Translational Diffusion of Transient Radicals Studied by the Transient Grating Method

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Abstract
Diffusion coefficients (D) of various radicals created by the photoinduced hydrogen abstraction reactions from alcohols (ethanol and 2-propanol) as well as those of the parent molecules are measured by using the transient grating (TG) method. Dependence of D on the viscosity, molecular size, and temperature are investigated, and the results are interpreted in terms of microscopic aggregation of the radicals with solvents or solutes.

1. Introduction
Since translational diffusion process is sensitive to the microscopic structure in the solution, understanding the diffusion provides an important insight into the structure as well as the intermolecular interaction. Therefore, dynamics of molecules in solution have been one of the main topics in physical chemistry for a long time. Recently we have studied the diffusion process of transient radicals in solution by the TG method aiming to understand the microscopic structure around the chemically active molecules. This kind of study will be also important in a view of chemical reaction because movement of radicals plays an essential role in the reactions. Here we present anomalous diffusion of the radicals created by the photoinduced hydrogen abstraction reaction. The origin of the anomaly is discussed based on the measurements of the solvent, solute size, and temperature dependences.

2. Method
Interference between two coherent beams produces a sinusoidal pattern (grating) in a sample solution. At the bright region of the grating, reactants are excited to the excited states, and they abstract hydrogen atoms from the alcoholic solvents. Spatial modulation of the chemical species is probed by another cw laser (He-Ne laser). The diffracted signal, \( I_G(t) \), induced by grating with wavevector \( \vec{q} \) decays with the diffusion process and D can be calculated from the decay rate constant, \( k \), with \( D = k/\vec{q}^2 \). Assumptions made for deriving this relation are discussed in more detail in Refs. 2 and 3.

3. Results
First we show the method of the measurement by taking an example of benzoquinone (BQ). According to the photochemical investigations of BQ, the triplet state BQ abstracts hydrogen from alcohol to form transient species of benzosemiquinone radical (BQH) and 2-hydroxypropyl radical (HPr). Typical time dependence of the TG signal after the photoexcitation of BQ in 2-propanol is depicted in Fig. 1. The initial strong spike-like signal is due to the contribution of the thermal grating. The decay of the signal is determined by the thermal diffusion. After it decays to the baseline once, another slowly developing signal appears. Since this signal develops almost 2 orders of magnitude slower than that of the thermal grating, the time profile must reflect the molecular diffusion in the solution. The
square root of the TG signal is expressed well by a sum of two exponential functions with different signs of the pre-exponential factors

\[ I_{TG}^{1/2} = a_s \exp(-ks)t + a_f \exp(-kt) \]  

where subscripts s and f stand for the slow and fast components, respectively. The dip between the thermal grating and the population grating implies that the absolute signs and magnitude of the pre-exponential factors in eq. (2) are \( a_s > 0 > a_f \) and \( |a_s| > |a_f| \). Assignment of the chemical species in the TG signal is made based on the following facts. (a) All of these species have their absorption bands at shorter wavelengths than the light of the He-Ne laser. A theoretical consideration on the refractive index associated with the absorption bands states that the slow and fast components originate from the radical species (or the reaction products) and the parent molecules, respectively. (b) The slow component decays faster under the air saturated condition. (c) BQH is revealed to be the only stable radical during the TG measurement from the EPR and transient absorption spectrum. On the basis of these considerations, we conclude that the slower signal is due to the radical and the faster one comes from the parent molecule. Figure 2 shows the \( q^2 \) dependence of \( k_s \) and \( k_f \). The each slope of the plot gives \( D \) of the each chemical species. Similar arguments also hold for the other chemical species and also in ethanol. The determined \( D \) of the radicals (\( D_r \)) and parent molecules (\( D_p \)) are plotted against \( 1/t \) (\( r \); radius of the molecules) in Fig.3. It should be noted that \( D_r \) are generally smaller than \( D_p \). This is not an apparent result because the difference in the molecular volume between the parents and their radicals is just one hydrogen atom, which is negligible compared to the whole molecular volume. The relation, \( D_r < D_p \), holds for all the radicals regardless of the nature of the solute.

![Chemical structures and graphs](image)

**Fig. 1** (left) Time profile of the TG signal after the photoexcitation of benzoquinone in 2-propanol (dotted line) and the best fitted curve with eq. (1) (solid line).

**Fig. 2** (right) Plots of the observed decay rate constants \( k \) of BQH (squares) and of BQ (circles) vs. square of the wavevector, \( q^2 \).

**4. Discussions**

4.1. **Comparison of \( D \) with the calculated \( D \)**
The Stokes-Einstein equation, which describes $D$ of a diffusing molecule in a solution with viscosity $\eta$, is given by

$$D_{SE} = \frac{kT}{6\pi\eta r}$$  \hspace{1cm} (2)

where $r$ denotes the radius of a spherical molecule and $f$ is a factor for correction of the deviation from the spherical shape and of the boundary condition. The determined $D_r$ agrees well with this $D_{SE}$. On the other hand, we found that a semiempirical modification of eq. (2) proposed by Spernol and Wirtz\textsuperscript{5} reproduces $D_D$ very well. In the following, we discuss the origin of the difference in $D$ between the radicals and the parent molecules.

4.2. Molecular size effect and a radical diffusion model

Fig. 3 shows that $D_p$ almost constantly decreases with increasing molecular size. On the other hand, the $D_r$ plot first decreases with decreasing $1/r$ until $0.3 \times 10^{-10}$ m\(^{-1}\), and then it increases gradually ('inverted' region). In terms of the friction, this tendency can be treated as follows. The friction coefficient of a species $i$ (i.e., $p$ or $r$), $f_i$, is defined by

$$f_i = kT/D_i$$  \hspace{1cm} (3)

An excess friction, $\Delta f$, of the radical gained by the conversion from the parent molecule to the corresponding radical is given by

$$\Delta f = f_r - f_p$$  \hspace{1cm} (4)

When this quantity is calculated for each solvent and plotted against $1/r$, it apparently shows a decreasing trend with increasing $r$. The trend in the excess friction of the solutes studied herein may be accounted for by the following model. First we consider that the radical is diffusing accompanied with several solvent (or other solute) molecules and the effective molecular volume of the radical is defined by including the attached solvent molecules around the radical. Next we assume that an unpaired electron has the capability of increasing the effective molecular volume only by a certain amount $V$. Then we obtain a simple relation between $\Delta f$ and $r$ as,

$$\Delta f \propto 1/r$$  \hspace{1cm} (5)

This relation can explain the observed $1/r$ dependence of $\Delta f$ qualitatively. In this paper, the excess friction is treated as an apparent excess volume of the radical. However, since the radicals cannot be tightly bounded with solvent (or solute) molecules, a description that the radicals feel a larger friction from the surrounding molecules during the movement by the intermolecular interaction may be more adequate.

4.3 Solvent effect

Since the radical concentration is very low (10\textsuperscript{-5} M) in the measurement, we might neglect a possible radical-radical interaction. The radicals should be surrounded by the solvent molecules in our observing time scale. Thus, an attractive intermolecular interaction between the radical and solvents (or solute) is necessary for increasing the apparent volume. One possibility for such an interaction is a hydrogen bonding interaction. The effect is examined by measuring $D$ of benzophenone ketyl radical (BPK) in non-polar solvents. Producing BPK in nonreactive solvents, we add hydrogen donors. We find that the values of $D$ are inversely proportional to the viscosity of the solvents which is predicted from the SE relation (Fig.4). Therefore, we believe that the hydrogen bonding is not the origin of the interaction.

4.4 Temperature dependence

To examine the adequacy of the proposed diffusion model, $D_D$ and $D_r$ are measured at various temperatures. The temperature dependence of both $D$ can be well expressed by the Arrhenius relation with activation energies close to that of the viscosity of the solution. The similar $E_D$ of $D_r$ and $D_D$ indicates that both diffusions are governed by the molecular motion, not by chemical reactions. (If a chemical reaction is involved in the decay of the
TG signal, the activation energy of $D_r$ should be totally different from that of $D_p$ because of the activation energy of the reaction.) Further, we find that the small but non-negligible difference in $E_D$ between the radical and the parent molecules can be explained by the concept of the larger volume of the radical, which supports our radical diffusion model.

**Conclusion:** $D_s$ of various transient radicals are measured by the TG method. We found that $D_r$ are $2 \sim 4$ times smaller than $D_p$. The discrepancy is interpreted in terms of an attractive intermolecular interaction between the radical and solvents (or solute), which may create microscopic clusters in solution.

Fig.3 (left) $D_s$ of the parent molecules (a) and those of the transient radicals (b) in 2-propanol (closed circles and squares) and in ethanol (open circles and squares) against the reciprocal of the radii ($r^{-1}$) of the molecules. The solid lines represent $D_{SW}$ in (a) and $D_{SE}$ in (b).

Fig.4 (right) Plots of $D_p$ (circles) and $D_r$ (squares) for benzophenone in various solvents against viscosity. Solid line represents $D_{SE}$.

**References**