



# Contribution of hydrogen bonding to the slow diffusion of transient radicals

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Received 22 January 2003; in final form 19 February 2003

## Abstract

The translational diffusion of many transient radicals has been revealed to be different from that expected from the stable closed shell molecules. The origin of the slower diffusion of the radicals was investigated. In particular, participation of the hydrogen bonding to the diffusion process was considered from view points of excess friction and the solvent dependence.

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## 1. Introduction

Diffusion coefficients ( $D$ ) of transient radicals are fundamental and important quantities for analyzing chemical reactions. However, data on  $D$  of transient radicals have been very scarce until we applied the transient grating technique to photochemical reactions in solution. In a series of our papers, we have found that  $D$  of many transient radicals ( $D_r$ ) are slower than those of the parent molecules ( $D_p$ ) [1–12]. Although there have now been accumulated a number of data of  $D$  of tran-

sient radicals, factors that control the diffusion process of the radicals have not been clear yet. The origin of the slow diffusion was initially attributed to an enhanced intermolecular interaction between the radicals and the solvents [7]. Subsequently, theoretical studies suggested that the enhancement is due to the enhanced charge sensitivity of the radicals [13–15]. Recently, Autrey et al. [16] reported  $D$  of some aryl carbonyls and aryl alcohols in alcohols by the Taylor dispersion method. By a comparison of these values with those of radicals reported by our group, they concluded that molecules adding a hydrogen atom to the radical center is a good model to predict  $D$  of transient radicals and that the hydrogen bonding (HB) between the ketyl radicals and hydroxylic solvent is the only origin of the slow diffusion of the radicals in alcoholic solvents. They stated that ‘the diffusion coefficient of the ketyl radical in hydroxylic

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solvents is not anomalously slow, and there is little reason to suggest a unique interaction between ketyl radicals and the solvent other than hydrogen bonding'. In this Letter, we investigated the origin of the slower diffusion of the radicals from the view points of excess friction and the solvent dependence to consider a possible participation of the hydrogen bonding to the diffusion process.

## 2. Experimental

The experimental setup of TG is similar to that reported previously [1–12]. Briefly, the third harmonics of a Nd:YAG laser (Spectra Physics, GCR170) was split into two with a nearly equal intensity by a beam splitter and crossed at a sample to create the TG. Each excitation beam was focused by separated lenses. A He–Ne laser was used for the probe beam, which was sent to the grating region satisfying the Bragg condition. The signal was detected by a photomultiplier (Hamamatsu R928), and averaged by a digital oscilloscope (Tektronix 2430A) and a microcomputer. The wavenumber of the grating is determined from the decay rate of the species grating signal observed after the photoexcitation of methyl red in benzene and known decay rate constant. The experiment was carried out at 22 °C.  $D$  of stable molecules were measured by the Taylor dispersion method using a teflon capillary tube (0.5 mm inner diameter, 20 m long) with the concentration profile being detected by a differential refractometer (Hitachi, L-7490) [17,18]. Other details have been described elsewhere.

## 3. Results and discussion

In order to reveal a possibility of the participation of the hydrogen bonding, the solvent dependence of  $D$  may provide a good clue, because the HB effect can be minimized using non-polar solvents as shown later. First, we examined the solvent dependence of 4-methylacetophenone. Fig. 1 shows the TG signal of 4-methylacetophenone in ethanol and in cyclohexane. In the TG measurement, a sinusoidal modulation of the light

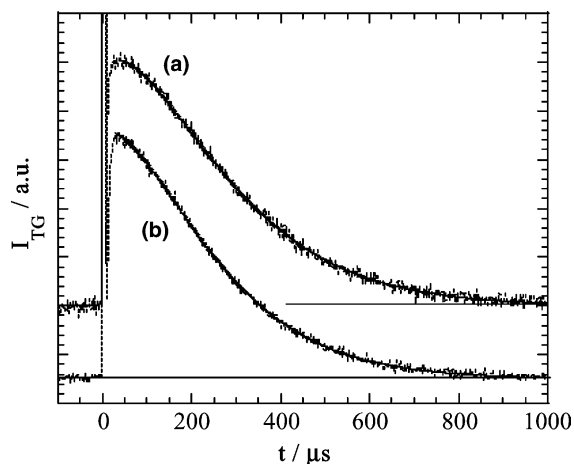


Fig. 1. Transient grating signals after photoexcitation of 4-methylacetophenone in ethanol (a) and cyclohexane (b).

intensity is produced by the interference of two light waves. The photoexcitation of the sample by this light creates the spatial modulation of the temperature (thermal grating) and the concentration of transient radicals (species grating), which lead to the sinusoidal modulation in the refractive index ( $\delta n$ ) at this probe wavelength. The creation and decay of the grating represent the molecular dynamics in the solution. The TG signal in the whole time range can be expressed by

$$I_{TG}(t) = \{ \delta n_{th} \exp(-D_{th}q^2t) - \delta n_p \exp(-D_pq^2t) + \delta n_r \exp(-D_rq^2t) \}^2,$$

where  $\delta n_{th}$ ,  $\delta n_p$ , and  $\delta n_r$  represents the refractive index changes by the thermal energy, parent molecule, and the radical, respectively.  $D_{th}$  denotes the thermal diffusivity of this solution and  $q$  is the grating wavenumber. The rise and decay parts of the TG signal in this time range represent the diffusion processes of the parent and the chemically created radical (4-methylacetophenone ketyl radical), respectively. Since the shape of the TG signal is very sensitive to the ratio  $R (= D_r/D_p)$ , the similarity of the TG signals in both solvents indicates that  $R$  should be very similar in these solvents (even though HB is not expected in cyclohexane). In fact,  $D_r$  of the ketyl radical was determined by a bi-exponential fitting of this curve under a condition that  $D_p$  is fixed to the value measured by the

Taylor dispersion method.  $D_p$  and  $D_r$  in cyclohexane are listed in Table 1.

Comparing these values, we immediately notice that  $D_r$  is smaller than  $D_p$  even in the non-polar solvent. This trend was previously reported for benzophenone ketyl radical in a variety of solvents [5]. We also show in Table 1 that  $D$  of  $\alpha$ -hydroxyethylbenzene in cyclohexane is similar to isopropylbenzene, which is a non-hydrogen bonding molecule. This similarity is reasonable because HB is not efficient in non-polar solvents. This conclusion agrees with the report by Chan and Chan [19].  $D$  of  $\alpha$ -hydroxyethylbenzene in cyclohexane is much larger than that of acetophenone ketyl radical in the same solvent. We have also reported that  $D_r$  is smaller than  $D_p$  in solvents such as cyclohexane, hexane, benzene, and methylcyclohexane [5]. If HB is the main cause of the slower diffusion, the ratio  $R$  should be enhanced in non-hydrogen bonding solvents. However,  $R$  is determined only by the viscosity of the solvents but not by the HB ability of the solvents.

Second, the friction due to HB and due to the radical is examined. The friction coefficient of species  $i$  is defined by  $f(i) = k_B T / D_i$ , where  $k_B$  is the Boltzmann constant, and  $T$  is the temperature. The excess friction,  $\Delta f$ , between  $i$  and  $j$  molecules is given by  $\Delta f = f(i) - f(j)$ . For example,  $\Delta f$  due to the  $\alpha$ -OH group of  $\alpha$ -hydroxyethylbenzene, which is an analogous molecule of acetophenone ketyl radical, can be calculated from  $D$  of ethylbenzene

and that of  $\alpha$ -hydroxyethylbenzene (Table 1),  $\Delta f(\alpha\text{-OH}) = f(\alpha\text{-hydroxyethylbenzene}) - f(\text{ethylbenzene}) = (2.0 \pm 0.08) \times 10^{-12}$  kg/s. Similarly,  $\Delta f$  of the  $p$ -OH of acetophenone is calculated as  $\Delta f(p\text{-OH}) = f(p\text{-hydroxyacetophenone}) - f(\text{acetophenone}) = (3.2 \pm 0.1) \times 10^{-12}$  kg/s.  $\Delta f(p\text{-OH})$  is larger than  $\Delta f(\alpha\text{-OH})$ , probably because of the different HB ability. This difference could result from the different  $pK_a$  ( $pK_a(\alpha\text{-OH}) \sim 15$  and  $pK_a(p\text{-OH}) \sim 10$ ) [20] as mentioned in [16]. The excess friction due to the radical character ( $\alpha$ -OH and radical center) of acetophenone ketyl radical is given by  $\Delta f(\text{ketyl}) = f(\text{acetophenone ketyl radical}) - f(\text{ethylbenzene}) = (3.9 \pm 0.5) \times 10^{-12}$  kg/s. This value is certainly larger than  $\Delta f(\alpha\text{-OH})$ , and also larger than  $\Delta f(p\text{-OH})$ . Therefore, it is reasonable to conclude that the excess friction due to the ketyl radical is not the same as that due to the OH group; that is,  $D$  of the acetophenone ketyl radical is smaller than that of  $\alpha$ -hydroxyethylbenzene, and even smaller than that of a hypothetical  $\alpha$ -hydroxyethylbenzene having more acidic  $\alpha$ -OH than the ketyl radical ( $pK_a \sim 10$ ). (The similar  $D$  of acetophenone ketyl radical to that of  $p$ -hydroxyacetophenone may be an accidental coincidence, because  $p$ -hydroxyacetophenone possesses two functional groups, i.e., OH group and C=O group and these two functional groups should make the excess friction of  $p$ -hydroxyacetophenone larger than that expected from the HB effect of the OH group. Due to this enhancement of the friction,  $D$  of  $p$ -hydroxyacetophenone becomes similar to that of acetophenone ketyl radical.)

Third, we have already reported that even radicals that possess no OH group diffuse slower than the parent molecules [9–11]. For example,  $D$  of diphenylmethyl radical is as low as about 30% of the diazo precursor and similar to benzophenone ketyl radical in cyclohexane [9]. These observations cannot be explained by the HB effect alone.

The above three observations certainly show that the radical character affects the diffusion process. However, Autrey et al. concluded that ‘there is little reason to suggest a unique interaction between ketyl radicals and the solvent other than hydrogen bonding’ based on the fact that  $D_r$  is similar to  $D$  of corresponding molecules with

Table 1  
Diffusion coefficients of acetophenone derivatives measured by the TD method and the radicals by the TG method at 21 °C

Solute	Solvent	$D$ ( $10^{-9}$ m <sup>2</sup> /s)
Acetophenone	Ethanol	1.14
Acetophenone ketyl radical	Ethanol	0.58
4-Methylacetophenone	Ethanol	1.10
	Cyclohexane	1.33
4-Methylacetophenone ketyl radical	Ethanol	0.59
	Cyclohexane	0.75
Ethylbenzene	Ethanol	1.34
$\alpha$ -Hydroxyethylbenzene	Ethanol	0.81
	Cyclohexane	1.23
Isopropylbenzene	Cyclohexane	1.28
$p$ -Hydroxyacetophenone	Ethanol	0.59

OH group only in alcohols [16]. We should stress here that their conclusion cannot be correct unless all of the characteristic features of the radical diffusion can be explained consistently. There is no direct evidence against or for a possibility that the ketyl radicals form HB with alcohols at present. The formation of HB should be examined by another spectroscopy. It would be interesting to think what explanation is possible if we assume that  $D$  of the ketyl radicals are smaller due to the HB contribution. We cannot explain the above observations unless the friction due to the radical in alcoholic solvents is smaller than that in non-polar solvents by unknown reason, or the frictions due to the radical character and due to HB are not additive. We will examine this effect further. In conclusion, HB cannot be the only origin of the slow diffusion of the radicals.

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