

## Comments on “Diffusion of Free Radicals in Solution. TEMPO, Diphenylpicrylhydrazyl, and Nitrosodisulfonate”

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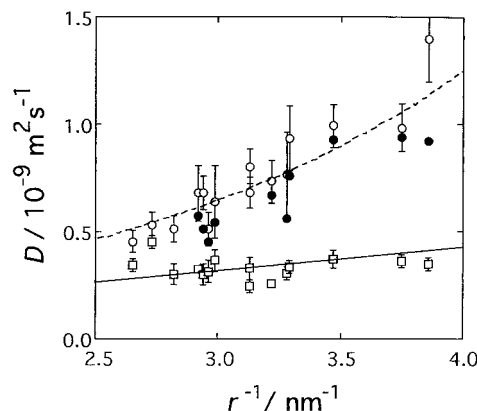
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Donkers and Leaist reported the diffusion constants of some stable free radicals ( $D_{\text{rad}}$ ) by the Taylor dispersion (TD) method.<sup>1</sup> At the same time,  $D$  of carbonyl, quinones, and azaromatic compounds were measured and compared with our data determined from the transient grating (TG) method.<sup>2–5</sup> They found that  $D_{\text{rad}}$  is similar to the nonradical molecules, and  $D$  of several stable (parent) molecules ( $D_{\text{par}}$ ) in some solvents seriously differ from those determined by the TG method. Although they have stated that “Direct comparison of the two sets of results may not be entirely appropriate”, the authors appear to question the slow diffusion of transient free radicals in their paper. In this comment, we point out that  $D$  of many stable free radicals have already been published, which showed that  $D$  of the radicals are close to  $D$  of the analogous closed-shell molecules, and discussed in terms of the chemical stability.<sup>6</sup> We also examine sources of the discrepancy between  $D$  determined by the TG and TD methods and emphasize that the transient (unstable) radicals actually diffuse slower than the stable molecules of similar sizes and shapes.

To begin with, sources of the discrepancy between the two methods are examined. Compared with the rather simple and stable setup of the TD method,  $D$  from the TG method have to be determined by taking account of several factors, and the accuracy is not generally as good as that from the TD method, although the TG method has a unique potential for transient species. There are two possible sources of the error in the TG measurement. First, we admit that the fitting of the double-exponential function leads to some uncertainties. In particular, since the time profile due to the parent molecule is superimposed on the decay of the radical signal, the error in  $D_{\text{par}}$  is more serious than  $D_{\text{rad}}$ . In Figure 1, we plot previously reported  $D_{\text{par}}$  and  $D_{\text{rad}}$  together with  $D_{\text{par}}$  determined by the TD method against  $r^{-1}$  ( $r$  = radius of the molecule) with statistical error bars. Considering the different method and experimental conditions for TG and TD, we think that most of  $D_{\text{par}}$  from the TG method agree reasonably with those from the TD method within the error range of  $D_{\text{par}}$ . Some serious disagreements are found in pyrazine (52%), xanthone (32%), and quinoline (38%). In these cases, we think that relatively small contribution of the parent molecules in the TG signal produces larger errors. In spite of these errors in  $D_{\text{par}}$ ,  $D_{\text{rad}}$  are more accurate because the signals due to the radicals are longer-lived without any contribution from the parent molecules. Indeed, even if we fix  $D_{\text{par}}$  to the values reported by Donkers and Leaist in the double-exponential fitting process (adjustable parameters are the relative intensity and  $D_{\text{rad}}$ ), the differences in  $D_{\text{rad}}$  are not so large (Table 1).

Second,  $D_{\text{par}}$  of benzophenone (BP) in nonpolar solvents<sup>3</sup> were not accurate enough for comparison with other data in pure solvents because the samples contained hydrogen donors, such as dimethylaniline, triethylamine, and 1,4-cyclohexadiene. Recently, we noticed that these donors produced additional TG signals, and  $D_{\text{par}}$  were less accurate. We also found that, instead of adding the hydrogen donors, the species grating signal can be observed by a slight increase of the excitation laser power

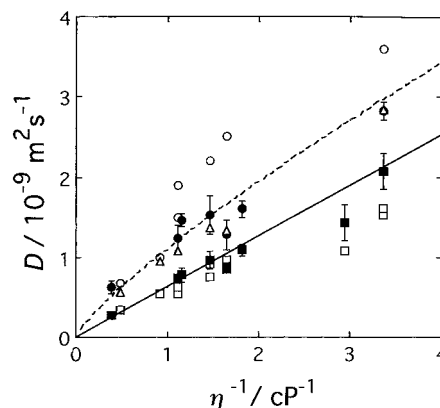


**Figure 1.** Molecular size dependence of  $D_{\text{par}}$  (open circles) and  $D_{\text{rad}}$  (squares) in 2-propanol with statistical error bars.  $D_{\text{par}}$  determined from the TD method are presented by closed circles. The broken line is  $D$  calculated from the equation proposed by Evans et al.<sup>7</sup> The solid line is  $D$  calculated from the Stokes–Einstein equation.

**TABLE 1: Diffusion Constants ( $D/10^{-9} \text{ m}^2 \text{ s}^{-1}$ ) of Some Hydrogen Abstracted Radicals<sup>a</sup>**

solute	solvent	$D_{\text{rad}}$	$D_{\text{rad}}^*$	$(D_{\text{rad}} - D_{\text{rad}}^*) / D_{\text{rad}}^* \times 100$
pyrazine	ethanol	$0.66 \pm 0.06$	$0.71 \pm 0.08$	-7
	2-propanol	$0.35 \pm 0.04$	$0.38 \pm 0.04$	-8
xanthone	2-propanol	$0.31 \pm 0.04$	$0.36 \pm 0.08$	-14
quinoline	2-propanol	$0.30 \pm 0.05$	$0.36 \pm 0.03$	-17

<sup>a</sup>  $D_{\text{rad}}$  are the previously reported values. They were calculated by the four-parameter fitting (rate constants of the radicals and of parent molecules, relative intensities) of the double-exponential function.  $D_{\text{rad}}^*$  are the radical diffusion constants that are calculated by the three-parameter fitting (rate constant of the radicals and relative intensities) of the double-exponential function. The rate constants for the parent molecules are fixed to those measured by the TD method.



**Figure 2.**  $D_{\text{par}}$  (open circles) and  $D_{\text{rad}}$  (open squares) of benzophenone in various solvents with hydrogen donors (in ethanol ( $\eta = 1.08$  cP) and 2-propanol ( $\eta = 2.04$  cP), no hydrogen donor was used) from the previous report,<sup>3</sup> and  $D_{\text{par}}$  (closed circles) and  $D_{\text{rad}}$  (closed squares) measured without the hydrogen donors are plotted against  $\eta^{-1}$ . (Since the species grating signal was not observed in benzene ( $\eta = 0.60$  cP) and acetonitrile ( $\eta = 0.34$  cP) without any hydrogen donor, diphenylmethanol was added in the solution (0.1 M). After the hydrogen abstraction of benzophenone from this donor, only one radical (benzophenone kethyl radical) is created.) The broken line is  $D$  calculated from the equation proposed by Evans et al.,<sup>7</sup> and the solid one is from the Stokes–Einstein equation.  $D_{\text{par}}$  from the TD method<sup>1</sup> is shown by triangles.

and sensitivity even in some nonpolar solvents. We carried out  $D$  measurement of BP in various solvents, and  $D_{\text{par}}$  and  $D_{\text{rad}}$  are plotted against  $\eta^{-1}$  ( $\eta$  = viscosity) in Figure 2.  $D_{\text{par}}$  agree with the values calculated from an equation proposed by Evans

et al.<sup>7</sup> and also those measured by the TD method<sup>1</sup> within a range of 20% to -5%. The values and  $D_{\text{par}}$  and  $D_{\text{rad}}$  of other solutes in various solvents will be reported in a separate paper.

We have already published  $D$  of stable free radicals and compared them with  $D$  of the transient radicals.<sup>6</sup> In nonpolar solvents,  $D$  of the free radicals are similar to those of the analogous closed-shell molecules, but this is not the case in polar solvents. We have found that  $D$  of the hydrogen abstracted radical from tetramethylcyclohexanone is smaller than  $D_{\text{par}}$ . In this case,  $D_{\text{par}}$  agrees well with  $D$  measured by the TD method. Evidently, from these data<sup>6</sup> and from Figures 1 and 2, the slower diffusion of the transient radicals should be genuine.

In conclusion, we examined the difference in  $D_{\text{par}}$  between the TG and TD methods and found that the errors in some data from the TG method were due to the fitting error and also from the contribution of other chemicals.  $D_{\text{par}}$  and  $D_{\text{rad}}$  of benzophenone in various solvents measured without hydrogen donors are presented. The main conclusion of the TG experiment, the slower diffusion of the transient radicals, should not be altered

or even supported by the "reasonable" agreement of  $D_{\text{par}}$  in many systems with  $D_{\text{par}}$  measured independently by the TD method.

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#### References and Notes

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