

ARTICLES

Diffusion of Free Radicals in Solution. TEMPO, Diphenylpicrylhydrazyl, and Nitrosodisulfonate

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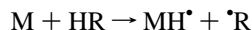
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Taylor dispersion and differential refractometry are used to measure diffusion coefficients (D) at 25 °C for dilute solutions of the stable free radicals: 2,2,6,6-tetramethyl-4-piperidinol (TEMPO) (in n -hexane); 1,1-diphenyl-2-picrylhydrazyl (in ethanol); and nitrosodisulfonate (in aqueous KOH solutions). For comparison, diffusion coefficients are measured for the respective nonradical analogues: 2,2,6,6-tetramethylpiperidine; 1,1-diphenyl-2-picrylhydrazine; and hydroxylaminedisulfonate. The limiting values of D for each free radical and its analogue differ by 5% or less. In contrast to this result, recent transient-grating measurements suggest that free radicals diffuse up to 4 times more slowly than their nonradical analogues. The accuracy of the grating data is checked by using Taylor dispersion to measure D values for 10 different analogues. Values of D from the grating measurements are found to be systematically too large by 25% on average, with a maximum error of 90%.

Introduction

The diffusion of free-radical intermediates is an important part of the kinetics of many chemical reactions.^{1–3} Measuring the diffusion of unstable free radicals is difficult because of the low concentrations of these species and their fleeting existence. In a recent series of studies, Terazima and co-workers^{4–7} used transient-grating laser spectroscopy⁸ to measure the diffusion coefficients of parent molecules (M) and unstable free radicals (MH^\bullet) generated by photoinduced hydrogen abstraction from different organic solvents (HR):



Remarkably, the radicals (MH^\bullet) appeared to diffuse much more slowly than the parent molecules (M) in spite of the nearly identical sizes and chemical structures of the pairs of species. For example, the diffusion coefficient reported for the pyrazinyl radical ($C_4H_4N_2H^\bullet$) in 2-propanol is 4 times smaller⁵ than the diffusion coefficient of the pyrazine molecule ($C_4H_4N_2$). The slow diffusion of the free radicals was attributed to enhanced radical–solvent interactions which increases the effective radius of the diffusing radical.

The diffusion coefficient of a solution species is inversely related to its effective radius. It is surprising, therefore, that the addition of a hydrogen atom to a pyrazine molecule increases the effective radius of the resulting radical by a factor of 4, implying a striking 64-fold increase in the effective molecular volume. This result challenges our understanding of diffusion in liquids. It would be prudent, however, to independently verify the transient-grating diffusion measurements, especially the important pyrazinyl/pyrazine results. Although very few diffusion experiments can be extended to studies of unstable solution species, a number of established techniques can be used

to measure reliable diffusion coefficients for pyrazine and other stable molecular solutes. In the work reported here, the accuracy of the transient-grating measurements is assessed by using Taylor dispersion^{9,10} to measure the accurate diffusion coefficients for pyrazine and nine other organic solutes.

In a Taylor (peak-broadening) experiment, a narrow band of solute is injected into a carrier stream of solvent at the entrance to a long capillary tube. Diffusion coefficients are calculated from the broadened distribution of dispersed solute as it flows out of the tube, usually 1–3 h after injection. This technique is obviously many orders of magnitude too slow for studies of transient free radicals. Nevertheless, Taylor dispersion can be used to measure reliable diffusion coefficients for *stable* free radicals. In the present study, the dispersion method is used to measure diffusion coefficients for the stable free radicals: 2,2,6,6-tetramethyl-4-piperidinol (TEMP), 1,1-diphenyl-2-picrylhydrazyl (DPP), and nitrosodisulfonate (NDS^{2-}). In addition, diffusion coefficients are measured for the respective nonradical analogues, 2,2,6,6-tetramethylpiperidine (TMP), 1,1-diphenyl-2-picrylhydrazine (DPPH), and hydroxylaminedisulfonate (HDS^{2-}), to see if the radicals and species of similar size and chemical structure (see Figure 1) diffuse at similar rates.

Experimental Section

Materials. Reagent-grade (>99% purity) ethanol, 2-propanol, n -hexane, cyclohexane, methylcyclohexane, and benzene were supplied by Caledon Laboratories. Water was purified by ion exchange and distillation.

Potassium hydroxylaminedisulfonate (K_2HDS), the analogue of potassium nitrosodisulfonate (K_2NDS), was prepared¹¹ by bubbling SO_2 through a solution of 5.2 g of KNO_3 and 7.6 g of potassium acetate dissolved in 13 g of water and mixed with 100 g of finely shaved ice. The K_2HDS product was recrystallized from aqueous ammonia and washed with cold water. The water contents of the K_2HDS and K_2NDS (Fremy's salt, Aldrich) were uncertain, so the purity of each salt was determined by

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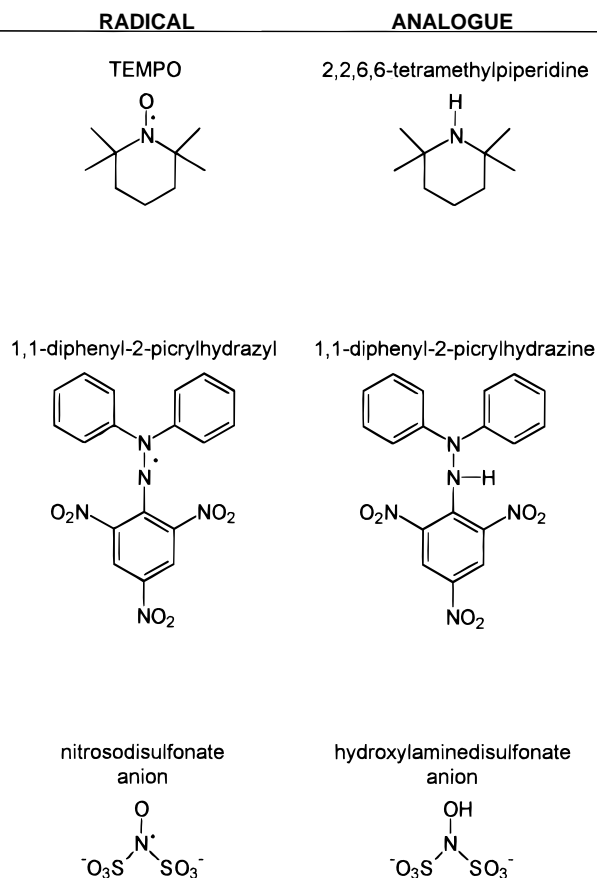


Figure 1. Stable free radicals and nonradical analogues.

passing weighed samples through a chloride ion-exchange column followed by titration with silver nitrate. Tracer diffusion of the NDS^{2-} and HDS^{2-} ions was measured in aqueous solutions of KOH prepared by dilution of a standardized stock solution of carbonate-free KOH. The other solutes were used as received from Aldrich or Sigma. Solutions were prepared in calibrated volumetric flasks.

Taylor Dispersion Equipment. Teflon and stainless steel dispersion tubes were used in this work. The inner radius of each tube ($r \approx 0.04$ cm) was calculated from the tube length ($L \approx 3000$ cm) and the weight of the tube when empty and when filled with water of known density. Each tube was coiled into a 75-cm-diameter helix and held at 25.00 ± 0.05 °C in a thermostat. Metering pumps (Gilson model Minipuls 3) maintained steady laminar flows of the carrier solutions. At the start of each run, a 20- μL sample of solution was injected into the carrier solution at the tube entrance through a Teflon valve (Rheodyne Model 50). A differential refractometer (Waters Model 410 or Gilson Model 131) detected the dispersed solute at the tube outlet. The refractometer output voltage, $v(t)$, was measured at timed intervals with a digital voltmeter (Hewlett-Packard Model 3478A). Mean flow speeds (u) and sample retention times ($t_R = L/u$) were typically 0.4 cm s^{-1} and 8000 s, respectively.

Binary Diffusion Measurements. The mutual diffusion coefficients (D) of the two-component solutions (e.g., pyrazine dissolved in 2-propanol) were measured^{9,10} by injecting at time $t = 0$ a small volume (ΔV) of solution containing solute at concentration $\bar{c} + \Delta c$ into a carrier solution of composition \bar{c} . The injected solute spreads out as it flows along the tube, producing the concentration distribution¹²

$$c(t) = \bar{c} + \Delta c_{\max}(t_R/t)^{1/2} \exp[-12D(t - t_R)^2/r^2t] \quad (1)$$

at the tube outlet. The eluted concentration profile closely resembles a Gaussian peak of variance $r^2 t_R/24D$ and height $\Delta c_{\max} = (2\Delta c \Delta V/\pi r^3 u)(3D/\pi t_R)^{1/2}$ centered on the retention time t_R .

Least squares was used to fit the working equation¹⁰

$$v(t) = a_0 + a_1 t + \Delta v_{\max}(t_R/t)^{1/2} \exp[-12D(t - t_R)^2/r^2t] \quad (2)$$

to the measured refractometer voltages. The eluted concentration profile closely resembles a Gaussian peak of variance $r^2 t_R/24D$ and height $\Delta c_{\max} = (2\Delta c \Delta V/\pi r^3 u)(3D/\pi t_R)^{1/2}$ centered on the retention time t_R . In addition to D and the peak voltage (Δv_{\max}), the retention time and the linear baseline ($a_0 + a_1 t$) were optimized to allow for small drifts in the flow rate and the detector signal, respectively.

The operation of the dispersion equipment was checked by measuring D for 0.100 mol L^{-1} aqueous solutions of sucrose, urea, and KCl. Agreement with accurate diffusion coefficients determined previously by optical interferometry^{13–15} was within 2%.

Tracer Ionic Diffusion Measurements. Dispersion measurements on aqueous K_2NDS solutions yield the binary diffusion coefficient of the salt,¹⁶ which depends on the mobilities of both the K^+ and NDS^{2-} ions. In the present study, however, the diffusion coefficient of the NDS^{2-} radical is more important. It was measured by dispersing trace amounts of K_2NDS in a supporting electrolyte, aqueous KOH. At the start of each tracer run, a sample of solution containing dilute K_2NDS (at concentration Δc) and KOH (at concentration \bar{c}_{KOH}) was injected into a carrier solution of KOH (at concentration \bar{c}_{KOH}).

Mutual diffusion in aqueous $\text{K}_2\text{NDS}/\text{KOH}$ solutions is coupled.¹² In the dispersion experiments, for example, the diffusion potential generated by the initial gradient in K_2NDS drives a coupled flow of the KOH supporting electrolyte, even though the initial gradient in KOH is zero. As a result, the refractive index profile across the eluted peak resembles two overlapping Gaussians¹⁷ of normalized weights W_1 and $1 - W_1$:

$$v(t) = a_0 + a_1 t + \Delta v_{\max}(t_R/t)^{1/2} \left[W_1 \exp\left[-\frac{12D(t - t_R)^2}{r^2 t}\right] + (1 - W_1) \exp\left[-\frac{12D_{\text{KOH}}(t - t_R)^2}{r^2 t}\right] \right] \quad (3)$$

D is the tracer diffusion coefficient of the NDS^{2-} ion, and D_{KOH} is the binary diffusion coefficient of the supporting electrolyte. For improved accuracy, D and D_{KOH} were evaluated by simultaneously fitting eq 3 to pairs of dispersion peaks: a tracer peak generated by an initial concentration difference in K_2NDS as described above and a binary peak ($W_1 = 0$) produced by injecting excess KOH into the aqueous KOH carrier stream.

The same procedure was used to measure tracer diffusion of the hydroxylaminedisulfonate (HDS^{2-}) ion in KOH solutions. KOH was used as the supporting electrolyte because the HDS^{2-} ion is stable under alkaline conditions. Also, the diffusion coefficient of KOH is about 3 times larger than the tracer diffusion coefficients of the HDS^{2-} and NDS^{2-} ions. Consequently, the Gaussian profiles generated by tracer diffusion of the ions were considerably broader than the Gaussian generated by the diffusion of KOH, and the separate contributions could be accurately resolved by the fitting procedure. Details of the measurement of tracer ionic diffusion by the dispersion method have been reported.¹⁷

TABLE 1: Binary Diffusion Coefficients of Organic Molecules in Ethanol and 2-Propanol Solvents at 25 °C Determined by Taylor Dispersion

solute	$\bar{c}/\text{mol L}^{-1}$	$D/10^{-5} \text{ cm}^2 \text{ s}^{-1}$	
		in ethanol	in 2-propanol
pyrazine	0.000	0.98	1.55
	0.005	0.97	1.51
	0.010	0.97	1.50
	0.025	0.98	1.49
phenazine	0.000	0.57	0.92
	0.010	0.57	0.91
	0.020	0.57	0.91
	0.000	0.54	0.94
xanthone	0.010	0.54	0.91
	0.020	0.54	0.90
	0.000	0.71	1.14
quinoxaline	0.010	0.70	1.11
	0.020	0.71	1.14
	0.000	0.48	0.81
acridine	0.010	0.48	0.81
	0.020	0.47	0.79
	0.000	0.59	0.95
quinoline	0.005	0.59	
	0.010	0.59	0.97
	0.020	0.59	0.98
	0.000	0.81	1.29
acetophenone	0.005	0.80	
	0.010	0.81	1.28
	0.020	0.82	1.27
	0.000	0.98	1.45
benzaldehyde	0.005	0.97	1.42
	0.010	0.97	1.44
	0.020	0.97	1.43
benzoquinone	0.000	0.98	1.48
	0.005	1.00	
	0.010	0.99	1.51
	0.020	0.99	1.52

Results and Discussion

Five to 10 injections were made into each carrier stream. Diffusion coefficients calculated from replicate peaks were usually reproducible within $\pm 1\%$. Solutions of at least two different compositions ($0.003 \leq |\Delta c| \leq 0.050 \text{ mol L}^{-1}$) were injected to verify that the values of D were independent of Δc and, therefore, represented differential diffusion coefficients at the carrier solution concentration (\bar{c}).

Comparison of Diffusion Coefficients from Transient-Grating and Taylor Dispersion Measurements. The dispersion method was used to measure binary mutual diffusion coefficients for pyrazine and nine other organic solutes in ethanol and 2-propanol solvents. The diffusion of benzophenone in cyclohexane, methylcyclohexane, *n*-hexane, and benzene was also measured. Tables 1 and 2 give the average values of D determined at each carrier stream composition.

Organic molecules, especially planar aromatics,¹⁸ can self-associate in solution. As a qualitative test for aggregation, the diffusion of each solute was measured at three or four different carrier stream concentrations from 0.000 to 0.030 mol L⁻¹. Association in these solutions was judged to be unimportant because none of the D values dropped appreciably with increasing concentration.

In Tables 3–5, the diffusion coefficients from the dispersion measurements are compared with the corresponding values determined previously^{4–6} by the transient-grating method. The grating measurements were made on 0.010 mol L⁻¹ solutions of each solute at room temperature, about 23 °C. To adjust the dispersion data from 25 to 23 °C, a minor correction (about –4%) calculated from the Stokes–Einstein equation¹² has been applied to the dispersion D values: $D_{23\text{C}} = (296.15/298.15) \cdot (\eta_{25\text{C}}/\eta_{23\text{C}})D_{25\text{C}}$. Published solvent viscosities¹⁹ (η) were used to calculate the correction factors.

TABLE 2: Binary Diffusion Coefficients of Benzophenone in Different Solvents at 25 °C Determined by Taylor Dispersion

solvent	$\bar{c}/\text{mol L}^{-1}$	$D/10^{-5} \text{ cm}^2 \text{ s}^{-1}$
ethanol	0.000	0.98
	0.005	0.98
	0.010	0.97
	0.025	0.97
2-propanol	0.000	0.61
	0.005	0.59
	0.010	0.57
	0.025	0.55
benzene	0.000	1.37
	0.010	1.37
	0.020	1.42
cyclohexane	0.000	1.12
	0.005	1.12
	0.010	1.11
	0.025	1.09
methylcyclohexane	0.000	1.42
	0.010	1.39
	0.030	1.41
<i>n</i> -hexane	0.000	2.91
	0.005	2.90
	0.010	2.91
	0.025	2.86

TABLE 3: Comparison of Diffusion Coefficients of Organic Molecules in Ethanol at 23 °C Determined by Taylor Dispersion (TD) and Transient-Grating (TG) Methods

solute ^a	$D_{\text{TD}}/10^{-5} \text{ cm}^2 \text{ s}^{-1}$	$D_{\text{TG}}/10^{-5} \text{ cm}^2 \text{ s}^{-1}$	$100(D_{\text{TG}} - D_{\text{TD}})/D_{\text{TD}}$
pyrazine	1.48	2.0	35
phenazine	0.89	1.1	24
xanthone	0.90	1.1	22
quinoxaline	1.09	1.1	1
acridine	0.78	0.90	14
quinoline	0.92	1.1	19
acetophenone	1.24	1.3	5
benzaldehyde	1.39	1.5	8
benzophenone	0.95	1.11	6
benzoquinone	1.44	1.6	11

^a Concentration: 0.010 mol L⁻¹.

TABLE 4: Comparison of Diffusion Coefficients of Organic Molecules in 2-Propanol at 23 °C Determined by Taylor Dispersion (TD) and Transient-Grating (TG) Methods

solute ^a	$D_{\text{TD}}/10^{-5} \text{ cm}^2 \text{ s}^{-1}$	$D_{\text{TG}}/10^{-5} \text{ cm}^2 \text{ s}^{-1}$	$100(D_{\text{TG}} - D_{\text{TD}})/D_{\text{TD}}$
pyrazine	0.92	1.4	52
phenazine	0.54	0.64	18
xanthone	0.51	0.68	32
quinoxaline	0.67	0.73	9
acridine	0.45	0.51	13
quinoline	0.56	0.77	38
acetophenone	0.76	0.93	22
benzaldehyde	0.93	0.99	7
benzophenone	0.57	0.68	19
benzoquinone	0.94	0.98	5

^a Concentration: 0.010 mol L⁻¹.

It is clear from Tables 3–5 that the diffusion coefficients estimated from the grating measurements are consistently higher than those measured by the dispersion method. On average, the grating coefficients are 25% too large. A discrepancy of this magnitude is well outside the proven 2% accuracy of the dispersion measurements and the claimed 10% accuracy^{4–7} of the grating measurements.

The dispersion and grating data are in nearly perfect agreement for some systems, such as quinoxaline in ethanol. In other cases, the grating data are seriously in error. For example, the grating diffusion coefficient for benzophenone in benzene is

TABLE 5: Comparison of Diffusion Coefficients for Benzophenone^a in Different Solvents at 23 °C Determined by Taylor Dispersion (TD) and Transient-Grating (TG) Methods

solvent	$D_{TD}/10^{-5}$ $\text{cm}^2 \text{s}^{-1}$	$D_{TG}/10^{-5}$ $\text{cm}^2 \text{s}^{-1}$	$100(D_{TG} - D_{TD})/D_{TD}$
ethanol	0.95	1.0	6
2-propanol	0.57	0.68	19
benzene	1.34	2.5	87
cyclohexane	1.08	1.5	40
methylcyclohexane	1.36	2.2	62
<i>n</i> -hexane	2.84	3.6	27
acetophenone	1.24	1.3	5

^a Concentration: 0.010 mol L⁻¹.

about 90% too large. Moreover, the average error in the grating results for benzophenone in different solvents is +40%. The wide scatter in the accuracy of the grating diffusion coefficients (0–90%) seems to rule out a simple calibration error. It does not appear that the operation of the grating experiment was checked by measuring the diffusion of solutes for which D is accurately known.

The pyrazine/2-propanol system is of particular interest. According to the grating measurements,⁵ the diffusion coefficient of pyrazine in 2-propanol ($1.4 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$) is 4 times larger than the diffusion coefficient of the pyrazinyl radical ($0.31 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$). However, the more accurate dispersion measurements reported here give $0.92(\pm 0.02) \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$ for the diffusion coefficient of 0.010 mol L⁻¹ pyrazine. The pyrazine diffusion coefficient from the grating studies is therefore 50% too large. Using the revised D value, pyrazine still appears to diffuse much more rapidly than the pyrazinyl radical, by a factor of 3. It should be mentioned, however, that the uncertainty in the diffusion coefficient of the pyrazinyl radical used in this comparison is unknown and potentially very large.

In the transient-grating experiments, an excitation pulse from crossed laser beams generates a pattern of bright and dark interference fringes and a corresponding “picket-fence” profile in the initial concentration of each photogenerated species. The nonuniform composition creates a refractive-index grating which diffracts a delayed probe beam from another laser. As diffusion smooths out the concentration grating, the intensity of the diffracted signal drops to zero. Diffusion coefficients of the unstable free radicals (MH[•]) and the parent molecules (M) were estimated^{4–7} by least-squares analysis of the multiexponential decay of the diffracted signal.

The practical difficulty of fitting accurate parameters to multiexponential decays is well-known.²⁰ Unless the data are extremely precise, it is usually impossible to resolve decay constants that differ by 20% or less, especially if the baseline must also be fitted. Moreover, the errors in the fitted parameters tend to be strongly correlated. It might be feasible to use the relatively accurate values of D reported in this paper to evaluate the transient decay constants for the parent molecules. This calibration procedure would allow a more reliable determination of other decay constants in the transient-grating signals.

Diffusion of Stable Free Radicals and Nonradical Analogues. To shed more light on the transport properties of free radicals, the dispersion technique was used to measure diffusion coefficients for stable free radicals and nonradical analogues. Table 6 summarizes the results for the diffusion of 2,2,6,6-tetramethyl-4-piperidinol (TEMPO) free radical and its analogue, 2,2,6,6-tetramethylpiperidine (TMP), in *n*-hexane solutions. The dispersion measurements indicate that the TEMPO radical diffuses slightly more slowly (by about 4%) than TMP at a given concentration.

TABLE 6: Diffusion Coefficients of TEMPO and 2,2,6,6-Tetramethylpiperidine (TMP) in *n*-Hexane Solutions at 25 °C

$\bar{c}/\text{mol L}^{-1}$	$D(\text{TEMPO})/10^{-5} \text{ cm}^2 \text{s}^{-1}$	$D(\text{TMP})/10^{-5} \text{ cm}^2 \text{s}^{-1}$
0.000	2.93	3.08
0.010	2.85	2.94
0.020	2.78	2.89
0.030	2.66	2.95

TABLE 7: Tracer Diffusion Coefficients of Nitrosodisulfonate (NDS²⁻) and Hydroxylaminedisulfonate (HDS²⁻) Ions in Aqueous KOH Solutions at 25 °C

$\bar{c}_{\text{KOH}}/\text{mol L}^{-1}$	$D(\text{NDS}^{2-})/10^{-5} \text{ cm}^2 \text{s}^{-1}$	$D(\text{HDS}^{2-})/10^{-5} \text{ cm}^2 \text{s}^{-1}$
0.005	1.12	1.08
0.010	1.10	0.98
0.025	1.06	0.94
0.050	1.01	0.85
0.100	0.98	

Solute–solute interactions, changes in the solution viscosity, and nonideal thermodynamic behavior can profoundly influence the rates of diffusion.¹² To avoid these complications in the interpretation of D , it is convenient to refer to the limiting diffusion coefficient (D^0) at zero solute concentration. The D^0 values of $(2.93 \pm 0.06) \times 10^{-5}$ and $(3.08 \pm 0.06) \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$ for TEMPO and TMP were determined by injecting dilute solutions of each solute into pure *n*-hexane carrier streams.

Only a few diffusion measurements were made on the 1,1-diphenyl-2-picrylhydrazyl radical (DPP) and the 1,1-diphenyl-2-picrylhydrazine (DPPH) analogue because of the high cost and poor solubility of these materials. Injecting dilute solutions of DPP or DPPH into pure ethanol carrier solutions gave $(0.57 \pm 0.02) \times 10^{-5}$ and $(0.55 \pm 0.03) \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$ for the respective D^0 values. In this case, the radical appears to diffuse slightly more rapidly than its analogue, but the difference is not significant.

Table 7 gives the tracer diffusion coefficients measured for the nitrosodisulfonate (NDS²⁻) radical ion and the hydroxylaminedisulfonate (HDS²⁻) analogue in aqueous solutions of KOH. In dilute solutions, ionic diffusion coefficients are linear functions of the square root of the ionic strength.^{12,16} Linear extrapolation of D against the square root of \bar{c}_{KOH} gives $(1.15 \pm 0.04) \times 10^{-5}$ and $(1.12 \pm 0.07) \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$ for the respective limiting diffusion coefficients of the aqueous NDS²⁻ and HDS²⁻ ions.

In sharp contrast to the transient-grating results, the dispersion measurements reported here indicate that free radicals and nonradical analogues have similar diffusion coefficients. Direct comparison of the two sets of results may not be entirely appropriate because the radicals employed in the grating studies were highly unstable. Nevertheless, the dispersion results are consistent with a large body of diffusion data which suggest the solution species of similar sizes and chemical structure have similar diffusion coefficients. This behavior is illustrated in Table 8 for pairs of aqueous solution species.

Conclusions

In no way do the Taylor dispersion measurements reported in this paper rule out the slow diffusion of unstable free radicals suggested by transient-grating studies.^{4–7} However, the dispersion results for the stable molecules establish that the diffusion coefficients from the transient-grating measurements are subject to large and unexplained systematic errors of up to 90%. The revised diffusion coefficients could be used for calibration purposes in future transient-grating studies. In addition, the dispersion results show that certain stable free radicals and their

TABLE 8: Limiting Diffusion Coefficients of Aqueous Species at 25 °C

species	$D/10^{-5}$ $\text{cm}^2 \text{s}^{-1}$	species	$D/10^{-5}$ $\text{cm}^2 \text{s}^{-1}$
1-propanol ^{21,22}	1.06	2-propanol ²²	1.03
1-butanol ²³	0.97	2-butanol ²¹	0.94
urea ¹⁴	1.38	thiourea ²⁴	1.34
sucrose (C ₁₂ H ₂₂ O ₁₁) ¹³	0.52	maltose (C ₁₂ H ₂₂ O ₁₁) ²⁵	0.52
2-aminobenzoic acid ²⁶	0.84	3-aminobenzoic acid ²⁶	0.77
3-aminobenzoic acid ²⁶	0.77	4-aminobenzoic acid ²⁶	0.84
ammonia ²⁷	2.08	ammonium ion ¹⁶	1.96
acetic acid ²⁸	1.20	acetate ion ¹⁶	1.09
benzoic acid ²⁸	0.90	benzoate ion ¹⁶	0.86
phosphoric acid ³⁰	0.87	H ₂ PO ₄ ⁻ ion ³¹	0.86

nonradical analogues diffuse at nearly identical rates in solution. This piece of information may be of value in the development of a theory for the transport of free radicals in solution.

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