J. Phys. Chem. A **2001,** *105,* 5948−5953

Comparison of Diffusion Coefficients of Aryl Carbonyls and Aryl Alcohols in Hydroxylic Solvents. Evidence that the Diffusion of Ketyl Radicals in Hydrogen-Bonding Solvents Is Not Anomalous?

Tom Autrey,* Pramod Kandanarachchi, and James A. Franz

Pacific Northwest National Laboratory, Operated by Battelle Memorial Institute, P.O. Box 999, MS#K2-44, Richland, Washington 99352

Received: July 31, 2000; In Final Form: February 14, 2001

The diffusion coefficients of benzyl-, sec-phenethyl-, and diphenylmethyl alcohol and the corresponding arylcarbonyls (benzaldehyde, acetophenone, and benzophenone) were measured by Taylor's dispersion method in both ethyl and isopropyl alcohol. The experimental values are compared to published transient grating measurements of the corresponding aryl ketyls (benzyl-, *sec*-phenethyl-, and diphenylmethyl-ketyl radical). The diffusion coefficients of the aryl alcohols are between 50 and 70% slower than the corresponding aryl ketones. The slower rate of diffusion is attributed to the capability of alcohol to participate as a hydrogen-bond donor with the solvent ($\mathrm{ROH\text{- - -}O{<}^{H}_{R}}$). The ketone can only act as a weak hydrogen-bond acceptor, lacking acidic hydrogens to participate in hydrogen-bonding interactions with the solvent. On the other hand, the diffusion coefficient of the aryl alcohols and the corresponding aryl ketyls are comparable within expected experimental error. This work shows that the diffusion of ketyl radicals is not anomalously slow and that aryl alcohols are significantly better models than the corresponding aryl ketones for analyzing the diffusion of aryl ketyls in both ethyl and isopropyl alcohol. The standard empirical recipes of Spernol−Wirtz and Wilke−Chang do not adequately account for the interactions between the solutes and the hydroxylic solvents ethyl and isopropyl alcohol.

Introduction

We are interested in identifying a stable family of compounds that may be used to estimate the diffusion coefficient of ketyl radicals in a variety of organic solvents. Knowledge of the chemical and physical properties of ketyl radicals is important to understand their role as novel hydrogen atom donors and to appreciate their possible involvement in thermal degradation pathways in lignin.[1,2] In previous work, we used a competing radical self-termination pathway to obtain the activation barrier for unimolecular scission of a lignin model compound.[3] The von Smoluchowski equation was used to calculate the temperature-dependent rate parameters of radical self-termination as our basis reaction. Estimates of the temperature-dependent diffusion coefficient of substituted aryl radicals used in the von Smoluchowski equation were obtained with the prescriptions of Spernol and Wirtz (SW).[4,5] Implicit in our analysis was the assumption that the diffusion coefficient of the radical ($\mathrm{R^{\bullet}}$) could be accurately modeled with the corresponding stable hydrocarbon (RH), i.e., adding a hydrogen atom to the parent radical would not significantly change the physical characteristics that dictate diffusion. Therefore, the simple recipe of adding a hydrogen atom to the radical center (eq 1) to obtain a stable model for a radical is preferable to subtracting a hydrogen atom from the position α-to the radical center (eq 2). For example, when toluene is used as a model for benzyl radical, i.e., addition of a hydrogen atom to the radical center, there is little difference between the observed diffusion coefficient of the radical, measured by transient grating (TG) methods, and the diffusion coefficient of the model, toluene, measured by dispersion methods.[6] Donkers and Leaist have shown that the diffusion coefficient for a stable radical species 1,1-diphenyl-2-picrylhydrazyl and the corresponding "hydrocarbon," 1,1-diphenyl-2-picrylhydrazine, i.e., $\mathrm{R(\bullet) + H(\bullet) \rightarrow RH}$, are the same within experimental error.[7] This conventional approach, adding a hydrogen atom to the radical center to provide a comparative model for radical diffusion, has been justified for several radicals based upon the agreement between observed diffusion control radical self-termination rates and the rates predicted by empirical methods employing the D of the stable model,[8−12] even for ketyl radicals in alcoholic solvents.[9,13] Isopropyl alcohol was chosen as a model for isopropyl ketyl radical specifically because they were both believed to form hydrogen bonds with the solvent. However, much recent work has appeared suggesting a slow diffusion rate for some organic radical intermediates, generating an apparent controversy.[7,14−16] Specifically, interactions between ketyl radicals and organic solvents were suggested to decrease the observed rates of diffusion compared to both the calculated and the experimental diffusion rates of the parent ketones.[17,18] It was argued that the effective radius of the radical was greater than the radius of the parent ketone because of a special interaction between the π unpaired electron of the radical and the solvent. Of special significance was the suggestion that the decrease in observed diffusion coefficients should not be attributed to hydrogen bonding between the hydroxyl group of

$$\mathrm{RCH(\bullet)OH + H(\bullet) \rightarrow \underset{\text{Conventional model}}{RCH_2OH}} \qquad (1)$$

$$\mathrm{RCH(\bullet)OH - H(\bullet) \rightarrow \underset{\text{Unconventional model}}{RC(H){=}O}} \qquad (2)$$

10.1021/jp004291+ CCC: $20.00

the ketyl radical and the hydroxylic solvent. Subsequent theoretical work[19−21] was published attributing the slow diffusion of radicals to an "electric sensitivity." These conclusions are quite surprising in light of the recent work published independently by Tominaga and co-workers[22] and Chan and Chan[23] showing that organic molecules with hydroxy-substituents diffuse slower than the corresponding parent compounds because of the hydrogen-bonding interactions with hydroxylic solvents. In addition, convention suggests that whenever a hydrogen atom is attached to a heteroatom, there is a significant probability for hydrogen-bond formation. If any results are of great surprise, it would be that a ketyl radical does not form a hydrogen bond with a hydroxylic solvent.

We believe that addressing two issues will help to resolve this apparent anomaly: (1) following the conventional recipe of adding a hydrogen atom to the radical center to obtain a suitable model, i.e., comparing the diffusion of a ketyl radical to the corresponding alcohol, as previously practiced and (2) selecting an empirical model that is designed to account for interactions between solute and solvents. Accordingly, we believe that the corresponding aryl alcohol I should be considered as a model for comparisons with the aryl ketyl II, rather than the parent aryl ketone III, as has been the recent practice.

$$\underset{\text{I}}{\mathrm{ArCH(OH)R}} \qquad \underset{\text{II}}{\mathrm{ArC(\bullet)(OH)R}} \qquad \underset{\text{III}}{\mathrm{ArC({=}O)R}}$$

In this work, we report the results of experimentally measured diffusion coefficients of aryl alcohols (ArCH(OH)R): benzyl alcohol, phenethyl alcohol, diphenylmethanol, hydroxyxanthone, hydroquinone) and aryl carbonyls (ArC(═O)R: benzaldehyde, acetophenone, benzophenone) in two solvents, ethyl- and isopropyl alcohol, using the Taylor's dispersion method.[24] The results are compared with the reported experimental diffusion coefficients of the corresponding aryl ketyl radicals (ArC(•)(OH)R) measured by TG methods.[18,25] We assume that a radical center α- to a hydroxyl group will not significantly alter the interaction with the solvent and predict that the corresponding family of aryl alcohols will provide an improved model for estimating the diffusion coefficient of ketyl radicals. In addition, a hydrodynamic empirical approach that is reported to account for solute solvent interactions D_{WCh} (Wilke and Chang [WCh]),[26] is used to estimate diffusion coefficients of the aryl alcohol models and compared with the experimental data and D_{SW}, the diffusion coefficient calculated with the recipe of SW.[27] Given that the SW recipe corrects only for differences in the molecular sizes between solutes and solvents and assumes no associative interactions between solutes and solvents, it is not expected to provide a satisfactory agreement with experimental observation. At question is whether the WCh-modified Stokes−Einstein equation is adequate to predict the diffusion coefficient of aryl alcohols (or transient ketyl radicals) in hydroxylic solvents.

Importantly, the suggested absence of hydrogen bonding between ketyl radicals and hydroxylic solvents has consequences to the field of free radical chemistry beyond radical diffusion addressed in this work. It has long been believed that both the lifetime and the product distribution of ketyl radicals generated by intramolecular hydrogen atom abstraction are directly affected by hydrogen bonding of the aryl ketyl radical to solvents such as methanol![2,28−33] In addition, thermochemical estimates of the heats of formation of ketyl radicals are based upon the assumption that there is little difference between hydrogen bonding of the ketyl radicals and the corresponding alcohols in solvents capable of forming hydrogen bonds.[34,35] If ketyl radicals do not form a hydrogen bond with hydroxylic solvents, then alternative explanations are required to explain Norrish II photochemistry, and published thermochemical data for ketyl radicals needs to be reevaluated.

Methods and Materials

Experimental Diffusion Coefficients. The Taylor's dispersion method[24,36,37] was used to measure the diffusion coefficient of the stable compounds in both ethyl and isopropyl alcohol. The apparatus used in this work has been described previously.[38] Briefly, a 10-μL sample of the solute dissolved in the solvent (0.05−0.1 M) was injected (Waters Associates U6K injector) onto a coiled column (Upchurch Scientific − stainless steel length 22.8-m, coil diameter 21 cm, tubing ID 0.546 ± 0.008 mm or − PEEK tubing length 15 m, coil diameter 21 cm, tubing ID 0.494 ± 0.008 mm) held at temperature in a Neslab RTE−211 constant-temperature bath. The solvent (helium purged) was pumped through the column at a flow rate between 0.1 and 0.3 mL/min (Waters Associates high-performance liquid chromatography [HPLC] pump), and the solute was detected at the end of the column with a Waters 410 differential refractometer. The signal from the detector was digitized and collected on a National Instruments PCI 6110E multifunction IO card and stored on a PC for analysis. Least-squares analysis of a Gaussian curve through the digitized data provides the variance (σ^2) of the solute distribution. An average of three individual measurements was used to obtain the experimental diffusion coefficients. The diffusion coefficient is proportional to the variance according to ($D_{TD} = r^2t/24\sigma^2$)[12] where r is the internal radius of the stainless steel tubing, t is the retention time in seconds at the maximum peak intensity, and σ is the variance determined from a least-squares fit of a Gaussian curve through the experimental data. The internal radius of the tubing was determined experimentally from the length of the tubing and the volume of solution eluted for a given retention time t after injection of our solute and by comparison with a literature standard.[39] Diffusion coefficients can be determined by this dispersion method so long as the condition ($t > 50\ r^2/3.8^2\ D_{ab}$) is met, where t is the retention time, r is the internal radius of the tubing, and D_{ab} is the diffusion coefficient of solute a in solvent b. For our experiment apparatus and diffusion coefficients greater than 0.25×10^{-5} cm^2/s, the retention time must be greater than 15 min. All diffusion data collected were for experimental retention time greater than 18 min, typically between 25 and 35 min.

Materials. Ethanol (100% Rossville Gold Shield) and 2-propanol (Aldrich Spectrophotometric >99.5%) were sparged with helium before and during the experiment. Benzophenone, acetophenone, diphenylmethanol, and sec-phenethyl alcohol were recrystallized. Benzaldehyde, benzyl alcohol, and p-hydroquinone were purchased from Aldrich and used as received.

Calculations. Molar volumes of the aryl alcohols where calculated with PC Model (Ver 7.00) from Serena Software and according to the methods of le Bas as discussed in Reid.[40]

Results and Discussion

Experimental Measurements of the Diffusion Coefficients by Dispersion Methods. The experimental diffusion coefficient $D_{exp/TD}$ of diphenylmethanol, sec-phenethyl alcohol, benzyl alcohol, 9-hydroxyxanthene, hydroquinone, benzophenone, acetophenone, and benzaldehyde measured by the Taylor's dispersion method (TD) in ethyl- and isopropyl alcohol are summarized in Table 1. Several observations are notable. It is immediately apparent that $D_{exp/TD}$ of the stable aryl alcohols (ArCH(OH)R) are significantly slower than $D_{exp/TD}$ of the

TABLE 1: Comparison of the Experimental Diffusion Coefficient ($D_{Exp/TD}$) Measured by Taylor's Dispersion Method with the Diffusion Coefficient Estimated by the Methods of Spernol and Wirtz (D_{SW}) and Wilke and Chang (D_{WCh}), and the Diffusion Coefficient Determined by TG ($D_{Exp/TG}$) in Isopropyl Alcohol at 21 °C

solvent IPA	solute	$\times 10^{-5}$ cm^2/s							TG/TD[d] (%)
		D_{TD}	D_{TG}[a]	D_{sw}	D_{WCh}	D_{WCh*}[b]	pK_a	exp/lit[c] (%)	
	benzophenone	0.56	0.68	0.49				8	
	diphenylmethanol	0.37		0.51	0.37	0.34			11
	ketyl radical		0.33				9.25		
	acetophenone	0.76	0.98	0.61				7	
	s-phenethyl alcohol	0.44		0.60	0.47	0.43			23
	ketyl radical		0.34				10.1		
	benzaldehyde	0.80	0.99	0.63	0.54	0.49		−9	
	benzyl alcohol	0.45		0.60	0.52	0.47			18
	ketyl radical		0.37				10.5		
	xanthone	0.49	0.68				-	−4	
	hydroxy xanthene	0.38							
	ketyl radical		0.31						18
			0.36[e]						4
	benzoquinone	0.94							
	hydroquinone	0.28		0.48	0.56	0.52			−29
	ketyl radical		0.36						

[a] From refs 18 and 25. [b] Molar volumes from PC Model (Ver 7.00). [c] Ratio of aryl ketone literature value ref 7 to experimental value determined in this work. [d] $(D_{TD} - D_x)/D_{TD}$. [e] New reevaluated diffusion coefficient, ref 14.

corresponding aryl ketones (ArC(═O)R), even though there is little difference in molecular size. The ratio of the diffusion coefficients of the aryl ketones determined by Donkers and Leaist and the values measured in this work are the same within experimental error. Likewise, there is little difference between the diffusion coefficient of the aryl alcohols determined by the dispersion method, $D_{exp/TD}$ (ArC(OH)R), and the diffusion coefficient of the corresponding ketyl radicals determined by the TG method, $D_{exp/TG}$ (ArC(•)(OH)R), suggesting that the diffusion coefficients of the ketyl radical and the corresponding alcohols are the same within experimental error.[41] Of special significance is a comparison of our measured diffusion coefficient of hydroquinone with the reported TG value for the ketyl radical, benzosemiquione (BQH$^•$) formed from irradiation of benzoquinone in ethyl- or isopropyl alcohol.[18] Diffusion of hydroquinone in both ethyl- and isopropyl alcohol is slower than the diffusion of corresponding ketyl radical BHQ$^•$. If p-hydroquinone is used as a model, we would assume that ketyl radicals diffuse faster (not slower) than this parent compound.

A recent reevaluation of the diffusion coefficient of the ketyl radical of xanthone measured by TG methods suggested that the approach of fitting a double exponential TG signal yields consistently low values for the ketyl radical diffusion coefficient.[14] When experimental values for the corresponding ketones were used in the fitting analysis, the diffusion coefficient of the ketyl radical of xanthone increased from 0.31 to 0.36 $\times 10^{-5}$ cm^2/s (an increase of ca. 14%). Our experimental value for the corresponding alcohol, 9-hydroxyxanthene, 0.38 ± 0.02 $\times 10^{-5}$ cm^2/s compares quite favorably with the reevaluated diffusion coefficient.

We suggest that hydrogen bonding between the alcohol (or ketyl radical) and the solvent attenuates the rate of diffusion through solvents containing hydroxylic substituents. The rate of diffusion of p-hydroquinone is slower because of an additional hydroxyl group not present in the BHQ$^•$ ketyl radical. If hydrogen bonding does affect diffusion, then we would expect that the corresponding alcohol (ArCH(OH)R) would be a better model for the ketyl radical (ArC(•)(OH)R) than the corresponding ketone (ArC(═O)R) in experimental dispersion measurements. This approach of using an alcohol to model the diffusion coefficient of a ketyl radical is consistent with the approach of Lehni and Fischer.[9] Of direct relevance is their suggestion that the isopropyl ketyl radical does hydrogen bond with the hydroxylic solvent, and the hydrogen-bonding interaction between the ketyl radical and the hydroxylic solvent is no different than the interaction expected from isopropyl alcohol and the hydroxylic solvent. They propose that isopropyl ketyl radical and 2-propanol undergo comparable hydrogen-bonding interactions with associating solvents, e.g., 2-butanol, 3-methylpentanol, and 2-propanol. They used the measured diffusion coefficients of 2-propanol in a series of associating solvents to accurately model the observed rate of self-termination of isopropyl ketyl radical. Another trend that does not appear consistent with the radical solvent interaction is the comparison of the stable radical TEMPO (>N−O$^•$) with the reduced model TEMP (>N−H).[16] In hydroxylic solvents, the radical diffuses faster, not slower, than the model! However, if hydrogen bonding of the solute with the solvent is important, then the TEMP would be expected to diffuse slower, consistent with the experimental observation.

The diffusion-coefficient measurements of the aryl alcohols measured in this work and the diffusion-coefficient measurements of the aryl ketyls measured by TG methods[18] are consistent with hydrogen bonding between the solute and the solvent. The presence of a hydroxyl group in both the aryl alcohol and the aryl ketyl measurably decreases the rate of diffusion in hydroxylic solvents compared to a model compound without a hydroxyl substituent, i.e., the corresponding aryl ketone. In general, the more basic (and less polarizable) the acceptor, the stronger the hydrogen bond with a hydrogen-bond donor (HBD) (the hydroxylic solvent). The parent ketone is a weaker base (R═OH$^+$) (and more polarizable) than the corresponding alcohol (ROH$_2^+$)[42] and consequently, the hydrogen-bonding interaction of the ketone with the hydroxylic solvent is lower than either the alcohol or ketyl radical. In general, the hydrogen-bonding potential of a donor is proportional to the pK_a of the HBD. If true for ketyl radicals, benzaldehyde ketyl radical (pK_a = 10.5)[43] will form a stronger hydrogen bond with a hydroxylic solvent than benzyl alcohol (pK_a = 15.4).[44]

Empirical Methods to Estimate Diffusion Coefficients. Given the present experimental results and conventional chemical intuition suggest that ArCH(OH)R is an improved model for ArC(•)(OH)R diffusion measurements, we undertook a comparison of two different empirical methods to estimate diffusion coefficients. Empirical calculations offer an attractive alternative for estimating diffusion coefficients of transient radical species. A variety of prescriptions to estimate the diffusion of radicals in various solvents has been critically examined.[11] In general, two adjustments must be considered to correct for the observed deviations from the hydrodynamic Stokes–Einstein diffusion model: (1) a correction for sizes and/or molecular weights of both the solvent and the solute and (2) a correction for the interactions of the solute with the solvent. The SW prescription, shown in eq 3, employs an empirically derived microfriction factor to correct the hydrodynamic Stokes–Einstein diffusion coefficient for differences between the solute and solvent molecular size

$$D_{\mathrm{SW}} = (T/\eta)\ (k/6\pi\ r_{\mathrm{a}}\ f) \tag{3}$$

where (T/η) is the ratio of temperature to solvent viscosity, k is Boltzman's constant, r_{a} is the molecular radius of the solute, and f is a microfriction factor. Associative interactions between solute and solvent are assumed negligible in the SW treatment. On the other hand, WCh[26] derived an empirical recipe to account for the interactions between solutes and hydroxylic solvents as shown in eq 4

$$D_{\mathrm{WCh}} = (T/\eta)(7.4 \times 10^{-10}\ V_{\mathrm{A}}^{\ -0.6}\ \kappa_{\mathrm{B}} M_{\mathrm{B}})^{1/2} \tag{4}$$

where V_{A} is the le Bas molar volume of the solute, κ_{B} is a solvent-specific association parameter,[45] and M_{B} is the solvent molecular. The association parameter is used to yield an effective solvent molecular weight. This treatment suggests that hydrogen-bonding solvents have a larger effective molecular volume with respect to diffusive properties. The WCh correction provided a satisfactory correlation with experimental determinations of greater than 80 stable molecules in a variety of solvents, including methanol and ethanol; however, none of the solutes investigated contained hydroxylic substituents.[26] The empirical corrections suggested by Gainer and Metzner (GM)[46] provide a more universal approach to account for both hydroxylic solvents and solutes. The GM recipe uses an exponential correction to account for differences in activation energies of diffusion and viscosity using experimental enthalpies of vaporization for the solvent and solutes. However, the lack of experimental enthalpies of vaporization for a significant number of aryl alcohols limited our ability to critically examine the GM approach.

The estimated diffusion coefficients using the methods of Spernol Wirtz (D_{SW}) and Wilke and Chang (D_{WCh}) are shown in Table 1 with the experimental data. D_{sw} of both the ketone (ArC(=O)R) and the alcohol (ArCH(OH)R) are quite similar, as expected, for a model that accounts for molecular size differences and not solvent–solute interactions. On the other hand, the SW calculated values for the aryl alcohols are consistently higher (overestimate) the diffusion coefficient of the aryl alcohols. This is likely due to the inability of the SW recipe to account for the hydrogen-bonding interactions between the solute and the solvent. We used two different methods, the le Bas and the PC Model, to calculate the solute molecular volume in our estimate of D_{WCh}. In the original WCh work, the le Bas molar volumes were used; however, in this work, we found that molecular volumes calculated with the PC Model provided better agreement with experimental results. As a control and to further test the WCh recipe, we compared the D_{WCh} estimates for the corresponding ketones and alcohols and found little difference. The agreement between the PC Model/WCh recipe and the experiment diffusion coefficients of ArCH(OH)R may be fortuitous and suggests that further development of empirical methods to account for hydroxylic solute molecules in hydroxylic solvents is warranted.

Recent efforts in molecular dynamics (MD) methods to understand the effects of solvent–solute interactions on diffusion have provided theoretical determinations to be compared with experimental measurements of diffusion coefficients for pyrazine and the pyrazinyl radical in polar solvents.[19–21] We expect that a MD model that would account for hydrogen-bonding interactions between the radical and an alcoholic solvent would also show slower diffusion of the radical relative to the parent pyrazine. Tominaga and co-workers[22] have developed an empirical approach to estimate the effective volume (V_{eff}) of cyclohexanol derivatives in ethanol. Their analysis suggests that two ethanol solvent molecules may be hydrogen bound to one cyclohexanol solute molecule. The greater the effective volume (proportional to *effective* radius), the slower the diffusion coefficient as expected from the SW modified Stokes–Einstein equation (eq 3).

Analysis of the Origin of the Slow Diffusion. The authors of recent theoretical work note that a remarkable difference exists in diffusion coefficient between the ketone and the ketyl radical, given that the structures only differed by one hydrogen atom.[20] We agree, in fact, that one should expect an enormous difference in many physical and chemical properties, especially the properties that depend on hydrogen-bonding interactions. In most cases, when a hydrogen atom is attached to a heteroatom, it has the capability to form hydrogen bonds; we see no reason to assume otherwise for a ketyl radical in light of the absence of any arguments to the contrary.

Tominaga and co-workers[22] found the diffusion coefficient of cyclohexanol to be ca. 35% slower than the diffusion coefficient of cyclohexanone in ethanol and ca. 50% slower in hexanol. They argued that the diffusion of the alcohol was slower than the ketone because of hydrogen bonding of the hydroxyl group with the solvent. One of the most interesting findings of their work was the difference between the diffusion coefficients of 1,2- and 1,4-cyclohexanediols. The 1,2-cyclohexanediol was faster than the diffusion of the 1,4-cyclohexanediol because the intramolecular hydrogen bonding in the 1,2-diol limited the hydrogen-bonding interaction with the solvent. This observation suggests that if the ketyl radical of δ-methoxyvalerophenone ($\mathrm{PhC^{\bullet}(OH)CH_2CH_2XCH_3}$, X = oxygen) was investigated by TG methods, then the diffusion coefficient could be observed to be measurably faster than the corresponding alkyl derivative ($\mathrm{X = CH_2}$) because of intramolecular hydrogen bonding. If the interaction between the ketyl radical and the solvent is caused by an electronic sensitivity, then the two solutes would be predicted to diffuse with comparable rates.

If the pK_{a} is an indication of the HBD capability of the solute, then the ketyl radical could form a stronger hydrogen bond with the hydroxylic solvent than the corresponding aryl alcohols. Examining the trends in Tables 1 and 2 could lead one to conclude that the diffusion of the ketyl radical is measurably less than the corresponding parent alcohol, i.e., because they form stronger hydrogen bonds with the solvent. However, it has recently been reported that when the TG data are reevaluated with an independent measure of the parent ketone diffusion coefficient, the originally cited values of the radical diffusion increase by ca. 7–17%.[14] The only reevaluated diffusion coefficient that we can directly compare is 9-hydroxyxanthene and the ketyl radical derived from irradiation of xanthone. In this case, the diffusion coefficient of the ketyl radical and the aryl alcohol are the same. If the other ketyl radicals respond accordingly, then it could be argued that the diffusion coefficient

TABLE 2: Comparison of the Experimental Diffusion Coefficient ($D_{\mathrm{Exp/TD}}$) Measured by Taylor's Dispersion Method with the Diffusion Coefficient Estimated by the Methods of Spernol and Wirtz (D_{SW}) and Wilke and Chang (D_{WCh}), and the Diffusion Coefficient Determined by TG ($D_{\mathrm{Exp/TG}}$) in Ethyl Alcohol at 21 °C

solvent EtOH	solute	$\times 10^{-5}$ cm^2/s							
		D_{TD}	D_{TG}[a]	D_{sw}	D_{WCh}	$D_{\mathrm{WCh*}}$[b]	pK_a	exp/lit[c] (%)	TG/TD[d] (%)
	benzophenone	0.93	1.00	0.96			-	8	
	diphenylmethanol	0.64		1.06	0.61	0.56			14
	ketyl radical		0.55				9.25		
	acetophenone	1.19	1.3	1.25			-	3	
	s-phenethyl alcohol	0.78		1.26	0.78	0.71			26
	ketyl radical		0.58				10.1		
	benzaldehyde	1.31	1.5	1.27			-	17	
	benzyl alcohol	0.82		1.26	0.86	0.78			20
	ketyl radical		0.66				10.5		
	benzoquinone								
	hydroquinone	0.62		0.94	0.92	0.57			8
	ketyl radical		0.57						

[a] From refs 18 and 25. [b] Molar volumes from PC Model (Ver 7.00). [c] Ratio of aryl ketone literature value, ref 7, to experimental value determined in this work. [d] $(D_{\mathrm{TD}} - D_x)/D_{\mathrm{TD}}$.

of the ketyl radical and the corresponding alcohol are the same. We are ready to concede that the diffusion coefficient of the ketyl radical may be measurably slower than the corresponding alcohol because we suspect that the hydrogen bond formed between the ketyl radical and the solvent may be even greater than the hydrogen bond formed between the aryl alcohol and the solvent. However, because the *slow* diffusion rate of the ketyl radical is relative and importantly-it is not unexpected-there is little need to invoke a special interaction between the radical and the solvent; hydrogen bonding between the ketyl radical and the hydroxylic solvents is sufficient to explain the observed results.

Conclusions

We have provided arguments that no anomalous interaction occurs between aryl ketyls and hydroxylic solvents. The diffusion of ketyl radicals is slower than the diffusion of the parent ketones because the ketyl radicals are expected to be good HBDs and ketones are not. We have also provided arguments that aryl alcohols ArCH(OH)R are significantly better models than ketones Ar(C═O)R for comparing diffusion coefficients with the corresponding ketyl radicals ArC(•)(OH)R. The diffusion coefficients of aryl alcohols examined in this work measured by dispersion techniques compare favorably to the diffusion coefficients of the corresponding ketyl radicals measured by TG techniques. We believe that the agreement will become even greater when the previous experimental results[17] are reevaluated[14] using experimental values for the aryl ketones. We have no reason to doubt the accuracy of the TG method to measure the diffusion coefficient of the ketyl radical when the data are fit using experimental measured diffusion coefficients for the parent precursor molecule. These results strongly suggest that little difference exists in the interaction between the radical and the corresponding alcohol with hydroxylic solvents. Consequently, the diffusion of ketyl radicals in hydroxylic 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.

Acknowledgment. Support for this work from the Office of Science, Office of Basic Energy Sciences, U.S. Department of Energy is gratefully acknowledged. The work was conducted at Pacific Northwest National Laboratory, which is operated for the U. S. Department of Energy by Battelle under Contract No. DE-ACO6-76RL0 1830. Support for P.K. was provided through AWU−NW under grant DE-FG06-89ER-75522 with the U.S. Department of Energy. Tom Autrey thanks Derek Hopkins and John Price of the Environmental Molecular Science Laboratory for providing the data-acquisition software.

References and Notes

(1) Huang, Y.; Page, D.; Wayner, D. D. M.; Mulder, P. *Can. J. Chem.* **1995**, *73*, 2079.
(2) Scaiano, J. C.; Netto-Ferreira, J. C.; Wintgens, V. *J. Photochem. Photobiol. A: Chem.* **1991**, *59*, 265.
(3) Autrey, S. T.; Alnajjar, M. S.; Nelson, D. A.; Franz, J. A. *J. Org. Chem.* **1991**, *56*, 2197.
(4) Franz, J. A.; Bushaw, B. A.; Alnajjar, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 268.
(5) Franz, J. A.; Linehan, J. C.; Birnbaum, J. C.; Hicks, K. W.; Alnajjar, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 9824.
(6) Okamoto, K.; Hirota, N.; Terazima, M. *J. Phys. Chem. A* **1997**, *101*, 5269.
(7) Donkers, R. L.; Leaist, D. G. *J. Phys. Chem. B* **1997**, *101*, 304.
(8) Saltiel, J. A.; Atwater, B. W. *Advances in Photochemistry*; Wiley-Interscience: New York, 1988, Vol. 14.
(9) Lehni, M.; Fischer, H. *Int. J. Chem. Kinetics* **1983**, *15*, 733.
(10) Fischer, H.; Paul, H. *Acc. Chem. Res.* **1987**, *20*, 200.
(11) Schuh, H.-H.; Fischer, H. *Helvetica Chimica Acta* **1978**, *61*, 2130.
(12) Huggenberger, C.; Lipscher, J.; Fischer, H. *J. Phys. Chem.* **1980**, *84*, 3467.
(13) Munger, K.; Fischer, H. *Int. J. Chem. Kinet.* **1984**, *16*, 1213.
(14) Okamoto, K.; Hirota, N.; Terazima, M. *J. Phys. Chem.* **1997**, *101*, 5380.
(15) Terazima, M. *Res. Chem. Intermed.* **1997**, *23*, 853.
(16) Terazima, M.; Tenma, S.; Watanabe, H.; Tominaga, T. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3057.
(17) Terazima, M. *Acc. Chem. Res.* **2000**, *33*, 687.
(18) Terazima, M.; Okamoto, K.; Hirota, N. *J. Chem. Phys.* **1995**, *102*, 2506.
(19) Morita, A.; Kato, S. *J. Chem. Phys.* **1998**, *108*, 6809.
(20) Morita, A.; Kato, S. *J. Am. Chem. Soc.* **1997**, *119*, 4021.
(21) Biswas, R.; Bhattacharyya, S.; Bagchi, B. *J. Phys. Chem. B.* **1998**, *102*, 3252.
(22) Tominaga, T.; Tenma, S.; Watanabe, H. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1863.
(23) Chan, M. L.; Chan, T. C. *J. Phys. Chem.* **1995**, *99*, 5765.
(24) Taylor, S. G. *Proc. R. Soc. London A* **1953**, *219*, 186.
(25) Terazima, M.; Okamoto, K.; Hirota, N. *J. Phys. Chem.* **1993**, *97*, 13 387.
(26) Wilke, C. R.; Chang, P. *A. I. Ch. E. J.* **1955**, *June*, 264.
(27) Spernol, V. A.; Wirtz, K. *Naturforsch. A* **1953**, *8*, 522.
(28) Wagner, P. J. *Acc. Chem. Res.* **1989**, *22*, 83.
(29) Wagner, P. J.; Giri, B. P.; Scaiano, J. C.; Ward, D. L.; Gabe, E.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 5483.
(30) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.
(31) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 5898.
(32) Scaiano, J. C. *Acc. Che. Res* **1982**, *15*, 252.
(33) Caldwell, R. A.; Majima, T.; Pac, C. *J. Am. Chem. Soc.* **1982**, *104*, 629.
(34) Kanabus-Kaminska, J. M.; Gilbert, B. C.; Griller, D. *J. Am. Chem. Soc.* **1989**, *111*, 3311.

(35) Laarhoven, L. J. J.; Mulder, P.; Wayner, D. D. M. *Acc. Chem. Res.* **1999**, *32*, 342.

(36) Pratt, K. C.; Wakeham, W. A. *Proc. R. Soc. London A* **1975**, *342*, 401.

(37) Pratt, K. C.; Wakeham, W. A. *J. Chem Soc., Faraday Trans. 2* **1977**, *73*, 997.

(38) Alnajjar, M. S.; Garrossian, M. S.; Autrey, S. T.; Ferris, K. F.; Franz, J. A. *J. Phys. Chem.* **1992**, *96*, 7037.

(39) This method of measuring the ID of the tubing is preferrable to using the manufacture stated ID. When we used the ID specified by the manufacturer, we obtained lower diffusion coefficient values. With our experimental measured ID, we obtained good agreement for the ketone diffusion coefficients with the values reported by Donkers and Leaist in ref 7. We thank a referee for pointing this out.

(40) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.

(41) The transient grating measurements of a few representive radicals have recently be adjusted upwards between 7 and 17%.

(42) Deno, N. C.; Wisotsky; Max, J. *J. Am. Chem. Soc.* **1963**, *85*, 1735.

(43) Hayon, E.; Ibata, T.; Lichtin, N. N.; Simic, M. *J. Phys. Chem.* **1972**, *76*, 2072.

(44) Stewart, R. *Organic Chemistry*; Academic Press: New York, 1985; Vol. 46.

(45) k_b is 1 for nonassociating solvents, 1.5 for ethanol, and ca. 1.7 for 2-propanol.

(46) Gainer, J. L.; Metzner, A. B. *A. I. Ch. E.-I. Chem. E.* **1965**, *Symposium Series No. 6*, 74.