Frictional effects on barrier crossing in solution: Comparison with the Kramers' equation

Robert M. Bowman and Kenneth B. Eisenthal
Department of Chemistry, Columbia University, New York, New York 10027
David P. Millar
Research Institute of the Scripps Clinic, Department of Molecular Biology, La Jolla, California 92307

(Received 15 January 1988; accepted 5 April 1988)

In our efforts to examine the validity of the Kramers' equation, the rate constants of the excited state isomerization of 1,1′-binaphthyl in *n*-alkane solvents were measured at room temperature using picosecond spectroscopy. These data, and data measured previously in *n*-alcohols, were compared with Kramers' model using two forms for the friction. When a hydrodynamic model for the friction was used, good agreement was found for the alcohol data only. When the isomerization friction is assumed to scale linearly with the friction for overall reorientational motion, we find excellent agreement for both the alcohol and alkane solvents. In addition, the friction in alkanes is found to be considerably larger than that of alcohols of comparable viscosity. This provides a direct indication that the molecular aspects of the solute–solvent interaction play a role in the barrier crossing process.

INTRODUCTION

The dynamics of unimolecular reactions in the condensed phase differ fundamentally from the gas phase by virtue of the coupling of reactive motion to the medium degrees of freedom. The coupling is manifested in the dependence of the reaction rate on the transport properties of the medium, such as shear viscosity. A question of current interest concerns the applicability of stochastic models,[1–14] such as Kramers' model[1,2] in describing the reactant–medium coupling.

In the Kramers' model the motion of a particle in a one-dimensional potential coupled to a heat bath is considered. The escape of the particle over a barrier in the potential constitutes the reaction. The particle–bath coupling is described by two related contributions: a random fluctuating force acting on the particle, which describes the stochastic features of the particle–bath interaction, and a frictional force obtained from a systematic effect of the fluctuating forces that retards the particle. The result of these coupling mechanisms on the particle motion consists of two mutually opposing effects, the activation of the particle to the barrier region by bath–particle energy transfer, and the retarding effect of diffusional recrossings of the barrier. The interplay of these effects leads to a nonmonotonic dependence of the reaction rate on friction. In condensed phases, however, the recrossing effect is usually dominant and the rate decreases with increasing friction. Kramers' solution of the problem in this latter regime, i.e., where energy activation to the top of the barrier is not rate limiting, yielded the justly celebrated equation known by his name.

To experimentally test the Kramers' model or any model of chemical reaction in dense media, it is necessary to compare the measured rate constants with measured values of the coupling of the medium to the reaction coordinate(s). In the Kramers' model the solute–solvent interaction is contained in the static friction constant. Since we do not know how to measure the friction experienced by motion along the reaction coordinate we must adopt some model of the friction which can be related to measurable quantities. We note therefore that to carry out a meaningful test of the Kramers' model requires a realistic model of the friction. At the present time there is no general satisfactory frictional model and indeed this is an area of active research. We therefore must proceed with caution since we are using frictional models to test the Kramers' equation.

One model that has had some success in describing molecular motions in liquids is a hydrodynamic formulation of the friction, wherein the friction for the reactive motion is expressed in terms of the solvent shear viscosity, the solute size and shape, and the boundary conditions of the solute–solvent interaction, e.g., slip or stick. A common experimental approach based on this friction/viscosity connection is to measure the reaction kinetics at different viscosities. These different viscosities can be obtained by changing the pressure on a single solvent,[15] or by using the different members of a solvent family, e.g., *n*-alcohols. A number of picosecond laser studies of the photoisomerization dynamics of large molecules like 1,1′-binaphthyl (1,1′-BN),[16,17] diphenylbutadiene (DPB),[18,19] *trans*-stilbene,[20,23] among others[24–28] have been carried out in this latter way. In attempting to fit the viscosity dependence of the photoisomerization rate with Kramers' equation using static (frequency independent) hydrodynamic friction, deviations were noted for *t*-stilbene,[21] DPB,[18] and DODCI,[29] whereas we found excellent agreement for the photoisomerization of 1,1′-BN in alcohol solvents.[17] This latter result for 1,1′-BN supports the Kramers' model and possibly the validity of the hydrodynamic approximation. We cannot be more definitive on this latter point since a linear dependence of friction on viscosity does not establish that the friction experienced in the motion is due to hydrodynamic contributions alone.[3,31]

0021-9606/88/140762-08$02.10 © 1988 American Institute of Physics

Downloaded 09 Apr 2005 to 128.59.115.179. Redistribution subject to AIP license or copyright, see http://jcp.aip.org/jcp/copyright.jsp

The principal ideas that have been proposed to explain the deviations from Kramers' behavior are multidimensional effects and non-Markovian behavior, i.e., a frequency dependent friction that expresses a time correlation, or memory, in the solvent forces acting on the isomerizing molecule.[4,10,32] For 1,1'-BN, the torsional motion is very nearly one-dimensional. On the other hand, molecules like *t*-stilbene and DPB most certainly experience multidimensional effects because of their more complicated motions, i.e., bond breakage accompanying the isomerization. This could cause the coupling of other motions into the twisting motion, resulting in the breakdown in Kramers' one-dimensional approximation. Unlike multidimensional effects, if non-Markovian effects were important they would be equally likely in all of these molecules since they all have relatively high barrier frequencies. Yet, 1,1'-BN agrees quite well with the Kramers' picture.

To further explore the issues we have extended our studies of 1,1'-BN beyond alcohols, the single success of the Kramers' model, to alkanes, a solvent class that is considerably different from alcohols. We also report on our results based on an idea proposed by Fleming and co-workers[29] and Hochstrasser and co-workers,[22] that the isomerization friction be approximated by the friction acting on the rotational motion of the whole molecule. We can utilize this idea in the present work since the reorientation friction for rotational diffusion is directly related to the solute reorientation time. This latter relation taken together with the aforementioned idea allows the isomerization friction to be estimated from a separately measured quantity, the orientational relaxation time, free of the assumptions of a particular frictional model, e.g., a hydrodynamic one. It is of course to be noted that this approach substitutes one assumption for another and will be judged in terms of its successful application to experimental results.

EXPERIMENTAL

The technique and apparatus employed in measuring the kinetics of 1'1-BN isomerization have been described in detail in our previous work[17] and will only be briefly described here, except where differences exist in the present configuration.

Picosecond pulses were generated by a synchronously mode-locked, cavity-dumped Rhodamine 6G laser pumped by an actively mode-locked CW Argon laser. The dye laser repetition rate was 2.1 MHz. A second beam waist in the dye laser cavity was located in a jet stream of the saturable absorber DODCI and resulted in shorter pulse durations and suppression of satellite pulses. The pulse duration was determined by SHG autocorrelation[33] to be 2.5 ps. The laser wavelength was 615 nm.

A portion of the laser output was frequency doubled in a $LiIO_3$ crystal to produce pump pulses at 307.5 nm for excitation of 1,1'-BN to the S_1 excited state. The time course of the excited state isomerization was monitored by transient absorption of a time-delayed 615 nm probe pulse, which detects via an $S_1 \rightarrow S_n$ transition the population of excited molecules that have isomerized. The pump and probe linear polarization directions were orthogonal, since this configuration was most sensitive to the absorption change associated with isomerization.[16,17] The 5×10^{-3} M solution of 1,1'-BN flowed through a 1mm path length cuvette. The pump beam was modulated at kHz frequencies by a mechanical chopper and the resultant probe intensity modulation, due to transient absorption induced by the pump, was detected by a photodiode and lock-in amplifier. Under the low excitation intensity conditions of this experiment, the lock-in output was directly proportional to the absorbance change. The lock-in output was acquired by a microcomputer which also controlled the probe pulse delay. The data were averaged by repetitive scans of the delay interval.

The reorientation dynamics of 1,1'-BN were investigated by picosecond polarization spectroscopy.[34] Flowing solutions of the 1,1'-BN were excited with a linearly polarized UV pump pulse and probed by a visible pulse, as before. In this experiment, however, the probe was initially polarized at 45° to the pump and, after passage through the sample, the intensity of the probe passed by a polarizer that was crossed with the initial probe polarization was detected as function of probe delay time. To avoid errors that can arise due to birefringent optics,[35] we carefully tested our optical components and used high extinction polarizers (10^{-6}–10^{-7}). To further insure the validity of the rotation times obtained we note, that in all of our previous studies, the rotation times obtained by measuring the transmitted parallel and perpendicular components are the same as found by the crossed polarizer method used here. In the absence of birefringence effects, this signal is proportional to the square of the dichroism associated with the transient absorption. At delay time t the signal is

$$S(t) = \text{const}[r(t)p(t)]^2, \qquad (1)$$

where $r(t)$ is the absorption anisotropy and $p(t)$ describes the time dependence of the excited-state population. The anisotropy is proportional to the dipole correlation function associated with overall motion,[36]

$$r(t) = 0.4\langle P_2[\hat{\mu}(0)\cdot\hat{\mu}(t)]\rangle. \qquad (2)$$

All experiments were performed at 20 °C. Alcohol and alkane solvents were distilled prior to use. Solvent shear viscosities were obtained from standard tables.[37]

Isomerization on the S_1 excited state potential surface was monitored by $S_1 \rightarrow S_n$ transient absorption. The form of the transient absorption signals and their analysis have been considered in detail in our previous work.[16,17] Since the pump and probe polarization directions were orthogonal, it was necessary to also consider the influence of anisotropic absorption and overall molecular reorientation on the kinetics of the transient absorption. Magic angle polarization, which suppresses this additional time dependence, could not be used since the transient absorption component associated with isomerization became too small for accurate measurement.[16,17] In the alcohol solvents overall reorientation of 1,1'-binaphthyl was much slower than isomerization and its effect on the transient absorption kinetics was minor. However, in the alkane solvents overall reorientation was faster and its effect on the rise time of transient absorption should be considered. In this case it can be shown that transient absorption follows an equation of the form[35]

Downloaded 09 Apr 2005 to 128.59.115.179. Redistribution subject to AIP license or copyright, see http://jcp.aip.org/jcp/copyright.jsp

$$A(t) = a(1 - ce^{-t/\tau_{\rm iso}})(1 + 0.2e^{-t/\tau_{\rm or}}) , \tag{3}$$

where a is an amplitude parameter and c is the fraction of the amplitude due to the slowly rising component of transient absorption, i.e., the part associated with the isomerization. The pump and probe transitions have orthogonal polarization.[16] This equation only considers the slowly rising component and is valid for time after the fast rise is complete ($\geqslant 3$ ps). Equation (3) was fitted to the transient absorption curves using the $\tau_{\rm or}$ value measured for the same solvent and adjusting $\tau_{\rm iso}$ to achieve the best fit. Excellent fits were achieved in all cases. The Marquardt gradient-expansion algorithm[38] was used in abstracting both the isomerization and rotation times. The results are presented in Table I. The isomerization times of 1,1'-binaphthyl in alcohols have previously been presented by us, and are reanalyzed in this paper. The data for alkane solvents have not been reported previously.

COMPARISON WITH KRAMERS' MODEL USING HYDRODYNAMIC FRICTION

In the intermediate and high friction regimes, which are relevant to solution phase isomerization, the Kramers' expression for the reaction rate is[1]

$$k = \frac{Z^\ddagger}{Z'} \frac{\omega}{2\pi\omega'} [(\beta^2/4 + \omega'^2)^{1/2} - \beta/2] e^{-Q/k_BT} , \tag{4}$$

where $Z^\ddagger$ and Z' are partition functions evaluated at the barrier and well, respectively, with the reaction coordinate removed, ω and ω' are the frequency of the well and barrier, respectively, Q is the barrier height, and $\beta = \xi_{\rm iso}/I_{\rm iso}$ is the reduced isomerization friction. $\xi_{\rm iso}$ is the isomerization friction and $I_{\rm iso}$ is the moment of inertia for isomerization. For 1,1'-binaphthyl $I_{\rm iso} = 9.84 \times 10^{-45}$ kg m^2.[3,17]

To analyze our data in terms of the Kramers' equation the isomerization friction in each solvent must be known. One way to do this, as we noted earlier is to use a hydrodynamic model. For this case the isomerization friction is related to the measurable solvent shear viscosity η by the following equation[3,39]:

$$\xi_{\rm iso} = 4\pi\eta d r^2 , \tag{5}$$

where for the case of 1,1'-binaphthyl d is the radius of a naphthyl group approximated as a sphere, and r is the radius of gyration. A slip boundary condition is assumed. Using this hydrodynamic relation, the Kramers' rate can be calculated as a function of solvent shear viscosity and fitted to the experimental data.

FITTING OF ALCOHOL DATA USING HYDRODYNAMIC FRICTION

For isomerization of 1,1'-binaphthyl and alcohol solvents, we have shown that excellent agreement with the Kramers' model is obtained when Eq. (5) is used, a two parameter fit of the viscosity dependence of the isomerization rate is shown in Fig. 1. The two parameters are

$$\frac{Z^\ddagger}{Z'} \frac{\omega}{2\pi} e^{-Q/k_BT} \tag{6}$$

and

$$\frac{2\pi d r^2}{\omega' I_{\rm iso}} . \tag{7}$$

To extract molecular information from the parameters we assume that $Z^\ddagger$ equals Z', which is reasonable if there are no large frequency shifts in the vibrational modes. For the case of 1,1'-BN the absorption spectroscopy and the emission at low temperatures indicate that the naphthalene chromophores are weakly interacting in the reactant configuration which supports the approximation that $Z^\ddagger$ equals Z'. For the torsional mode ω we use the value of 5.7 ps^{-1} obtained experimentally from the fluorescence excitation spectrum of 1,1'-BN in a supersonic jet.[40] Using these approximations we find that the first parameter yields the barrier height Q. The value of 460 cm^{-1} obtained is in good agreement with a value of 480 cm^{-1} obtained from spectroscopic data.[41] For

TABLE I. Reorientation and isomerization times of 1,1'-binaphthyl.

Solvent	Viscosity (cP)	$\tau_{\rm or}$ (ps)	$\tau_{\rm iso}$ (ps)
Ethanol	1.08	61 ± 4	12.2 ± 1.0
n-Propanol	2.23	98 ± 5	13.9 ± 1.0
n-Butanol	2.95	113 ± 8	15.0 ± 1.0
n-Pentanol	4.33	156 ± 8	17.6 ± 1.0
n-Hexanol	5.27	176 ± 17	19.2 ± 1.0
n-Heptanol	6.90	255 ± 17	24.0 ± 2.0
n-Octanol	8.95	325 ± 23	27.0 ± 2.0
n-Pentane	0.227	27 ± 2	12.2 ± 1.1
n-Heptane	0.409	41 ± 2	16.0 ± 1.1
n-Octane	0.539	48 ± 2	17.9 ± 1.5
n-Decane	0.907	67 ± 4	19.6 ± 1.8
n-Dodecane	1.50	90 ± 3	29.2 ± 2.0
n-Tetradecane	2.18	119 ± 7	34.5 ± 3.6
n-Pentadecane	2.86	128 ± 8	36.1 ± 3.7
n-Hexadecane	3.44	167 ± 6	41.0 ± 3.0

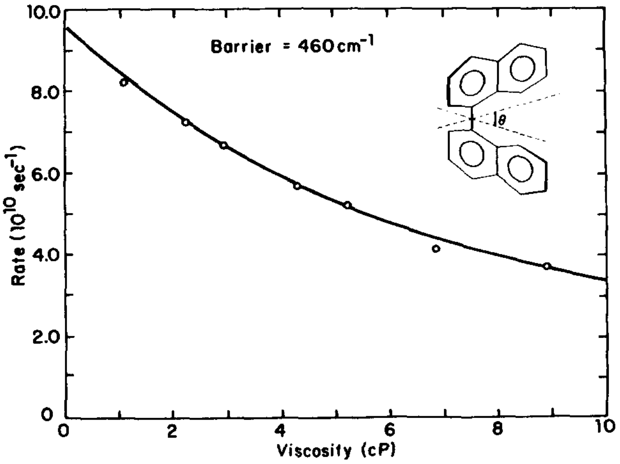

FIG. 1. Barrier crossing rate vs solvent shear viscosity in *n*-alcohols. The circles are experimental data. The line is the best fit of Kramers' equation, Eqs. (4) and (5). See the text for details.

Downloaded 09 Apr 2005 to 128.59.115.179. Redistribution subject to AIP license or copyright, see http://jcp.aip.org/jcp/copyright.jsp

the second parameter we use x-ray data from crystalline 1,1'-BN to obtain an $r = 1.2$ A and an $I_{\rm iso} = 9.8 \times 10^{-45}$ kg m^2. This leaves d and ω'. If we use for the radius of the naphthyl moiety, the value $d = 3.0$ Å, obtained from diffusion data for naphthalene in solution, we find that the barrier frequency ω' is 23 ps^{-1}. Alternatively we can assume that the potential is piecewise parabolic, an assumption which relates the values of Q and ω'. Proceeding in this way, the independent parameters are Q or ω', and d. This yields, as we found in our first paper, that for $Q = 460$ cm^{-1}, $\omega' = 22$ ps^{-1} and $d = 2.8$ Å. We thus see that either approach gives essentially the same results, which we note are physically reasonable. It is furthermore to be noted that although the barrier height Q is only about a factor 2.5 greater than $k_B T$ the validity of the rate constant law[6] still holds. This can be seen most clearly in the theoretical study[6] (see Fig. 6 of that paper) of isomerization dynamics where a barrier height of about 500 cm^{-1} yielded a plateau value for $k(t)$, i.e., one could still define a time independent rate constant. At a value of Q equal to 250 cm^{-1} the rate constant law was no longer applicable.

FITTING OF ALKANE DATA USING HYDRODYNAMIC FRICTION

The same fitting procedure used for the alcohols has been applied to the data for 1,1'-BN isomerization in alkanes, with the results shown in Fig. 2. We see that unlike the excellent agreement in alcohols, the Kramers' equation with hydrodynamic friction does not quantitatively fit the viscosity dependence of the isomerization rate in alkane solvents. As we noted earlier similar deviations were reported for isomerization of *t*-stilbene,[21] DPB,[18] and DODCI[29] when the Kramers' equation was used with hydrodynamic friction. The issue to be resolved, based on the results obtained for 1,1'-BN in alkanes, is whether it is the Kramers' model that is invalid, e.g., the failure of the assumption of a frequency independent friction, or the failure of the hydrodynamic model of the friction that we use in the Kramers' model.

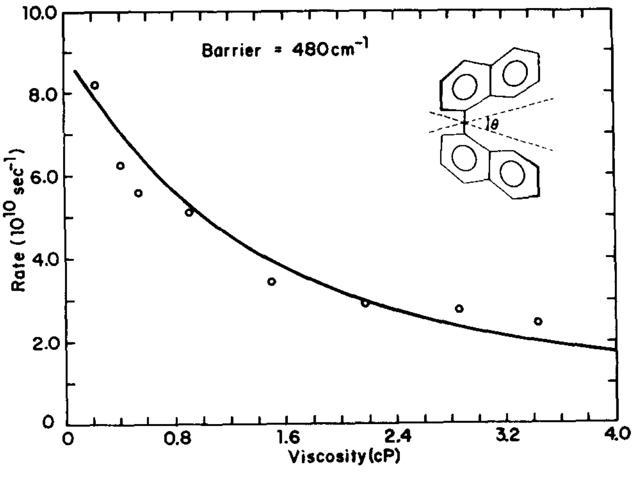

FIG. 2. Barrier crossing rate vs solvent shear viscosity in *n*-alkanes. The circles are experimental data. The line is the best fit of Kramers' equation, Eqs. (4) and (5). See the text for details.

COMPARISON WITH KRAMERS' MODEL USING REORIENTATIONAL FRICTION

To try to separate these possibilities we return to the idea that the isomerization friction is proportional to the reorientational friction, i.e., the friction experienced by the molecule in its overall rotational motion. This reorientational friction can be obtained in each solvent by measurement of the orientational relaxation time of 1,1'-binaphthyl in that solvent. An advantage of this approach is that it incorporates into the isomerization friction microscopic details that may be lacking in a particular friction model.

Following this approach we assume that the isomerization friction is linearly proportional to the overall friction

$$\xi_{\rm iso} = f\xi_{\rm or}\,, \tag{8}$$

where f is a proportionality constant that scales the generally different effectiveness of solute–solvent interactions in the isomerization motion with that for the overall rotational motion of the molecule. The next step is to relate the orientational friction with the measured reorientation time $\tau_{\rm or}$. Such a relationship, obtained by Hubbard[42] for a spherical particle in the rotational diffusion limit, is given by

$$\xi_{\rm or} = 6k_B T\tau_{\rm or} \tag{9}$$

(where k_B is Boltzmann's constant). The reduced friction β, appearing in Kramers' equation, can now be written

$$\beta = \frac{\xi_{\rm iso}}{I_{\rm iso}} = \frac{6k_B Tf\tau_{\rm or}}{I_{\rm iso}}\,. \tag{10}$$

This provides a model-independent estimate of the friction, although the absolute magnitude of the friction is uncertain to the extent that f is unknown. We note that f will also contain a correction for the nonspherical shape of 1,1'-BN. We turn now to our measurement of the rotational relaxation time which is the quantity needed to give us the reduced friction β in each of the solutions studied.

REORIENTATION DYNAMICS OF 1,1'-BN: MEASUREMENT OF $\tau_{\rm or}$

The transient dichroism signal $S(t)$, Eq. (1), exhibited a rapid rise of dichroism followed by a slower decay. The rise was associated with the isomerization process and the decay was due to the overall reorientation of the isomerized molecules, this later process being slower than the isomerization. For times after the rise is complete, the signal $S(t)$ is associated only with the population of isomerized molecules, so that $P(t)$, Eq. (1), is given by e^{-t/τ^*}, where τ^* is the lifetime of the isomerized excited molecules, which is typically 3 ns.[43] The single exponential decay of $S(t)$ implies that the rotational correlation function associated with reorientation of the isomerized molecules is also a single exponential decay. Thus, in this case, $S(t)$ is given by

$$S(t) = \mathrm{const}(e^{-t/\tau_{\rm or}}e^{-t/\tau^*}) = \mathrm{const}\, e^{-t/\tau_m}\,, \tag{11}$$

where $\tau_{\rm or}$ is the overall reorientation time and τ_m is the measured decay time of $S(t)$. From Eq. (11) we see that the reorientation time is obtained from the measured decay time as follows:

$$1/\tau_{\rm or} = 1/2\tau_m - 1/\tau^*\,. \tag{12}$$

Downloaded 09 Apr 2005 to 128.59.115.179. Redistribution subject to AIP license or copyright, see http://jcp.aip.org/jcp/copyright.jsp

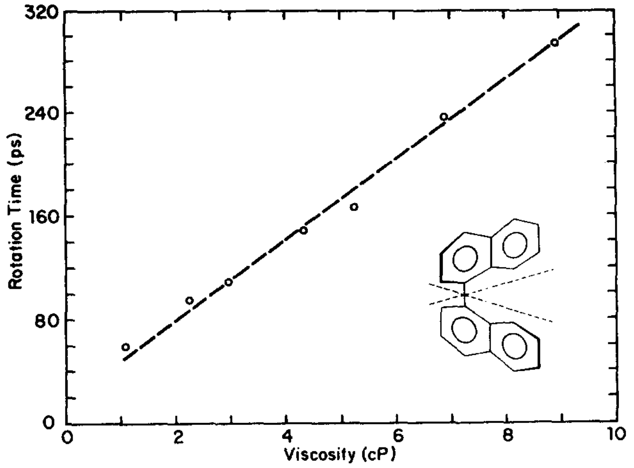

FIG. 3. Rotation time vs solvent shear viscosity in *n*-alcohols. The circles are experimental points. The line is a linear least-squares fit to the data. See the text for details.

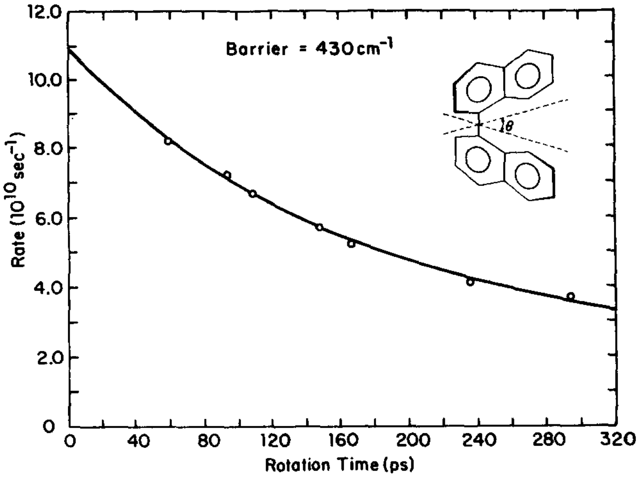

FIG. 5. Barrier crossing vs rotation time in *n*-alcohols. The circles are experimental points. The line is the best fit of Kramers' equation, Eq. (13). See the text for details.

The results of these measurements of the rotational correlation times are shown in Figs. 3 and 4. There is clearly a difference in the viscosity dependence of the rotation times between the two solvent classes. For the alcohols, τ_{or} is proportional to viscosity, but in the alkanes, the relationship between τ_{or} and viscosity is nonlinear, showing some saturation effects at higher viscosities. While this difference between solvent series is quite interesting, it is not the main concern of this paper and will be addressed in a future communication.[44]

KRAMERS' EQUATION USING ORIENTATIONAL RELAXATION MEASUREMENTS

Kramers' equation can now be written in a more useful form for comparison with experiment, as follows:

$$k = A\left[(1 + B^2\tau_{or}^2)^{1/2} - B\tau_{or}\right], \qquad (13)$$

where

$$A = \frac{Z^\ddagger}{Z'}\frac{\omega}{2}e^{-Q/k_BT}$$

and

$$B = \frac{3k_BTf}{I_{iso}\omega'}.$$

The isomerization rate is plotted in Figs. 5 and 6 versus τ_{or} for both alcohol and alkane solvents, respectively, and gives an excellent fit to the Kramers' equation, using A and B as adjustable parameters. The best fit parameter values in each case are

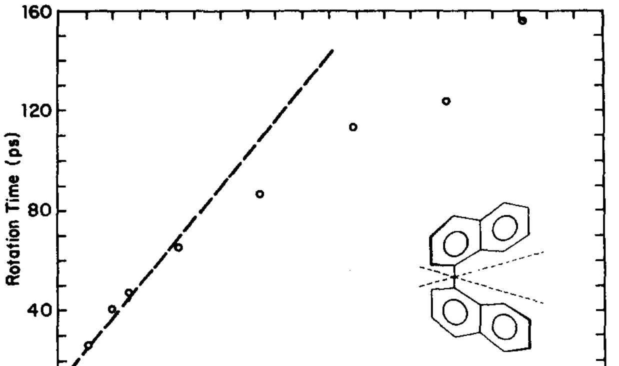

FIG. 4. Rotation time vs solvent shear viscosity in *n*-alkanes. The circles are experimental points. The line is a linear least-squares fit to the four lowest viscosity points. See the text for details.

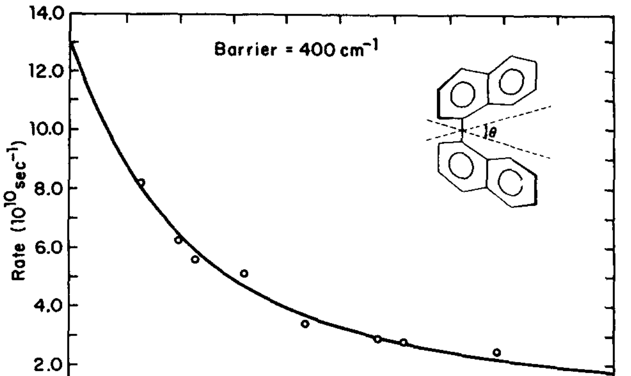

FIG. 6. Barrier crossing rate vs rotation time in *n*-alkanes. The circles are experimental points. The line is the best fit of Kramers' equation, Eq. (13). See the text for details.

Downloaded 09 Apr 2005 to 128.59.115.179. Redistribution subject to AIP license or copyright, see http://jcp.aip.org/jcp/copyright.jsp

$$\text{Alcohols: } A = 10.8\times 10^{10}\ \text{s}^{-1}, \quad B = 4.63\times 10^{9}\ \text{s}^{-1},$$
$$\text{Alkanes: } A = 12.8\times 10^{10}\ \text{s}^{-1}, \quad B = 1.82\times 10^{10}\ \text{s}^{-1}.$$

These parameter values can be used to estimate the potential surface parameters, providing certain assumptions are made. First, $Z^{\ddagger}/Z'$ will be close to 1 provided there are no large frequency shifts of the vibrational modes of the molecule during isomerization, which we have argued previously is reasonable for 1,1'-binaphthyl. Second, the well frequency is assumed to equal the measured free-molecule value of 5.7 ps^{-1} [40] for both solvents. With these assumptions we obtain the following potential parameters:

$$\text{Alcohols: } Q = 430\ \text{cm}^{-1}, \quad \frac{\omega'}{f} = 271\ \text{ps}^{-1},$$
$$\text{Alkanes: } Q = 400\ \text{cm}^{-1}, \quad \frac{\omega'}{f} = 69.0\ \text{ps}^{-1}.$$

The estimate of the barrier height in alcohols is in reasonable agreement with our previous estimate of 460 cm^{-1} using a hydrodynamic fit and with an independent estimate from spectroscopic data of $Q = 480\ \text{cm}^{-1}$. The spectroscopic data also show very little variation with solvent[41] which is consistent with our barrier height estimates. We are presently performing isoviscosity experiments at different temperatures, in the alcohols, to measure the barrier height independently. There appears to be no strong polarity or solvent dependence of the barrier height for 1,1'-binaphthyl. This is in contrast to *t*-stilbene[45] and DPB[19] which exhibit much lower barrier heights in alcohols than in alkanes, and *p*-dimethylaminobenzonitrle where polarity-induced barrier effects are found to occur not only between different solvent types, but also within a solvent family and with temperature changes in a given solvent, as well.[46] The insensitivity of 1,1'-binaphthyl isomerization to solvent polarity is consistent with quantum calculations of the S_1 excited state, which indicate that the interaction between the naphthyl groups is of excitonic rather than charge transfer character.[47]

DEPENDENCE OF FRICTION ON SOLVENT CLASS: MOLECULAR EFFECTS

Our results show that the ratio ω'/f is significantly different for the two solvents, being smaller for the alkanes. This could indicate a substantial flattening of the barrier in alkane solvents. However, since the barrier is apparently only slightly lower in alkane solvents, this degree of flattening could only result from a large increase in the equilibrium torsion angle separation between the excited-state isomers, for which there is no evidence. The possibility of a marked change in the barrier anharmonicity is also unlikely, based on the insensitivity of the spectra to solvent. Only a small reduction in ω' is expected in the alkanes on the basis of the barrier height estimates. The different ω'/f ratios must therefore predominantly reflect differences in the friction scaling factor f, defined in Eq. (8). We can use our data in fact to estimate f, provided that an estimate of ω' can be made. One possibility is to consider certain model potentials for which simple relationships exist between the various potential parameters. We have previously considered a continuous piecewise-parabolic potential that incorporates the existing data on the S_1 state torsional potential.[17] The barrier frequency can be calculated from the barrier height for this model and, when the present estimates of the barrier height are used, the model potential yields $\omega' = 15.0\ \text{ps}^{-1}$ for alcohol solvents and $\omega' = 11.9\ \text{ps}^{-1}$ for alkane solvents. As expected, the barrier frequency is only slightly less in the alkanes. Finally, using these estimates of ω' and the best-fit values of ω'/f, we obtain $f = 0.055$ for alcohol solvents and $f = 0.17$ for alkane solvents. Both of these values suggest that the isomerization friction is substantially smaller in magnitude than the friction for overall reorientation which may at first seem surprising. The result is clarified if we estimate f by another method. Such an estimate is provided by the ratio $f_h = \xi_{\text{iso}}/\xi_{\text{or}}$, where the friction constants are calculated from the hydrodynamic expressions, Eqs. (5) and (9). Using τ_{or} as given by the modified Debye–Stokes–Einstein equation for rotational diffusion,[39]

$$\tau_{\text{or}} = \frac{\kappa s V}{k_B T}\eta \tag{14}$$

we find that

$$f_h = \frac{\xi_{\text{iso}}}{\xi_{\text{or}}} = \frac{4\pi d r^2}{6\kappa s V}. \tag{15}$$

κ is a constant that depends on the boundary conditions[48] and s is the Perrin shape factor.[49] CPK space-filling models were made of the twisted form of 1,1'-BN and a volume of 300 Å^3 was found. From this model, 1,1'-BN was found to be closest in shape to an oblate rotor. Using a slip boundary paper and an axial ratio of 0.48 we found κ equal to 0.261. The Perrin shape factor s was equal to 1.17 using the same axial ratio value. The values of r and d have been mentioned previously.

Although these hydrodynamic expressions are not quantitatively accurate, the ratio may contain less error and should at least provide an order-of-magnitude estimate of f. Using Eqs. (5), (9), and (14) the result is $f_h = 0.09$, which is similar in magnitude to the above estimates, suggesting that the small value of f is associated in large part with geometric differences between isomerization and overall reorientation. If geometry was the only factor, however, and we assume, as seems plausible, that the geometry of 1,1'-BN in alkanes and alcohols is the same, then the values of f would have been the same. Our results suggest that the friction associated with rotation and isomerization are larger in alkanes than in alcohols of comparable viscosity. These interesting results on the different friction experienced in alcohols compared with alkanes provide a direct indication that molecular aspects of the solute–solvent interaction play a role in the isomerization dynamics of molecules in solution. We note that at equal viscosities the size and mass of the alkane is much larger than that of the alcohol, e.g., propanol (C_3H_7OH) and the much larger tetradecane ($C_{14}H_{30}$) have about the same viscosities; this could be responsible for differences in the local friction. In addition, the large sizes of several of the alkanes, which are comparable to or larger than the solute molecule, could contribute to a breakdown in the continuum approximation. This latter point could be responsible for the observed deviation of the orientational relaxation from a linear dependence on the alkane viscosity. A

Downloaded 09 Apr 2005 to 128.59.115.179. Redistribution subject to AIP license or copyright, see http://jcp.aip.org/jcp/copyright.jsp

related view is that the boundary conditions, which reflect the solute-solvent coupling, could differ from one alkane to another. The strength of this coupling can be expressed by a variation in the size of the solute for the different alkane solvents.[50]

We wish to remind the reader that these observations about the scaling coefficient f were obtained using the following approximations:

(i) $Z^{\ddagger}/Z' = 1$ is appropriate for isomerization of 1,1'-binaphthyl in both alkane and alcohol solvents.

(ii) The torsional potential is piecewise parabolic with the same energy difference and equilibrium torsion angle difference of the excited-state isomers in both alkanes and alcohols.

(iii) $\omega = 5.7\ \text{ps}^{-1}$ in both solvents.

(iv) The barrier height and frequency is the same in all members of a solvent series.

(v) Apart from barrier height differences between series, any remaining difference in the isomerization rate in alkanes and alcohols is due to a difference in β/ω'.

(vi) The isomerization friction is proportional to the overall reorientation friction $\xi_{\text{iso}} = f\xi_{\text{or}}$ in both solvent series.

The fifth assumption is the most crucial. It is by attributing the faster rate falloff in the alkane series to the differences in friction that we are led to different f values for the two solvents. If the barrier height were increasing monotonically across the alkane series a similar effect might be seen, although there is no evidence available at present to support this possibility.

DISCUSSION

The key finding of this work is that the Kramers' equation provides an excellent fit to the isomerization data of 1,1'-binaphthyl for such different solvents as alcohols and alkanes when a realistic estimate of the isomerization friction is used. Furthermore, the barrier heights obtained are in good agreement with other estimates, which supports the physical significance of the fits. We find from our experimental results that the decay of the orientational decay function $\langle P_2[\hat{\mu}(0)\cdot\hat{\mu}(t)]\rangle$ is exponential in form, at least over four to ten reorientation lifetimes, depending on the solvent. Thus by estimating the isomerization friction from the solute reorientation time, we are using a zero-frequency bulk property.

Our data can thus be accommodated within a Markovian model, and there is no need to invoke frequency-dependent friction to explain our results. Such effects have been invoked to explain poor Kramers' fits when a hydrodynamic model is used for the isomerization friction.[18,32] In the case of 1,1'-binaphthyl in alkane solvents such deviations are also observed but result from a breakdown of the linearity of the friction with the alkanes viscosities rather than of the Markovian assumption. Indeed, the previously reported deviations for *t*-stilbene have been reanalyzed and ascribed to the same cause as described here[20,22]—the Kramers' equation fitted the data when the friction was estimated from the reorientation time. We thus see that the Kramers' model based on Markovian friction is apparently sufficient to explain the isomerization data for these molecules.

Contrary to these results, it has been found that in the ground state isomerization of DODCI, a fit of Kramers' equation fails, even when the friction is estimated from τ_{or}.[29] The isomerization barrier in this case is very much higher than for 1,1'-binaphthyl, DPB or *t*-stilbene. The barrier frequency is presumably also much higher, so that non-Markovian effects are expected to be more severe for DODCI.

We ask at this point why does a Markovian model appear to work for 1,1'-binaphthyl in alcohols and alkanes, as well as *t*-stilbene and stiff diphenylbutadine in alkane solvents, since for these systems the barrier frequencies are high? The Markovian assumption is expected to be valid when the solvent motion is much faster than the reactant's motion on the potential barrier.[4] That is, $\tau_s^{-1} > \omega'$, where τ_s is the solvent correlation time. Our estimates of ω' based on the model potential are $\sim 10^{13}\ \text{s}^{-1}$, which requires that $\tau_s < 0.1$ ps. This time scale is commensurate with the collision time in the liquid state but is probably too short to characterize the full collective behavior associated with hydrodynamic friction.[5] The success of Kramers' model may perhaps be due to a significant contribution of collisional dynamics to the isomerization friction of 1,1'-binaphthyl in alcohol and alkane solvents. The possible importance of collisional friction is also seen in the reorientation dynamics of 1,1'-binaphthyl in alkanes, where there are nonhydrodynamic contributions to the rotational friction. Although τ_{or} scales linearly with viscosity in alcohols, we cannot conclude that the friction is necessarily hydrodynamic in origin. As has been shown theoretically by Hynes *et al.*[30] and Berne *et al.*,[31] friction can have a significant collisional contribution and still scale linearly with the shear viscosity. The possibility that collisional friction is important in 1,1'-BN, while being speculative at this stage, deserves further consideration as it may provide a better understanding of both the reorientation and isomerization data.

There is an alternative explanation for the different isomerization and rotational relaxation of 1,1'-BN in alcohols that we wish to mention briefly. For the alcohols, a complex solvent due to hydrogen bonding and dipolar interactions, there is the possibility that there is significant friction on the time scale of the inverse barrier frequency $(\omega')^{-1}$. This could have the effect of greatly extending the barrier crossing time, i.e., many crossings and recrossings, and thereby enable the slower solvent motions responsible for hydrodynamic behavior to contribute to the isomerization friction. In the alcohols, unlike the alkanes, the collective motions associated with the extensive hydrogen bonding would likely contribute to the increased importance of hydrodynamic friction relative to collisional contributions. Thus the reorientational motion would scale linearly as expected if the friction was hydrodynamic, as would the isomerization friction if the barrier crossing time was significantly slower than the inverse barrier frequency.

CONCLUSIONS

The medium effects on the isomerization dynamics of 1,1'-binaphthyl in solution can be understood within the context of the Kramers' model. However, caution is re-

Downloaded 09 Apr 2005 to 128.59.115.179. Redistribution subject to AIP license or copyright, see http://jcp.aip.org/jcp/copyright.jsp

quired in estimating the friction that should be used in the Kramers' model. The use of a friction model such as hydrodynamics may be inappropriate and can lead to erroneous conclusions, such as the apparent breakdown of the Markovian assumption. Kramers' equation works well when the measured reorientation times of 1,1'-binaphthyl are used to estimate the isomerization friction. The scaling factor *f*, however, is larger in the alkanes than the alcohols, which provides an indication that molecular aspects of the solute–solvent interaction also play a role in the isomerization dynamics of 1,1'-binaphthyl in solution. It should be noted, however, that the successful use of reorientation times to estimate the isomerization friction is an empirical procedure which emphasizes the need to develop realistic models of friction in condensed phases.

ACKNOWLEDGMENTS

The authors wish to gratefully acknowledge the National Science Foundation and The Air Force Office of Scientific Research for their support, and also to thank B. J. Berne and J. T. Hynes for helpful discussions.

[1] H. A. Kramers, Physica **7**, 284 (1940).
[2] T. Fonseca, J. A. N. F. Gomes, P. Grigolini, and F. Marchesoni, Adv. Chem. Phys. **62**, 289 (1985).
[3] J. S. McCaskill and R. G. Gilbert, Chem. Phys. **44**, 389 (1979).
[4] R. F. Grote and J. T. Hynes, J. Chem. Phys. **73**, 2715 (1980).
[5] R. F. Grote, G. van der Zwan, and J. T. Hynes, J. Phys. Chem. **88**, 4676 (1984).
[6] J. A. Montgomery, Jr., D. Chandler, and B. J. Berne, J. Chem. Phys. **70**, 4056 (1978).
[7] M. Borkovec and B. J. Berne, J. Chem. Phys. **82**, 794 (1985).
[8] J. E. Straub, M. Borkovec, and B. J. Berne, J. Chem. Phys. **83**, 3172 (1985); **84**, 1788 (1986).
[9] B. Carmelli and A. Nitzan, Phys. Rev. Lett. **51**, 233 (1983).
[10] B. Carmelli and A. Nitzan, J. Chem. Phys. **80**, 3596 (1984).
[11] A. Nitzan, J. Chem. Phys. **86**, 2734 (1987).
[12] J. L. Skinner and P. G. Wolynes, J. Chem. Phys. **69**, 2143 (1978); **72**, 4913 (1980).
[13] D. K. Garrity and J. L. Skinner, Chem. Phys. Lett. **95**, 46 (1983).
[14] J. Lee, S.-B. Zhu, and G. W. Robinson, J. Phys. Chem. **91**, 4273 (1987).
[15] D. L. Hasha, T. Eguchi, and J. Jones, J. Am. Chem. Soc. **104**, 2290 (1984).
[16] C. V. Shank, E. P. Ippen, O. Teschke, and K. B. Eisenthal, J. Chem. Phys. **67**, 5547 (1978).
[17] D. P. Millar and K. B. Eisenthal, J. Chem. Phys. **83**, 5076 (1985).
[18] S. P. Velsko and G. R. Fleming, J. Chem. Phys. **76**, 3553 (1982).
[19] K. M. Keery and G. R. Fleming, Chem. Phys. Lett. **93**, 322 (1983).
[20] S. H. Courtney, S. K. Kim, S. Canonica, and G. R. Fleming, J. Chem. Soc. Faraday Trans. 2 **82**, 2065 (1986).
[21] G. Rothenberger, D. K. Negus, and R. M. Hochstrasser, J. Chem. Phys. **79**, 5360 (1983).
[22] M. Lee, A. J. Bain, P. J. McCarthy, C. H. Han, J. N. Haseltine, A. B. Smith III, and R. M. Hochstrasser, J. Chem. Phys. **85**, 4341 (1986).
[23] R. M. Hochstrasser, Pure Appl. Chem. **52**, 2683 (1980).
[24] S. Russo and P. J. Thistlethwaite, Chem. Phys. Lett. **106**, 91 (1984).
[25] V. Sundstrom and T. Gillbro, Chem. Phys. Lett. **110**, 303 (1984).
[26] E. Akesson, V. Sundstrom, and T. Gillbro, Chem. Phys. **106**, 269 (1986).
[27] S. R. Flom, A. M. Brearly, M. A. Kalhow, V. Nagarajan, and P. F. Barbara, J. Chem. Phys. **83**, 1993 (1985).
[28] S. R. Flom, V. Nagarajan, and P. F. Barbara, J. Phys. Chem. **90**, 2085 (1986).
[29] S. P. Velsko, D. M. Waldeck, and G. R. Fleming, J. Chem. Phys. **78**, 249 (1983).
[30] J. T. Hynes, R. Kapral, and M. Weinberg, J. Chem. Phys. **69**, 2725 (1978).
[31] J. O'Dell and B. J. Berne, J. Chem. Phys. **63**, 4606 (1973).
[32] B. Bagchi and D. W. Oxtoby, J. Chem. Phys. **78**, 2735 (1983).
[33] D. P. Millar and A. H. Zewail, Chem. Phys. **72**, 381 (1982).
[34] C. V. Shank and E. P. Ippen. Appl. Phys. Lett. **26**, 62 (1975).
[35] D. Waldeck, A. J. Cross, Jr., D. B. McDonald, and G. R. Fleming, J. Chem. Phys. **74**, 3381 (1981).
[36] T. J. Chuang and K. B. Eisenthal, J. Chem. Phys. **57**, 5094 (1972).
[37] *Handbook of Chemistry and Physics*, 54th ed., edited by R. C. Weast (Chemical Rubber, Cleveland, 1978).
[38] P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw–Hill, New York, 1969).
[39] J. Happel and H. Brenner, *Low Reynolds Number Hydrodynamics* (Prentice–Hall, Englewood Cliffs, 1965).
[40] H. T. Jonkman and D. A. Wiersma, Chem. Phys. Lett. **97**, 261 (1983).
[41] R. M. Hochstrasser, Can. J. Chem. **39**, 459 (1961).
[42] P. S. Hubbard, Phys. Rev. **131**, 1155 (1963).
[43] X. Luo, G. S. Beddard, G. Porter, and R. S. Davidson, J. Chem. Soc. Faraday Trans. 1 **78**, 3477 (1982).
[44] R. M. Bowman, D. P. Millar, and K. B. Eisenthal (in preparation).
[45] V. Sundstrom and T. Gillbro, Chem. Phys. Lett. **109**, 538 (1984).
[46] J. Hicks, M. Vandersall, Z. Babarogic, and K. B. Eisenthal, Chem. Phys. Lett. **116**, 18 (1985).
[47] M. F. M. Post, J. K. Eweg, J. Langelaar, J. D. W. van Voorst, and G. ter Maten, Chem. Phys. **14**, 165 (1976).
[48] C.-M. Hu and R. Zwanzig, J. Chem. Phys. **60**, 4354 (1974).
[49] G. R. Fleming, J. M. Morris, and G. W. Robinson, Chem. Phys. **17**, 91 (1976).
[50] R. Zwanzig and A. K. Harrison, J. Chem. Phys. **83**, 5861 (1985).

Downloaded 09 Apr 2005 to 128.59.115.179. Redistribution subject to AIP license or copyright, see http://jcp.aip.org/jcp/copyright.jsp