THE ROLE OF TRANSLATIONAL FRICTION IN ISOMERIZATION REACTIONS

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The hydrodynamic friction used in many comparisons of isomerization reactions with Kramers' theory is shown to be related to the translational friction. The fractional viscosity dependence of the translational friction of naphthalene is shown to account for the failure of hydrodynamic models for 1,1'-binaphthyl in alkanes. The success of the reorientational model of friction is also discussed. Finally, an idea developed by Zwanzig and Harrison is used in rationalizing the fractional dependences.

1. Introduction

The use of Markovian models, such as Kramers' [1], to predict isomerization rate constants has been the subject of intense study. It often turns out, that the success or failure of these models is determined by the form of the friction used in describing the solvent–solute coupling. While much debate has taken place about the applicability of these equations to ultrafast dynamics, recently, good agreement has been found when the "appropriate" friction is used [2–4]. It is important to try to understand the possible reasons for the success of a particular frictional model, if we are to understand why the Kramers' picture is or is not applicable to isomerization dynamics.

One of the most popular frictional models is hydrodynamics, where the simple assumption is made that the isomerizational friction is proportional to the shear viscosity of the particular solvent. However, in a number of cases, the experimental measurements could not be satisfactorily fitted to the Kramers model using such a hydrodynamic description of the friction. Agreement was obtained if the isomerizational friction, ξ_{iso}, is assumed to be proportional to the reorientational friction [2–5], ξ_{or}, which in turn can be related to the orientational relaxation time, τ_{or}, via the Hubbard relation [6], as shown below:

$$\xi_{iso} \sim \xi_{or} \sim \tau_{or}. \qquad (1)$$

In this paper, we examine the use of rotational fric-

tion as a measure of the solute–solvent coupling, and go back to an idea first proposed by Zwanzig and Harrison [7] involving a solvent-dependent hydrodynamic radius.

2. Discussion

The principal assumption in invoking hydrodynamics in isomerization reactions is that the friction experienced by the isomerizing moiety in crossing the barrier is proportional to the viscosity, η, as previously stated. In this view, the motion along the isomerization coordinate is the translational diffusion across the barrier. Implicit in this assumption, is that the isomerizational friction can be directly related to the *translational* friction, ξ_{trans}, developed by Stokes and Einstein. The commonly used relationship between the isomerizational friction and the translational friction for a sphere of hydrodynamic radius d rotated at a distance r from a fixed axis, using a slip boundary condition is [8,9]

$$\xi_{iso} = \xi_{trans} r^2 = 4\pi\eta dr^2. \qquad (2)$$

Thus, if information about the translational diffusion of the isomerizing moiety is known for the solvents of interest, a prediction can be made about the use of hydrodynamics in Kramers' equation.

This can be tested for the case of 1,1'-binaphthyl (1,1'-BN) in alkanes. It was previously found that using the hydrodynamic model for friction in the

Kramers equation gives poor agreement with experimentally measured isomerization rate constants in alkanes [4]. The translational diffusion coefficient of naphthalene, the isomerizing moiety in 1,1'-BN, has been measured in hydrocarbon oils [10], and is found to have the dependence

$$D \sim \eta^{-0.69}. \tag{3}$$

The diffusion coefficient, D, is inversely proportional to the translational friction, resulting in the relationship

$$\xi_{trans} \sim \eta^{0.69}. \tag{4}$$

Since the translational diffusion of naphthalene does not obey the traditional Stokes–Einstein equation, it seems consistent that the Kramers equation using hydrodynamic friction should also fail.

However, the isomerization of 1,1'-BN in alkanes agreed well with Kramers' predictions when the reorientational model for friction was used [4]. The question remains as to why this model is successful where hydrodynamics fails. The solution becomes apparent when the viscosity dependence of the rotational relaxation times is explored. The dependence shown in fig. 1 is given by the relationship

$$\tau_{or} \sim \eta^{0.60}. \tag{5}$$

Thus, by finding a parameter that has almost the same viscosity dependence as the translational diffusion coefficient, we were able to find agreement
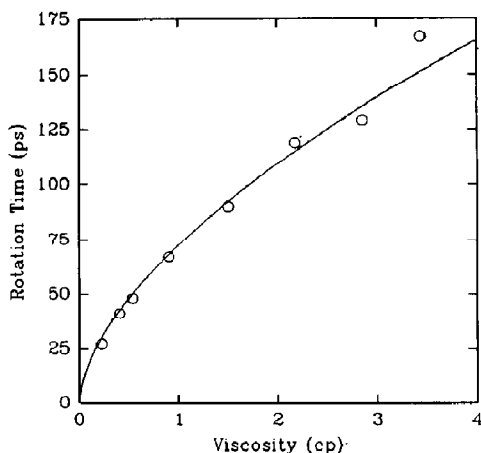

Fig. 1. The fractional dependence of τ_{or} on viscosity. The fitted curve obeys the equation $\tau_{or} = 72 \eta^{0.60}$.

with the Kramers model. Whether the choice of the rotational relaxation times was fortuitous or there is a more fundamental reason for its viscosity dependence is under investigation. We would like to note that the literature is filled with cases where the translational diffusion coefficient shows a non-linear dependence on shear viscosity [10–14]. In fact, this is still an area of active interest.

Similar studies were done for 1,1'-BN in alcohols [4,15]. In this case, both frictional models gave good agreement with Kramers' equation. Consistent with this is the linear dependence of viscosity with τ_{or} in alcohols. Unfortunately, there are no translational diffusion data in alcohols; we can only speculate that there is a linear relationship between the translational friction and shear viscosity.

It is important to try to understand why these non-linear viscosity effects arise; is it possible to reconcile them with hydrodynamics? In all of these cases it was assumed that this fractional dependence on viscosity was caused by a breakdown of hydrodynamics. Zwanzig and Harrison point out that one should not be so hasty in discarding hydrodynamics. They propose to modify the Stokes–Einstein equation by allowing the solute size, d, to vary from solvent to solvent. This varying effective hydrodynamic radius, as they refer to it, is related to the coupling strength between the diffusing solute molecule and the surrounding solvent molecules. This approach seeks to account for the variation in intermolecular interactions experienced by a molecule in different liquids, recognizing that the description of solute diffusion in terms of a hard sphere or ellipsoid with some boundary condition is inadequate.

In their treatment they noted that a non-linear viscosity dependence of the diffusion coefficient of xenon in alkanes [14] can be attributed to the exponential dependence of viscosity and the diffusion coefficient on an experimental parameter, e.g. carbon chain length. This leads to the introduction of an effective hydrodynamic radius that had an exponential dependence on carbon chain length. The radius of xenon was not assumed to be the same in each alkane solvent as in the traditional Stokes–Einstein equation. Thus, the solvent–solute coupling was allowed to change from one solvent to the next.

A similar approach can be used to explain the fractional dependence of τ_{or} on η. If we combine the
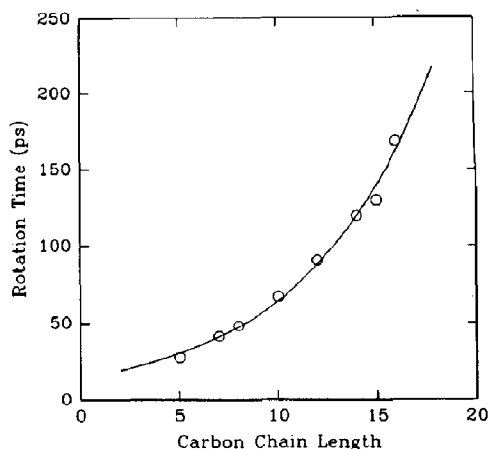
Fig. 2. The exponential dependence of τ_{or} on carbon chain length. The fitted curve obeys eq. (7) given in the text.

Zwanzig and Harrison result for the exponentional dependence of viscosity on chain length, n,

$$\eta = 7.36 \times 10^{-4} \exp(0.247n), \tag{6}$$

and our exponentional fit of τ_{or} versus chain length (as seen in fig. 2),

$$\tau_{or} = 13.8 \exp(0.154n), \tag{7}$$

it is possible to show that the original viscosity dependence of τ_{or} is preserved. From eqs. (6) and (7) the fractional dependence of τ_{or} on η is found to be 0.62. This number is close to the 0.60 experimentally measured seen in eq. (5). Now if we apply the modified Debye–Stokes–Einstein equation for rotational diffusion [16] along with eqs. (6) and (7) we can abstract an effective hydrodynamic volume, V, dependent on chain length,

$$V = 667 \exp(-0.093n)\ \text{Å}^3. \tag{8}$$

This effective volume measures the solute–solvent interactions, i.e. it is a convenient way to describe the strength of coupling between 1,1′-BN and a particular alkane solvent. The utility of this approach is that it gives a picture of solvent-dependent coupling as well as a simple method of explaining the fractional dependence on viscosity.

3. Conclusion

In this study, the connection between the isomerization friction experienced in crossing the barrier and the translational friction of the freely diffusing

molecule is demonstrated. This relationship suggests that measuring macroscopic diffusion coefficients would be helpful in elucidating the proper friction to use in the Kramers model or any other Markovian model. Finally, it appears that the naphthalene translational motion and 1,1′-BN rotational motion experience similar frictional forces in alkanes; neither of which obey traditional hydrodynamics. We find that one way to understand these fractional exponents in the context of hydrodynamics is to allow for the solute–solvent coupling to change as one progresses along the solvent series.

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