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We investigate the effect of the frequency dependence of friction on the rate of photochemical isomerization in solution. Recent experiments have shown a significantly smaller effect of viscosity on rates at high viscosities than that predicted by Kramers' theory. We show that this partial saturation of viscosity effects arises from the fact that the effective friction in the barrier region is much smaller than its zero frequency value at high viscosities. The fractional values of the exponent α (where $k_{iso} = A \, (\eta_s^0)^{-\alpha}$ and η_s^0 is the zero frequency shear viscosity) observed in recent experiments naturally arise when the frequency dependence of the friction is taken into account. The physical significance of these results is discussed.

I. INTRODUCTION

There has been considerable experimental[1-5] and theoretical[6-9] interest in recent years in the dynamics of photochemical isomerization processes in solution. These isomerization processes usually involve large amplitude motion of a bulky group twisting around a molecular axis; the rate of isomerization, therefore, depends critically on the frictional forces exerted by the solvent molecules on the twisting group. On the experimental side, recent advances in laser spectroscopy have made is possible to study ultrafast processes where isomerization rates lie in the picosecond regime,[1-4] thus allowing the study of the role of frictional forces on short time scales. On the theoretical side, several numerical calculations[9,10] have tested the validity of traditional Brownian motion approaches to the problem.

The best known and most widely used theory of isomerization dynamics is that of Kramers[11,12] who studied the effects of solvent frictional forces on the rate of chemical reaction by modeling the reactive motion as the passage of a solute particle over a potential barrier. Kramers' theory is based on the ordinary Langevin equation which neglects correlations in space and time of the solvent forces acting on the reactive motion. But when the motion near the top of the barrier takes place on a picosecond or subpicosecond time scale, the solvent forces at two different times can become correlated; i.e., memory effects become important and Kramers' theory can break down. Recent experimental work has given evidence for such a failure.[1-3] Kramers' theory can also break down if the potential surface is such that a multidimensional theory is necessary.

Recently, Fleming and co-workers[1-3] have carried out a systematic study of the effects of solvent frictional forces on the rate of isomerization in such organic molecules as DPB (diphenyl butadiene) and the dye molecule DODCI in alkane and alcohol solvents. They found that Kramers' expression with frequency independent hydrodynamic friction did not correctly describe the viscosity dependence of the twisting rate. If the low

viscosity rates were fit to Kramers' expression, then the experimental rates at high viscosities lay consistently higher than predicted by theory. On the other hand, if high viscosity points were fit to Kramers' expression then the theory predicted too low values for rates at low viscosities.[1-3] In other words, Kramers' theory does not have the correct curvature necessary to describe the experimental results at both low and high viscosities. Fleming and co-workers[1-3] also found that their experimental results could be fitted very well to a viscosity dependence of the following form

$$k_{iso} = A(\eta_s^0)^{-\alpha} \exp(-E_0/k_B T) , \qquad (1.1)$$

where A is a viscosity-independent constant and the activation energy E_0 is obtained by isoviscosity plots where the temperature is changed but the viscosity is held constant through the use of different solvents. The values of the exponent α lie in the range $1 \geqslant \alpha \geqslant 0.1$ with $\alpha = 0.26$ for ground state DODCI and $\alpha = 0.59$ for DPB in alkanes. Kramers' theory predicts a value of the exponent α close to unity in the high viscosity regime (i.e., in the Smoluchowski limit). This dramatic departure from Kramers' theory can be traced to a reduction of the viscosity effect (and therefore a leveling off of the rate) at high viscosities where Kramers' theory (if fitted to low viscosity values) differs from experimental values by more than one order of magnitude. Another interesting feature of these experimental results[1-3] is that the exponent α is well correlated with the frequency ω_b of the potential barrier. (ω_b is related to the curvature $|k_b|$ at the top of the barrier through $\omega_b = (|k_b|/\mu)^{1/2}$, where μ is the reduced mass for the motion.) If ω_b is small, then $\alpha \sim 1$ and Kramers' theory works, but if ω_b is large (which implies a sharp potential barrier) then α can be as small as 0.2. This indicates that the frequency dependences of solvent friction may play an important role in these isomerization processes and may be the primary reason for the failure of Kramers' theory.

Recently, Grote and Hynes[6] generalized Kramers' theory by including the frequency dependence of the friction. They started from a generalized (non-Markovian) Langevin equation for the velocity of the solute particle in the barrier region and showed that Kramers'

expression is modified in such a way that the new expression involves the friction not at zero frequency but at a finite frequency which depends on the barrier frequency ω_b. Since ω_b in isomerization dynamics can be quite large ($\omega_b \gtrsim 5 \times 10^{12}$ s^{-1}), the *effective* friction experienced by the reactive motion can be much smaller than the zero frequency friction. This, as we shall show later, can explain the dramatic reduction of the effect of viscosity at high viscosities observed by Fleming and co-workers.[1-3] Physically, this means that in long chain alkanes and also in alcohols, that part of the viscosity which arises from low frequency motions does not contribute to the motion across the barrier; the effective solvent friction in the barrier region is much smaller, and the rate of isomerization is higher than that predicted by Kramers' theory.

In this paper, we have looked into the implications of frequency dependent friction for rates of isomerization in solution. We have calculated these rates by using the Grote–Hynes theory.[6] For the frequency dependence of the friction, we have used the expression of Zwanzig and Bixon[13,14] for the translational friction on a spherical particle. For rotational friction, we have used the expression of Montgomery and Berne.[15] We have assumed simple Maxwell forms for the frequency dependences of shear and bulk viscosities, thus introducing the viscoelastic relaxation times τ_s and τ_v for shear and bulk viscosities. In the absence of experimental data for these quantities, we have used some reasonable approximations based on experimental results from ultrasonic absorption in liquids.[16-20] The main result of our calculation is that the observed "saturation effect" at high viscosities naturally arises in this theory. The numerical results can also be fitted very well to the form (1.1) with values of the exponent α in the range observed by Fleming and co-workers. An analysis of our frequency dependent friction shows that the effective friction is indeed much smaller in the barrier region for high viscosities than the zero frequency friction. We have also found that the exponent α depends on several other parameters not anticipated in Kramers' theory. We suggest that the Grote–Hynes theory[6] with frequency dependent friction can explain the experimental results of Fleming and co-workers.

The organization of the rest of the paper is as follows. In Sec. II, we briefly describe the Grote–Hynes generalization of Kramers' theory and also furnish the expressions necessary to evaluate the frequency dependent friction. In Sec. III, we present results and a discussion of their significance. Section IV concludes with a brief summary.

II. GENERALIZED KRAMERS' THEORY: FREQUENCY DEPENDENT FRICTION

A. Grote–Hynes theory

The well-known Kramers' theory for the effects of Brownian motion of bath particles on chemically activated processes in solution is based on the ordinary Langevin equation where the random force is given by Gaussian white noise so that the friction is frequency independent. For some chemically activated processes

in solution, there is a clear separation of time scale between the correlation time of the bath molecules and the rate of motion of the solute molecule so that the assumption of white noise holds and Kramers' theory gives a satisfactory description of the viscosity dependence of the rate constant. However, as discussed in the introduction, there can be situations where the assumption of Gaussian white noise can break down and Kramers' theory may not work.

Recently, Grote and Hynes[6] have extended Kramers' theory by removing the assumption of white noise. One very interesting result of their theory is that the rate constant depends on the friction at a frequency comparable to that of the barrier, ω_b. Since for many reactions the barrier frequency ω_b can be quite high, this friction can be much smaller than the zero-frequency friction. Thus Kramers' theory can vastly overestimate the effects of friction on those chemical reactions which involve sharp, high frequency barriers.

In order to include non-Markovian effects, Grote and Hynes[6] assumed the following generalized Langevin equation (GLE) for the dynamics along the reaction coordinate

$$\mu \frac{dv}{dt} = F(x) - \int_0^t d\tau \, \zeta(\tau) \, v(t - \tau) + f(t) \, , \tag{2.1}$$

where μ is the effective mass, v is the velocity along the reaction coordinate, $F(x)$ is the force arising from the potential in the barrier region, $\zeta(t)$ is the time-dependent friction, and $f(t)$ is the random force from solvent assumed to be Gaussian. $F(x)$ is assumed to arise from a static potential which is an inverted parabola, so that

$$F(x) = \mu \omega_b^2 x \, . \tag{2.2}$$

$\zeta(t)$ and $f(t)$ are related by the fluctuation-dissipation theorem

$$\zeta(t) = \beta \langle f(0) f(t) \rangle \, .$$

By using the probability distribution from the generalized Fokker–Planck equation, Grote and Hynes obtained, after some rather lengthy analysis, the following simple and elegant expression for the rate constant k,[6]

$$k = k^{\mathrm{TST}} (\lambda_r / \omega_b) \, , \tag{2.3}$$

where k^{TST} is the transition state rate constant given by

$$k^{\mathrm{TST}} = \frac{\omega_R}{2\pi} \exp(- E_0 / k_B T) \, ,$$

ω_R is the frequency of motion in the reactant well, and E_0 is the activation energy. λ_r is given by the following self-consistent relation

$$\lambda_r = \frac{\omega_b^2}{\lambda_r + \hat{\zeta}(\lambda_r)/\mu} \, , \tag{2.4}$$

where $\hat{\zeta}(\lambda_r)$ is the Laplace transform of the time dependent friction

$$\hat{\zeta}(\lambda_r) = \int_0^\infty dt \, e^{-\lambda_r t} \, \zeta(t) \, . \tag{2.5}$$

An alternative definition of λ_r is obtained in terms of the

velocity correlation function

$$\lambda_r = \omega_b^2 \int_0^\infty dt \; e^{-\lambda_r t} \langle v^2 \rangle^{-1} \langle v(0)v(t) \rangle \; ,$$

where the time correlation here is calculated in the absence of a barrier. Equation (2.3) predicts the transition state result for very weak friction ($\lambda_r \sim \omega_b$) and the Kramers' result for low barrier frequency [i.e., $\omega_b \to 0$, so that $\xi(\lambda_r)$ can be replaced by $\xi(0)$]. If the barrier frequency is large ($\omega_b \gtrsim 10^{13}$ s^{-1}) then the situation is not so straightforward. In this case, which often turns out to be the relevant one experimentally, the effective friction can be quite small even if the zero-frequency friction (proportional to viscosity) is very large.

Grote and Hynes[6] used some simple parametrized models to show that under certain circumstances k can be quite different from the predictions of Kramers' theory. In this paper, we have attempted to calculate both the frequency dependent friction and the reactive motion as explicitly as possible for real molecules in order to compare the predicted isomerization behavior with experiment.

B. Frequency dependent friction

Photochemical isomerization processes in molecules like DODCI, DPB, and 1,1'-binapthyl involve a twisting motion of bulky groups around a molecular axis. So, as a first approximation, we model this twisting motion as the rotational motion of a sphere of hydrodynamic radius R around a molecule-fixed axis; the center of the sphere is at a distance $(R+l)$ from the axis and l is related to the C–C bond length.

The friction experienced by the moving sphere consists of two parts: one contribution comes from the translational drag which is equal to $(R+l)^2\zeta_{tr}$, while the second is a pure rotational friction ζ_r due to rotation of the sphere around its own axis. Happel and Brenner[21] have shown that the coupling between rotational and translational friction for a sphere is zero, so the total friction is the sum of the two contributions

$$\zeta = (R+l)^2\zeta_{tr} + \zeta_r \; . \tag{2.6}$$

In writing Eq. (2.6), we have neglected the hydrodynamic interaction arising from the presence of the rest of the organic molecule which is considered fixed. Inclusion of this interaction would, however, make the rest of the work analytically intractable and extensive numerical work would be necessary. Moreover, recent calculations[7] have shown that inclusion of this hydrodynamic interaction does *not* change the result significantly.

Next, we need expressions for the frequency dependent frictions ζ_{tr} and ζ_r. For ζ_{tr}, we use the Zwanzig–Bixon[13] expression (including the corrections of Metiu, Oxtoby, and Freed[14]). In the Laplace plane, ζ_{tr} is then given by

$$\zeta_{tr}(p) = \left(\frac{4\pi}{3}\right) \eta_s(p) R X^2 \left[2(X+1)P + (1+Y)Q\right], \tag{2.7}$$

where

$$X = (p\rho_0/\eta_s)^{1/2} R; \quad Y = p\left[c^2 + \frac{p\eta_l}{\rho_0}\right]^{-1/2} R \tag{2.7a}$$

$$P = \frac{3}{\Delta} \, (3 + 3Y + Y^2) \tag{2.7b}$$

$$Q = \frac{3}{\Delta} \left[3 + 3X + X^2 + \frac{X^2(1+X)}{2+\beta/\eta_s}\right] \tag{2.7c}$$

$$\Delta = 2X^2 \left[3 + 3Y + Y^2\right] + Y^2\left[3 + 3X + X^2\right]$$
$$+ \frac{3X^2(1+X)(2+2Y+Y^2)}{2+\beta/\eta_s} \; . \tag{2.7d}$$

η_s is the frequency dependent shear viscosity, ρ_0 the solvent density, c the velocity of sound, and β the slip parameter, zero for pure slip and infinity for stick boundary conditions. The longitudinal viscosity $\eta_l(p)$ is related to the shear viscosity $\eta_s(p)$ and bulk viscosity $\eta_v(p)$ by

$$\eta_l(p) = \frac{4}{3} \, \eta_s(p) + \eta_v(p) \; . \tag{2.8}$$

Equation (2.7) is obtained by solving[13] the generalized Navier–Stokes equation and is known to give a satisfactory description of the velocity correlation function for small spherical molecules.

For rotational friction, things are somewhat different due to the fact that there is no friction for the perfect slip boundary condition, while the stick limit gives too large values of friction for small molecules. The correct approach is to consider a spheroidal shape since molecules are not perfect spheres. But for this case there is no analytic expression for $\zeta_r(p)$, and even the zero-frequency friction has to be evaluated numerically. This problem may not be serious for most cases since ζ_r generally is smaller than ζ_{tr} unless the bulky twisting group is either very large or carries a charge (as in DODCI)[22] so that the stick limit is appropriate. For the perfect stick limit the expression for frequency dependent friction has been given by Berne and Montgomery[15]

$$\zeta_r(p) = \frac{1 + X + \frac{1}{3}X^2}{1+X} \; 8\pi\eta_s(p) R^3 \; , \tag{2.9}$$

where X is given by Eq. (2.7a). For partial slip conditions, Berne and Montgomery have derived an expression for the frequency dependent rotational friction for rough hard spheres

$$\zeta_r(p) = \frac{1 + X + \frac{1}{3}X^2}{1 + X + 3\eta_s/\beta \; (1+X+X^2/3)} 8\pi\eta_s(p) R^3 \; . \tag{2.10}$$

Equation (2.10) is to be treated with care. It predicts a saturation effect at high viscosity even for zero-frequency friction

$$\zeta_r(0) = \frac{8\pi\eta_s(0) R^3}{1 + 3\eta_s(0)/\beta} \; .$$

However, such effects have not been observed even at very high viscosities for those molecules where barrier frequency is low so that the zero-frequency approximation is adequate. Therefore, we have used only the pure stick limit given by Eq. (2.9) or the pure slip limit where ζ_r vanishes; the former limit appears to hold for DODCI in alcohol solvents, while the latter is applicable to DPB.

In order to use Eqs. (2.7) and (2.9), we need expressions for $\eta_s(p)$ and $\eta_v(p)$ as functions of p. We assume

the simple Maxwell forms

$$\eta_s(p) = \frac{\eta_s^0}{1 + p\tau_s} \ , \tag{2.11a}$$

$$\eta_v(p) = \frac{\eta_v^0}{1 + p\tau_v} \ , \tag{2.11b}$$

η_s^0 and η_v^0 are the zero-frequency shear and bulk viscosities. The viscoelastic relaxation times τ_s and τ_v are physical constants connected to the rate of relaxation of shear and bulk modes of the solvent. In principle, these constants may be determined by fitting Eq. (2.11) to experimental data. But for liquids like the intermediate alkanes, and propanol, or butanol, almost no such data exists and in the frequency range in which we are interested ($\sim 5 \times 10^{12}$ s^{-1}), Brillouin spectra are of little help. We therefore used a semiempirical method to evaluate τ_s and τ_v. For the single relaxation of shear and bulk stresses assumed in writting Eq. (2.11), we have the following exact relations for τ_s and τ_v[16-18]

$$\tau_s = \frac{\eta_s^0}{G_\infty}; \quad \tau_v = \frac{\eta_v^0}{K_r} \ , \tag{2.12}$$

where G_∞ is the infinite frequency shear modulus and K_r is the relaxation part of the bulk modulus

$$K_r = K_\infty - K_0 \ . \tag{2.13}$$

K_0 and K_∞ are bulk moduli at zero and infinite frequency, respectively. Before discussing the theoretical methods available for evaluating G_∞ and K_r, let us consider the following facts observed in ultrasonic experiments on many organic liquids:

(1) For associated liquids like alcohols and also for other liquids at high viscosities, G_∞ and K_r are very weakly temperature dependent.[18,23] For many associated liquids, both G_∞ and K_r can be fitted by an equation of the form[18,23]

$$G_\infty = A - BT \ , \tag{2.14}$$

where B is a small constant. Over a temperature variation of 100 °C, G_∞ and K_r usually vary at most by a factor of 2 or 3.

(2) For a large number of organic liquids, the values of G_∞ and K_r are very close to each other, and in many hydrogen bonded liquids, an empirical relation of the form[16,18,23]

$$K_r \cong \tfrac{4}{3} G_\infty \tag{2.15}$$

holds with surprising accuracy. In fact, even though the values of G_∞ and K_r vary by factors of 10 or more from organic liquid to crystalline solid, the ratio K_r/G_∞ has been found to remain constant to within a factor of 1.5.

The similar variation of G_∞ and K_r is to be attributed to the same physical origin of these two quantities.

(3) For most organic liquids, the value of G_∞ (hence of K_r) is found to be close to 10^{10} dyn/cm^2.[18,20,23]

(4) The temperature dependences of η_s^0 and η_v^0 are quite similar[18,19] and much stronger than that of G_∞ and K_r. At high temperatures η_s^0 and η_v^0 can be fitted very well to an Eyring type exponential form[18] while at low

temperatures a free-volume equation gives a good fit to the experimental data.[18-20] Thus, over a range of 100 °C η_s^0 and η_v^0 can vary over two orders of magnitude, whereas G_∞ and K_r only change by a factor of 2 or 3.

(5) τ_s and τ_v have temperature variations similar to η_s^0 and η_v^0, which can easily be understood from Eq. (2.12) and the above experimental facts. At present, there is *no* theory which can account for all the above experimental facts, though there are some useful relations. Eyring's hole theory of viscosity[24,28] predicts the following simple relations for G_∞ and K_r

$$G_\infty = \frac{k_B T}{v_0} \exp[E_h/k_B T] \ , \tag{2.16a}$$

$$K_r = \frac{k_B T}{v_h} \exp[E_h/k_B T] \ , \tag{2.16b}$$

where v_0, v_h, and E_h are the volume of a molecule, the volume of a hole, and the energy required to form a hole of volume v_h. E_h can be found approximately from the relation

$$E_h = \frac{v_h}{v_0} E_{\text{vap}} \ ,$$

where E_{vap} is the energy of vaporization per molecule. Eyring's theory, however, has some severe limitations. First, for many liquids, it predicts the wrong temperature dependence for K_r.[18,23] Second, it becomes increasingly inaccurate at low temperatures and fails completely for associated liquids below 0 °C.[18,23] Since we are interested in studying effects at large viscosities through variation of temperature and we have to use temperatures well below 0 °C, we *cannot* use Eyring's theory. We know of no other theory which gives closed form expressions for G_∞ and K_r and which is accurate over the temperature range of interest.

Partly due to the absence of a theoretical expression and partly due to the extensive experimental evidence (1)–(5) above, we have used a constant value of 10^{10} dyn/cm^2 for G_∞ and Eq. (2.15) to find K_r. Since both η_s^0 and η_v^0 vary quite rapidly at low temperatures and since we are mainly interested in the effects at large viscosities, this seems entirely reasonable. Since both G_∞ and K_r vary slowly with temperature, we will have the correct temperature variation of τ_s and τ_v, a fact which is of crucial importance in our theory.

C. Validity of the Smoluchowski limit

Experiments of Fleming and co-workers[1-3] show that under certain situations the Smoluchowski limit (SL) of Kramers' equation (i.e., $1/\eta_s^0$ dependence of the rate) is not observed even at relatively high values of viscosity ($\eta_s^0 \sim 20$ cp). This is clearly in contradiction to the traditional belief that at high viscosities, when the correlation time $\tau(= \mu/\zeta_0)$ of bath degrees of freedom is small compared to ω_b^{-1}, one obtains Smoluchowski behavior. Since at the higher values of viscosity considered in Refs. 1 and 2, τ is much smaller than ω_b^{-1} (a typical value of τ for DPB at 20 cp is 10^{-15} s whereas ω_b^{-1} is about 10^{-13} s), the nonattainment of SL is noteworthy and deserves further investigation.

As we have already discussed in the previous sections

this departure from SL is correlated with the sharpness of the potential barrier. In fact, it can easily be explained if the frequency dependence of friction, hence of viscosity, is included in the description of the rate process. If the frequency dependence of viscosity can be approximately given by Eqs. (2.11) and (2.12), a new time constant related to the shear and bulk relaxation times τ_s and τ_v enters the problem. When η_s^0 and η_v^0 become very large, τ_s and τ_v become very large as well and frequency dependence of the friction becomes significant.

In this limit $p\tau_s \gg 1$, so that

$$\eta_s(p) \approx \frac{\eta_s^0}{p\tau_s} = \frac{G_\infty}{p} , \qquad (2.17a)$$

$$\eta_v(p) \approx \frac{\eta_v^0}{p\tau_v} = \frac{K_\tau}{p} , \qquad (2.17b)$$

i.e., $\eta_s(p)$ and $\eta_v(p)$ become almost independent of the zero-frequency viscosity η_s^0. So, if η_s^0 is varied by changing temperature, then $\eta_s(p)$ and $\eta_v(p)$ would change only through the weak dependence of G_∞ and K_τ on temperature. Therefore, the rate of isomerization would show only a weak dependence on η_s^0. This is markedly different from the *low* viscosity behavior where $p\tau_s \ll 1$ over the relevant values of p(i.e., close to λ_r) and frequency dependent rate theory predicts results similar to Kramers' theory. We shall show in the next section by numerical evaluation of rate constants that this indeed happens; i.e., there are two distinct regions of completely different slope in the plot of rate constant vs viscosity, and in contradiction to Kramers' theory, SL is *not* attained even at viscosities much larger than that predicted by Kramers' theory.

This immediately raises the important question: under what conditions can Smoluchowski behavior be observed? Experiments[2,3] indicate that SL is attained when ω_b is small, which is in agreement with the Grote-Hynes theory. The SL (within Kramers' theory) may only be obtained for a limited range of types of barriers. If the barrier is too high and sharp, frequency dependence is important and the SL may never be realized even at arbitrarily large shear viscosity. On the other hand, frequency dependence is unimportant for a low broad barrier but if the barrier becomes *too* low (on the order of $k_B T$) Kramers' theory begins to break down for an entirely different reason.

The inverse viscosity dependence of the rate can also appear in a completely different situation—in an isomerization process in the *absence* of potential barrier. We shall show in a future publication that this dependence can occur in the presence of an absorbing barrier along the potential surface.

III. RESULTS AND DISCUSSION

To find λ_r, we have to solve Eq. (2.4) iteratively and it is convenient to write it in the form

$$1 - x^2 = \frac{x}{\mu\omega_b} \xi(x\omega_b) , \qquad (3.1)$$

where $x = \lambda_r/\omega_b$ so that x is the multiplicative factor

which measures the deviation from k^{TST}. x is related to the reduced rate k_{iso}^* of Fleming and co-workers[1-3] by the following relation

$$k_{iso}^* \equiv k_{iso} \exp(E_0/k_B T) = \frac{\omega_R}{2\pi} x , \qquad (3.2)$$

where ω_R is the frequency of the reactant well and E_0 the barrier height.

In order to solve Eq. (3.1), we need experimental values for a large number of quantities: the barrier frequency ω_b, the variation of η_s^0, η_v^0, c, ρ_0 with temperature, the hydrodynamic radius R, and the moment of inertia μ. For η_s^0, η_v^0, c, and ρ_0 extensive tables of experimental values exist[19] over a range of temperatures. R and μ can be determined from the molecular structure of the twisting group. For DPB, we take $R = 3.6$ Å and the hydrodynamic parameter $\beta = 0$ (slip boundary condition[26]), while for DODCI we take $R = 5$ Å and $\beta = \infty$ (stick boundary condition[22]). In both cases we use $l = 1.5$ Å.

There is considerable uncertainty in which value of ω_b to use. This is due to the fact that one can determine only the combination $\omega_b\mu/\zeta_0$ by fitting the experimental data at low viscosities to Kramers' equation, but one needs to know at least one additional function of ω_b and ζ_0 in order to extract ω_b; until now this has not been possible. This is unfortunate, since the experiments of Fleming and co-workers as well as our theoretical calculations indicate that both the rate k and the exponent α depend critically on ω_b. Order of magnitude estimates of ω_b for DPB[1] and DODCI[2] suggest values in the range 6×10^{12} to 3×10^{13}, with the barrier frequency being distinctly higher in the ground state of DODCI than in the excited state. These numbers can only be used as estimates since there is uncertainty in fitting the data to a preexponential and an exponential form (a change in activation energy of 1 kcal/mol would change ω_b by a factor of about 5); in addition, the assumption $\omega_R = \omega_b$ was made to extract these numbers. In view of this, we have solved Eq. (3.1) by assuming reasonable values of ω_b without stressing too much a detailed numerical comparison with those given in Refs. 1 and 2.

Figure 1 shows the results of our theoretical calculations for x as a function of viscosity for DPB parameters with $\omega_b = 6 \times 10^{12}$ s^{-1}. For comparison, we have also drawn the results of Kramers' theory in the same figure. As can be seen from the graph, there is a marked slowing down in the decrease of the rate at high viscosities, a fact which is in qualitative agreement with experiment and is clearly absent in the Kramers' theory. In Fig. 1, we have used data for both octane and butanol. If ω_b is held fixed, then the results for these two liquids do not differ at all. However, it has recently been shown that ω_b of DPB can change significantly[3] from normal alkanes to polar liquids like alcohols. Thus, the effects of solvent interactions at least partly manifest themselves through values of ω_b.

As can also be seen from Fig. 1, our results can be fitted very well to a form like Eq. (1.1) with a value of the exponent α significantly less than unity. If we choose $\omega_b = 6.0 \times 10^{12}$ s^{-1},[1] then we find a value of the exponent $\alpha = 0.25$, whereas if we choose $\omega_b = 4.0 \times 10^{12}$ s^{-1}, we find

$\alpha = 0.64$. The experimental results give a value of α $= 0.59$ for DPB in alkanes. However, it is more important to look for the qualitative features than to fit the experimental data at this stage of research, since there are considerable uncertainties in our choice of values of the parameters involved. The basic qualitative feature is the breakdown of Kramers' theory at high viscosities. The generalization of Kramers' theory by Grote and Hynes seems capable of removing this failure from the older theory. The generalized theory correctly predicts the slowing down of the rate of decrease of K_{iso}^* at high viscosities. At low viscosities ($\eta_s^0 \lesssim 0.5$ cp); Kramers' theory and Grote–Hynes theory agree with each other, as well as with experiment.

In order to study the effect of frequency dependent friction, we have plotted the ratio $\zeta(p)/\zeta(p=0)$ as a function of p for various values of the shear viscosity in Fig. 2. At low viscosities, this ratio changes very slowly, staying close to unity (the Kramers limit). But as viscosity is increased, $\zeta(p)/\zeta(p=0)$ shows a sharper fall and at viscosities near 10 cp for DPB, the ratio goes to zero rapidly. This implies that if we use the zero-frequency viscosity then we vastly overestimate its effect; the effective friction at high viscosities is much smaller than its zero-frequency value. This is precisely the reason why the decrease of the rate slows down at high viscosities. Physically this means that many of the low frequency motions that contribute to $\zeta(p=0)$ do not affect the reactive motion across the barrier if the barrier frequency is sufficiently high. In the long chain alkanes, examples of low frequency motions are those rotations around the backbone which involve cooperative motions of serveral backbone atoms. These kinds of motion will not respond if the liquid is driven at high frequency.

We have also done a calculation appropriate to the ground state of DODCI. In this case the boundary condition appears to be stick and the barrier is quite sharp,
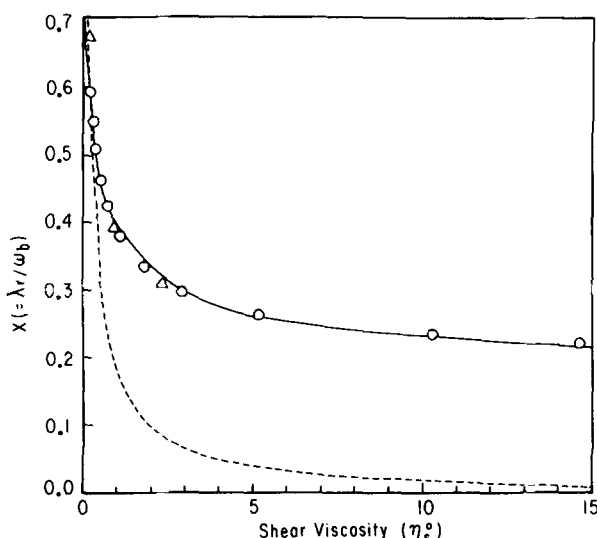

FIG. 1. Values of rate parameter $x(=\lambda_r/\omega_b)$ are plotted against shear viscosity η_s^0 for DPB in octane ($\triangle$) and in butanol (O). $\omega_b = 6.0 \times 10^{12}$ s^{-1}. The solid line is a fit of the data to Eq. (1.1) with $\alpha = 0.25$. The dashed line is the result from Kramers' theory for the same value of the barrier frequency.
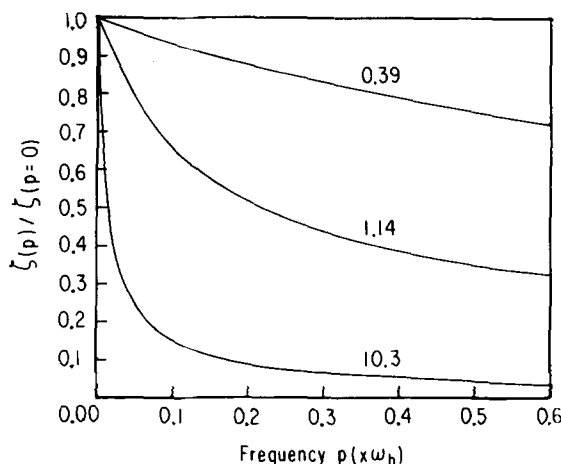

FIG. 2. Values of $\zeta(p)/\zeta(p=0)$ are plotted against frequency p for various values of the shear viscosity η_s^0. The values of η_s^0 (in cp) are indicated on the graph.

so we have chosen $\omega_b = 10^{13}$ s^{-1}. The qualitative features of the variation of x with viscosity are same as in Fig. 1, except that the slowing down effect is more pronounced. We find the value of $\alpha = 0.17$ for the exponent which is to be compared with the experimental value $\alpha = 0.26$. The rate constant is of the right order of magnitude; this is the case also for DPB.

There are some other interesting features which arise in the generalized theory but are absent in ordinary Kramers' theory. For example, the exponent depends significantly on the choice of stick or slip hydrodynamic boundary conditions. For example, $\alpha = 0.25$ for $\beta = 0$ for DPB, but $\alpha = 0.49$ for stick boundary condition for $\beta = \infty$ if we keep only translational friction in Eq. (2.6). Another interesting aspect is the dependence of α on radius R of the twisting group.

IV. CONCLUSION

Let us first summarize the basic features of this paper. We have used Grote-Hynes' generalization of Kramers' theory to investigate the effects of frequency dependent friction on the rate of photochemical isomerization processes in solution. For the frequency dependence of the friction, we have adopted the expression given by Zwanzig and Bixon for translational friction and that of Montgomery and Berne for rotational friction. We have found that both in the slip and in the stick limits, the frequency dependence of friction gives rise to a marked effect on the rate at high viscosities. This effect is absent in ordinary Kramers' theory where the rate goes to zero at high viscosities as $(\eta_s^0)^{-1}$. We have also shown that our results can be fitted quite well to an equation of the form (1.1) with values of the exponent α varying between 0.1 and 1, depending on the barrier frequency ω_b and the hydrodynamic boundary condition. The presence of these kinds of exponents has already been observed in the experiments of Fleming and coworkers who systematically studied the breakdown of Kramers' theory at high viscosities. Thus, our calculations provide a quantiative explanation of these experimental results.

There are, however, certain limitations in our work which are mainly due to the lack of experimental data on viscoelastic response at high frequencies. We believe that the approximations we have been forced to use do not affect the qualitative results of this paper. Due to this uncertainty in τ_s and τ_v and also, more importantly, in the value of the barrier frequency ω_b, we have not tried a quantitative fit to the experimental results. However, the values of our rate constants are of the right order of magnitude compared with experimental results.

As to the physical significance of these results, we have already pointed out that at high viscosities, the part of friction which arises from low frequency motion does not affect the reactive motion across the barrier due to the obvious fact that short time or high frequency motions play the dominant role in determining the dynamics in the barrier region for sharp barriers. This gives rise to a saturation effect manifested through the rate of decrease of the preexponential at high viscosities.

By definition, a frequency dependent friction implies a non-Markovian process. Theoretically, it is rather pleasing to see the dramatic effect this has on the rate of isomerization. Further theoretical and experimental research is necessary to fully understand the precise role of solvent forces and their correlations in time.

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