

at the 12th Experimental Nuclear Magnetic Resonance Conference, Gainesville, Fla., Feb 1971; C. H. Bradley, Ph.D. Thesis, University of California, Los Angeles, Calif., 1971.

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 (37) The exploration of pseudorotation paths involves the migration of a specific

carbon atom from a corner to an adjacent noncorner position (an elementary process)^{2,3} or series of such migrations. As a result of an elementary process three torsional angles change by about 120° : ± 60 to ∓ 60 , ± 60 to 180 , and 180 to ± 60 , where these values are approximate and may vary by 10 – 20° in some cases. One torsional angle passes through 0° and the other through 120° in a sequential rather than simultaneous fashion.

Intramolecular Excimer Study of Rates of Conformational Transitions. Dependence on Molecular Structure and the Viscosity of the Medium¹

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Abstract: Fluorescence spectra for compounds of the type $\text{ArCH}_2\text{XCH}_2\text{Ar}$ where Ar is phenyl, 1-naphthyl, or 4-biphenyl and X is $-\text{CH}_2-$, $-\text{O}-$, $-\text{NH}_2^+-$, $-\text{N}(\text{CH}_3)_2^+-$, or $-\text{N}(\text{COCH}_3)-$ were recorded as a function of temperature in heptane, ethanol, and ethylene glycol. All the compounds studied with the exception of dibenzylidimethylammonium chloride exhibited intramolecular excimer formation. The temperature dependence of the ratio of emission intensities of the excimer and the monomer (I_d/I_m) in the temperature range -70 to -40°C was interpreted in terms of the activation energy for the conformational transition required for excimer formation. Measurements of (I_d/I_m) in ethanol-ethylene glycol mixtures at 0°C were supplemented with excited lifetime determinations of the compounds forming intramolecular excimers and their analogues containing a single chromophore. The viscosity dependence of the rate of conformational transition derived from these data was interpreted in terms of Kramers' diffusion model of chemical reactions. Plots of the reciprocal rate constant against the viscosity of the medium exhibited the initial upward curvature predicted by Kramers and had limiting slopes increasing sharply with an increasing bulk of the chromophore. The temperature dependence of I_d/I_m of two of the model compounds was compared in ethanol and ethylene glycol solutions above 0°C . The difference in the apparent activation energies, E_a , for conformational transition in the two media derived from these data are not in accord with Kramers' theory which predicts E_a in very viscous solvents to be the sum of the barrier height and the activation energy for viscous flow ΔE_η^\ddagger . The results agree with analyses by Christiansen, by Marcus, and by Noyes, which predict that E_a should approach ΔE_η^\ddagger in media of high viscosity.

Until recently, ultrasonic absorption provided the only experimental method for the study of rates of conformational transitions of small molecules with low energy barriers in the liquid phase. Typical of such an investigation is the study of butane and its homologues by Piercey and Rao² which led to an estimate of the potential energy barriers for hindered rotation around the C–C bonds in the range of 3–4 kcal/mol. A number of other techniques (e.g., dielectric dispersion, depolarization of fluorescence, NMR relaxation) have been employed for the study of the conformational mobility of polymers,³ but they all depend on the fact that the rotational diffusion of the macromolecule is slow compared to the rate of conformational transitions—they are, therefore, not applicable to the study of small molecules.

The discovery of intramolecular excimer fluorescence⁴ has provided a new, powerful tool for the study of conformational changes with relaxation times in the range of 10^{-9} – 10^{-7} s. This is so since the conformation required for the sandwich complex between two aromatic chromophores which is responsible for excimer emission would have a prohibitive energy requirement in the absence of electronic excitation. We must assume, therefore, that a conformational transition has to take place during the lifetime of the excited state of one of the chromophores to bring it into proper juxtaposition with the second chromophore for excimer formation. Since this process is exothermic,⁵ the dissociation of the excimer is negligible at low temperatures and the relative emission intensity of excimer and normal fluorescence yields information on the ratio of the rate constants for excimer formation and monomer emission. This principle was first used by Klöpffer⁶ to estimate the rates of excimer formation from excited 1,3-diphenylpropane and 1,3-dicarbazolylpropane. Later work used time-resolved flu-

orescence decay techniques to determine rate constants for both excimer formation and dissociation.^{7–9}

The use of intramolecular excimer fluorescence as a measure of conformational mobility is particularly valuable in allowing us to study the rates of conformational transitions as a function of the nature of the solvent medium. This was first attempted by Klöpffer and Liptay;¹⁰ Avouris et al.⁷ tried later to find a correlation between such rates and the viscosity of the medium, but Johnson found in a detailed study on 1,3-dicarbazolylpropane that such correlations hold only within homologous series of solvents.⁹

In the present investigation we have used a series of compounds of the type $\text{ArCH}_2\text{XCH}_2\text{Ar}$ where Ar is phenyl, 1-naphthyl, or 4-biphenyl and X may be $-\text{CH}_2-$, $-\text{O}-$, $-\text{NH}_2^+-$, or $-\text{N}(\text{COCH}_3)-$. Excimer fluorescence was determined as a function of temperature in heptane, ethanol, and ethylene glycol and in ethanol-glycol mixtures at 0°C . In addition, fluorescent lifetimes were measured by the phase shift and the demodulation method. We attempted to define the dependence of the rate of conformational change on the nature of the bond around which hindered rotation takes place and on the bulk of the chromophore which experiences a frictional resistance to its motion through the solvent. The experimental data were discussed in terms of two alternative theoretical approaches, the first suggested by Kramers,¹¹ the second formulated by Christiansen,³⁹ Marcus,¹² and Noyes,¹³ for rates of chemical processes in viscous media.

Results and Discussion

Temperature Dependence of Fluorescence Behavior in Low-Viscosity Media. The temperature dependence of the fluorescence spectra of $\text{ArCH}_2\text{OCH}_2\text{Ar}$ with Ar = phenyl,

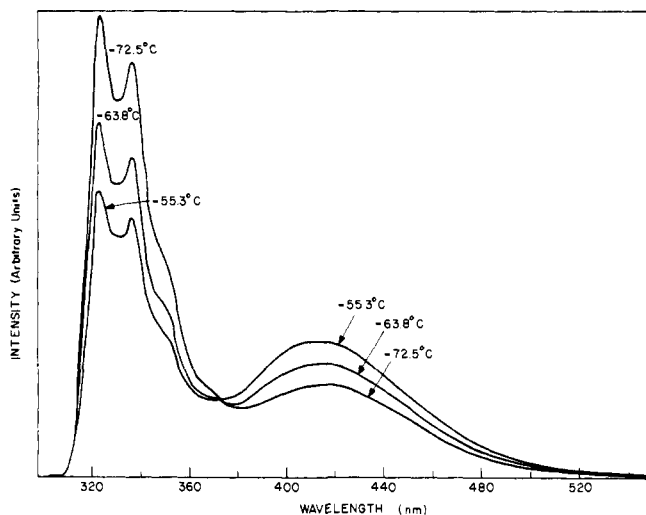


Figure 1. Fluorescence spectra of bis(1-naphthylmethyl) ether in the temperature range exhibiting an isolampsic point.

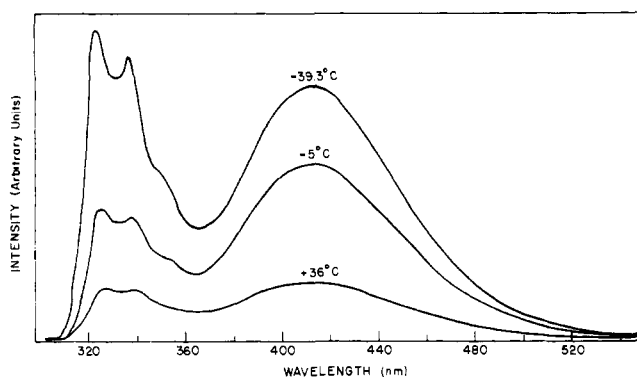


Figure 2. Fluorescence spectra of bis(1-naphthylmethyl) ether at -39.3 , -5 , and 36 °C.

1-naphthyl, and 4-biphenyl (Figures 1 and 2) in the temperature range from -70 to 70 °C is characteristic of all the compounds in the present study, and similar to that reported in previous work.^{8,14}

Below -60 °C the shape of the spectrum begins to resemble that of the respective analogue molecules with a single chromophore, i.e., arylmethylenolcohols. Between -70 and -50 °C there is a steady decrease in the monomer emission accompanied by an increase in the intensity of the red-shifted excimer band. In this temperature region there exists a well-defined isolampsic (isoemissive) point (Figure 1). For instance, in the case of bis(1-naphthylmethyl) ether, the emissive intensity is constant at 370 nm. Production of the intramolecular excimer is thus a thermally activated process and its rate competes with monomer fluorescence.

As the temperature is further increased, the spectra are no longer characterized by an isolampsic point. The intensity of both the monomer and excimer bands can be seen to decrease, although not in the same proportion (see Figure 2). Figure 3 gives a logarithmic plot of the ratio of excimer to monomer intensity ($\log I_d/I_m$) in absolute ethanol as a function of temperature for these compounds. The I_d/I_m ratio increases with temperature in the range in which excimer fluorescence is determined by the rate of excimer formation. At higher temperatures, I_d/I_m passes through a maximum at a temperature T_{\max} and decreases as the temperature is further raised, reflecting the excimer dissociation equilibrium.⁸

The intensity changes which characterize the formation and deactivation of the intramolecular excimer state can be described by the following kinetic scheme in analogy to the

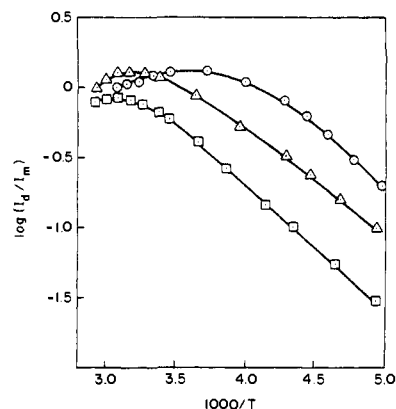
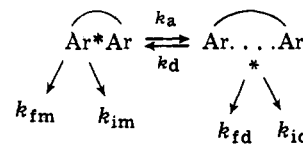
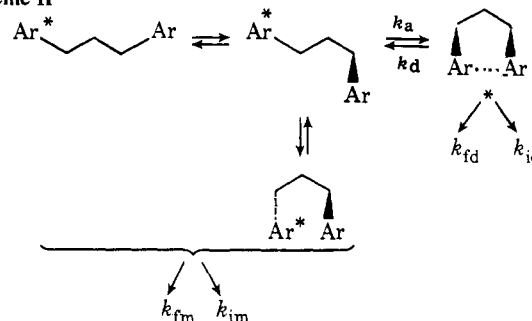


Figure 3. Temperature dependence of I_d/I_m : (O), bis(1-naphthylmethyl) ether; (Δ), dibenzyl ether; (\square), bis(4-biphenylmethyl) ether.

Scheme I



Scheme II



scheme characterizing systems in which intermolecular excimers are formed.^{7,8,12,13}

Here k_{fm} and k_{fd} are rate constants for fluorescence from monomer and excimer, k_{im} and k_{id} are the corresponding rate constants for internal quenching, while k_a and k_d characterize the rates of intramolecular excimer formation and excimer dissociation.

The solution of the rate equations assuming photostationary conditions leads to^{14,15}

$$I_d/I_m = Z(k_a/k_{fm}) \left[1 + \frac{k_{id} + k_d}{k_{fd}} \right]^{-1} \quad (1)$$

where Z relates the ratio of the peak heights to the ratio of the quantum yields of excimer and monomer emission.

The treatment based on Scheme I is, however, incomplete since it neglects the equilibrium between the various conformational states of the monomer formed by a molecule such as 1,3-diphenylpropane. Thus, we should consider Scheme II in which the rate constants for the radiative and nonradiative deactivation of the monomer do not depend on its conformational state. Since the excimer can form only from the monomer containing one gauche bond, eq 1 should be modified to

$$I_d/I_m = Z(k_a/k_{fm}) \left[1 + \frac{k_{id} + k_d}{k_{fd}} \right]^{-1} \alpha \quad (2)$$

where α is the fraction of the monomer in a conformation from which a single hindered rotation can lead to excimer formation.

The rate constants for the radiative emissions, k_{fm} and k_{fd} , are independent of temperature while k_d is negligible and

Table I. Fluorescence Behavior of ArCH₂XCH₂Ar Compounds

Ar ^a	X	solvent ^b	(I _d /I _m) ₂₅₀	E _a , kcal/mol	T _{max} , K	λ _m , nm	λ _d , nm	Δν, cm ⁻¹
P	CH ₂	E	0.42	3.9	320	283	329	4940
P	CH ₂	H	0.46	3.8	318	284	330	4910
P	O	E	0.54	3.7	316	283	333	5310
P	O	H	0.62	3.4	307	283	331	5120
P	NH ₂ ⁺	E	0.22	4.7	>339	280	333	5680
P	N(COCH ₃)	E	1.4 ₄	4.1	308	282	330	5160
P	N(COCH ₃)	H	1.4 ₁	3.6	298	283	331	5120
P	N(CH ₃) ₂ ⁺	E				284		
N	CH ₂	H	0.81	3.7	284	326	417	6690
N	CH ₂	E	0.60	3.8	291	326	418	6750
N	O	H	2.4 ₅	4.2	275	325	413	6560
N	O	E	1.1 ₅	4.2	275	323	415	6860
N	NH ₂ ⁺	E	0.71	5.5	284	326	406	6040
BP	O	E	0.20	4.1	322	319	380	5030
BP	O	H	0.40	3.8	312	319	380	5030

^a P = phenyl, N = 1-naphthyl, BP = 4-biphenyl. ^b H = heptane, E = ethanol.

k_{id}/k_{fd} constant in the low-temperature range of our investigations.¹⁶ Since the temperature dependence of α is much smaller than that of k_a ,¹⁷ we may write, in good approximation,

$$d \log (I_d/I_m)/d(1/T) = E_a/2.3R \quad (3)$$

where E_a is the activation energy for excimer formation and R is the gas constant.

The presence of an isolampsic point is commonly taken to signify that both the radiative rate constants and the internal conversion rate constants are temperature independent.^{14,18} However, Al-Wattar and Lumb¹⁹ have shown that under certain conditions isolampsic points exist even when the quantum efficiencies of monomer and excimer emission vary with temperature. On the other hand, various studies^{8,14} including the present one have arrived at linear plots of $\log(I_d/I_m)$ against $1/T$ well beyond the temperature range characterized by an isolampsic point. This implies that the disappearance of the isolampsic point is due to a temperature variation of k_{im} , which has, of course, no effect on I_d/I_m . Nevertheless, to minimize uncertainties of interpretation, all activation energies were calculated from the slope of the lowest part of the temperature plot. This was always far below T_{max} and within the temperature range exhibiting an isolampsic point.

The activation energies, T_{max} values, I_d/I_m at 250 K (a temperature well below T_{max} for the compounds studied), the wavelengths of the emission maxima of the monomer and excimer, λ_m and λ_d , and the frequency shift between the excimer and monomer $\Delta\nu$, all obtained in two solvents, ethanol and heptane, are summarized in Table I.

The following points may be noted: (1) All the activation energies for excimer formation fall within a narrow range, 3.4–4.2 kcal/mol, except for the two protonated amines, for which slightly higher values, 4.7 and 5.5 kcal/mol, were determined.²⁰ Thus, the energy barrier for the conformational transition is generally unaffected, in these low-viscosity solvents, by the spatial requirements of the aromatic chromophores or the exothermicity of the excimer formation. For instance, E_a is similar for phenyl and 1-naphthyl derivatives, although ΔH for excimer formation is 3 kcal/mol more negative for 1-methylnaphthalene than for toluene.⁵ In fact, the activation energies determined in the present study are essentially the same as those determined by ultrasonic techniques for the hindered rotation in paraffin hydrocarbons. We may then conclude that the effects due to the bulk of the chromophores and incipient excimer formation are both negligible or that their effects cancel each other.

(2) Our data indicate that solvation effects are not important

in determining the energy barrier for excimer formation. While E_a values tended to be slightly higher in ethanol solution, the average difference for six compounds studied in both ethanol and heptane was only 0.2 kcal/mol. While the I_d/I_m ratios for benzyl derivatives were similar in the two solvent media, the naphthyl and biphenyl compounds yielded significantly more excimer in ethanol solution.

(3) As noted previously,¹⁵ dibenzylamine does not fluoresce but the protonated compound exhibits monomer and excimer fluorescence. The excimer fluorescence in the acetylated dibenzylamine is much more intense than in the protonated species. This effect is similar to that noted earlier with dibenzylformamide.¹⁵ We shall discuss later the factors which may be responsible for this effect.

(4) In contrast to the protonated dibenzylamine and the protonated dibenzylmethylamine,²¹ the dibenzyl dimethylammonium ion exhibits no excimer emission. This is clearly due to a prohibitively high energy barrier in this highly crowded species. Space-filling molecular models bear out this interpretation.

(5) The shift in the emission maximum on excimer formation, $\Delta\nu$, is a measure of the attractive potential in the excimer conformation.^{22,40} There is no significant difference in the $\Delta\nu$ values for phenyl and biphenyl derivatives, suggesting that the second phenyl group does not contribute to excimer stability. On the other hand, the $\Delta\nu$ values for the naphthyl derivatives are larger, corresponding to an increased excimer stabilization.⁵

Viscosity Dependence of k_a . In the low-temperature range, where dissociation of intramolecular excimers may be neglected, αk_a can be obtained, in principle, from a comparison of the excited lifetime, τ , at a wavelength of monomer emission of a compound which can form intramolecular excimers and the excited lifetime, τ_0 , of an analogue compound containing a single chromophore:

$$\alpha k_a = 1/\tau - 1/\tau_0 \equiv k_a' \quad (4)$$

Since α may be assumed to be constant for media of similar polarity and varying viscosity if the conformational distribution of the monomer is not perturbed by the excimer formation, k_a' determined in such solvents should yield relative values of k_a .

In experiments carried out at 0 °C, a temperature well below T_{max} , it is justified to assume $k_d \ll k_a$. Unfortunately, eq 4 could be used for the direct determination of k_a' over the entire viscosity range from ethanol ($\eta = 0.018$ P) to ethylene glycol ($\eta = 0.53$ P) only for the naphthyl derivatives. In the case of bis(4-phenylmethyl) ether the τ and τ_0 values were too close to each other in the more viscous media to allow an estimate

Table II. Fluorescence Behavior and Excited Lifetimes of Bis(1-naphthylmethyl) Ether in Ethanol, Ethylene Glycol, and Their Mixtures at 0 °C

wt % glycol	viscosity, P	I_m/I_d	$10^{-7} k_a', s^{-1}{}^a$	$10^{-7} k_a'/(I_m/I_d)^b$
0	0.018	0.91	15.2 ± 1.9	13.8
52.6	0.083	2.1	8.04 ± 0.84	16
76.1	0.19	4.6	3.84 ± 0.54	17.8
100	0.53	14.1	1.09 ± 0.46	15.4

^a Based on $\tau_0 = 29.3 \pm 3.5$ ns obtained in glycerol containing less than 10% ethanol. ^b Mean value 15.7 ± 1.6 .

of k_a' , while in the case of the benzyl derivatives, for which the fluorescence yield is very low, only measurements in viscous media, in which the monomer emission is relatively intense, yielded reliable τ values.

In cases where a direct determination of k_a' proved difficult, the following argument was used to obtain its value indirectly. In our system radiative and nonradiative deactivation of the excited species would not be expected to be sensitive to the viscosity of the medium.⁸ We confirmed this assumption by finding that the excited lifetimes of compounds such as toluene, benzyl alcohol, and *N*-benzylmethylammonium chloride were very similar in ethanol and glycol solution. If we additionally assume that k_d is negligible, then eq 2 predicts the quantity $X \equiv k_a'I_m/I_d$ to be independent of the composition of ethanol-ethylene glycol mixtures. Data listed in Table II for bis(1-naphthylmethyl) ether show that X appears, in fact, to be constant within experimental error for a wide variation of k_a' . The same constancy of X may be assumed for the other compounds. Thus, if we determine X in any one medium, we may use I_d/I_m data, obtainable with high precision, to obtain k_a' in a medium *i* from

$$k'_{ai} = X/(I_m/I_d)_i \quad (5)$$

Table III lists the directly measured k_a' values as well as I_m/I_d ratios observed in ethanol and in ethylene glycol for various compounds forming intramolecular excimers. In Figure 4 $1/k_a'$ is plotted against the viscosity of the medium for dibenzyl ether, bis(1-naphthylmethyl) ether, and bis(4-biphenylmethyl) ether in ethanol-glycol mixtures. The plots are linear at high viscosities but we observe an upward curvature at low viscosities in the plots for the first two compounds. The plots have a finite intercept and a slope which increases with an increasing bulk of the chromophore, i.e., in the order of phenyl < 1-naphthyl < 4-biphenyl.

Table III. Values of I_m/I_d and of k_a' for Compounds of the Type $ArCH_2XCH_2Ar$ in Ethanol and in Ethylene Glycol at 0 °C

Ar	X	$10^{-7} k_a', s^{-1}{}^a$		I_m/I_d		η^*, P	$10^{-7} \alpha k_a^0, s^{-1}$
		ethanol	glycol	ethanol	glycol		
BP	O	6.2 ± 1.3		3.3	<i>d</i>	0.012	17
N	O	17.2 ± 1.8^c		0.91	14.2	0.035	25
P	O		24.3 ± 2.8	0.84	6.4	0.091	215
P	C		10.9 ± 1.3	1.02	5.4	0.140	63
N	C	4.38 ± 0.16^b		1.26	12.7	0.064	5.4
P	NH ₂ ⁺		12.0 ± 1.6	1.78	9.8	0.134	73
N	NH ₂ ⁺	9.8 ± 1.2		0.90	7.2	0.086	11.5
P	N(COCH ₃)		30.0 ± 3.8	0.29	2.5	0.078	307

^a The k_a' values were determined by eq 4 using the following τ_0 values (ns) obtained from the phase shift technique unless otherwise indicated: benzyl alcohol, 32 ± 2.6 (average of ethanol and glycol values); toluene, 33 ± 3.7 (average of ethanol and glycol values); *N*-acetylbenzylamine, 29 ± 1.7 (average of phase and modulation techniques); benzylmethylamine hydrochloride, 20 ± 2.2 (average of phase and modulation techniques); 1-methylnaphthalene, 81 ± 1.8 (modulation technique). The τ_0 for bis(1-naphthylmethyl) ether 29 ± 1 ns, bis(1-naphthylmethyl)-ammonium chloride, 46 ± 1.5 ns, and for bis(4-biphenylmethyl) ether, 9.8 ± 1.0 ns, were obtained from the excited lifetime in glycerol containing less than 10% ethanol. No excimer emission was observed in this medium. ^b The τ value obtained by modulation technique. ^c Datum obtained from mean value of $k_a'(I_m/I_d)$ appearing in Table II. ^d The excimer emission was too weak for determination of I_m/I_d . The k_a^0 and η^* values were based on the I_m/I_d in ethanol and $I_m/I_d = 13.2$ in an ethanol-glycol mixture containing 52.4 wt % glycol and having a viscosity of 0.083 P.

The temperature dependence of the I_d/I_m ratio in a viscous solvent, ethylene glycol, was determined for dibenzyl ether and bis(4-biphenylmethyl) ether. Unfortunately, this study had to be restricted to temperatures above 0 °C, since excimer emission is too weak in the viscous medium at lower temperatures. This introduces uncertainties in the interpretation of the results, since the temperature dependence of k_{id}/k_{fd} contributes to the temperature dependence of I_d/I_m . Figure 5 shows a comparison of the fluorescence behavior of the two compounds in the same temperature range in glycol and ethanol solution, showing that $\log(I_d/I_m)$ increases much more rapidly with increasing temperature in the more viscous solvent. At the same time the inversion temperatures, T_{max} , are shifted to higher values.

Theoretical Considerations.²³ **A. Kramers' Theory.** Rates of conformational transitions in viscous media may be treated by the approach introduced by Kramers' theory¹¹ for the rate at which a particle in a viscous medium moves from a potential energy well over a potential energy barrier ΔU^\ddagger , assumed to be larger than about $5RT$. With a Maxwell distribution of particles in the well, he obtained for the diffusion rate r across the potential energy barrier

$$r = (\omega'/2\pi\omega)(\sqrt{(f/2m)^2 + (2\pi\omega)^2} - f/2m) \exp(-\Delta U^\ddagger/RT) \quad (6)$$

where ω and ω' are the oscillation frequencies at the top of the barrier and the bottom of the well, respectively, f is the frictional coefficient of the particle, and m is its mass. Kramers' theory was later cited by Helfand²⁴ and by Iwata²⁵ in their discussions of hindered rotations in chain molecules and we shall use a similar approach to analyze the factors determining k_a .

Rotation around a given bond will lead to motion of the molecular residues attached at both ends of the bond with masses m_1, m_2 and frictional coefficients f_1, f_2 and we must therefore use a reduced mass $m_r = m_1m_2/(m_1 + m_2)$ and a reduced frictional coefficient $f_r = f_1f_2/(f_1 + f_2)$ in eq 6. The oscillatory frequencies are given by $\omega = (1/2\pi)(C/I)^{1/2}$, $\omega' = (1/2\pi)(C'/I)^{1/2}$, where C and C' are the force constants and I is the molecular moment of inertia around an axis parallel to the X-CH₂ bond. Taking also into account any entropy change, ΔS^\ddagger , which may be associated with the passage over the energy barrier, we obtain for k_a

$$k_a = (\omega'/q)[\sqrt{1+q^2} - 1] \exp(\Delta S^\ddagger/R) \exp(-\Delta U^\ddagger/RT) \\ = k_a^0[(1+q^2)^{1/2} - 1]/q \\ q = 4\pi m_r \omega / f_r \quad (7)$$

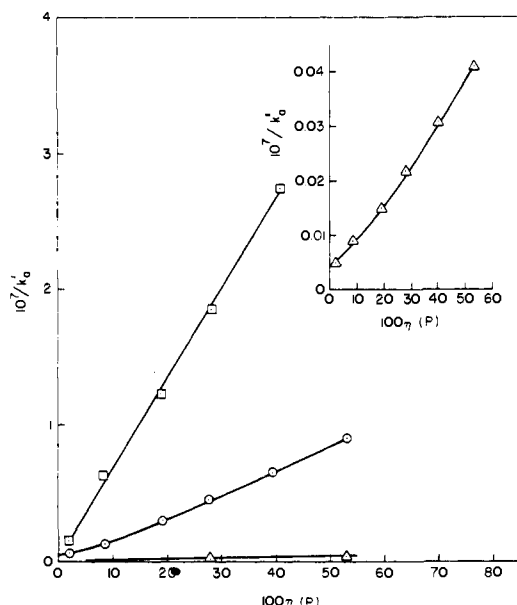


Figure 4. Viscosity dependence of k_a' : (\square), bis(4-biphenylmethyl) ether; (\circ), bis(1-naphthylmethyl) ether; (Δ), dibenzyl ether. Note change of scale in the insert and the significant upward curvature in the plots of the dibenzyl ether and bis(1-naphthylmethyl) ether data at low viscosities.

where k_a^0 is the rate constant for $q \rightarrow \infty$, i.e., in the limit of zero viscosity assuming that the Maxwell distribution is still maintained.²⁶ Since $k_a = k_a^0/2$ when $q = 4/3$ and since f is proportional to the viscosity, η , a characteristic viscosity η^* at which $k_a = k_a^0/2$ is given by

$$\begin{aligned} \eta^* &= (3/4)\eta q \\ &= (3\pi m_r \omega)(f_r/\eta)^{-1} \end{aligned} \quad (8)$$

Note that $k_a = k_a^0 q/2$ for $q \ll 1$, $k_a = k_a^0(q-1)/q$ for $q \gg 1$. Thus, eq 7 predicts the initial slope of $1/k_a$ against η to be half of the slope at large η values.

The parameter q may be obtained from rate constants in media of two viscosities

$$k_{aj}/k_{ai} = (q_i/q_j)[(1+q_j^2)^{1/2}-1]/[(1+q_i^2)^{1/2}-1] \quad (9)$$

But $q_i/q_j = \eta_j/\eta_i$ and $k_{aj}/k_{ai} = (\alpha_i/\alpha_j)(I_m/I_d)_i/(I_m/I_d)_j$. Assuming $\alpha_i/\alpha_j = 1$ and setting $\eta_j/\eta_i = P$, $(I_m/I_d)_i/(I_m/I_d)_j = K$, eq 9 leads to

$$\begin{aligned} q_j^2 &= (P^2 + 1 - 2PQ)/P^2(Q^2 - 1) \\ Q &= (K^2 + 1)/2K \end{aligned} \quad (10)$$

Values of η^* are then obtained from q and η in any medium from $\eta^* = (3/4)\eta q$.

Finally, we may inquire how the activation energy of viscous flow, ΔE_{η^\ddagger} , affects the observed activation energy E_a corresponding to the rate constant k_a . From eq 7,

$$\begin{aligned} -R d \ln k_a/d(1/T) &= \Delta U^\ddagger \\ -R d \ln [(1+q^2)^{1/2}-1]/q/d \ln q [d \ln q/d(1/T)] \\ &= \Delta U^\ddagger + \beta \Delta E_{\eta^\ddagger} \\ \beta &= d \ln [(1+q^2)^{1/2}-1]/q/d \ln q \\ &= (1+q^2)^{-1/2} \end{aligned} \quad (11)$$

so that $E_a = \Delta U^\ddagger + \Delta E_{\eta^\ddagger}$ in the limit of $q \rightarrow 0$, i.e., $\eta \rightarrow \infty$.

B. Theory of Christiansen, Marcus, and Noyes. An alternative theory of the effect of diffusion on chemical kinetics was formulated by Christiansen³⁹ and by Marcus,¹² and discussed in a Noyes review.^{13,41} In this treatment the rate at which two

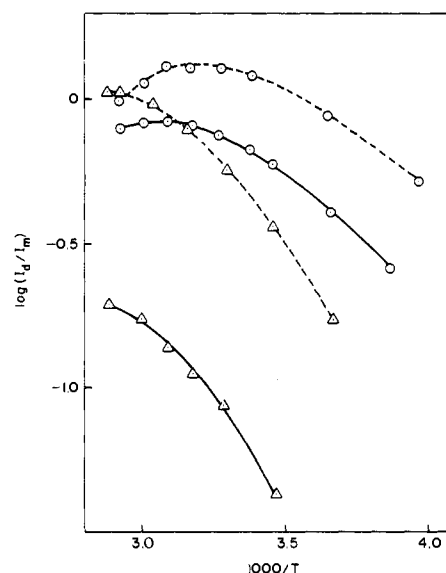


Figure 5. Temperature dependence of I_d/I_m in ethanol (\circ) and in ethylene glycol (Δ). Full lines: bis(4-biphenylmethyl) ether. Dotted lines: dibenzyl ether.

species, A and B, react with each other is treated as depending on the steady-state concentration of B in the immediate vicinity of A. If k_A is the rate constant which would correspond to a uniform distribution of B (so that the rate would be governed by the height of the activation barrier) and k_D is the rate constant for the diffusion-controlled process, then the observed rate constant k will be given by

$$1/k = 1/k_A + 1/k_D \quad (12)$$

and since k_D is inversely proportional to viscosity, $1/k$ is predicted to be linear in η . If we write eq 12 in the form

$$k = [A \exp(\Delta U^\ddagger/RT) + B \exp(\Delta E_{\eta^\ddagger}/RT)]^{-1} \quad (13)$$

then the apparent activation energy E_a becomes

$$E_a = \frac{A \Delta U^\ddagger \exp(\Delta U^\ddagger/RT) + B \Delta E_{\eta^\ddagger} \exp(\Delta E_{\eta^\ddagger}/RT)}{A \exp(\Delta U^\ddagger/RT) + B \exp(\Delta E_{\eta^\ddagger}/RT)} \quad (14)$$

so that this theory predicts that E_a is restricted to the range between ΔU^\ddagger and ΔE_{η^\ddagger} , approaching the activation energy for viscous flow in highly viscous media.

Comparison of Theory with Experimental Results. Using Kramers' theory for the interpretation of the k_a' and I_m/I_d data, we derived by eq 7-10 αk_a^0 and η^* values listed in the last two columns of Table III. The following features may be noted: (1) In the ether series, both αk_a^0 and η^* increase in the order biphenyl < naphthyl < phenyl. (2) Comparing compounds with $X = -CH_2-$ with the ethers, $X = -O-$, we find that the ethers are characterized by a lower η^* but much higher αk_a^0 values. (3) The *N,N*-dibenzylacetamide has η^* reduced by one-third and αk_a^0 increased by a factor of 2.5 compared to the dibenzylammonium ion.

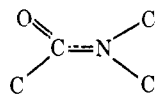
Since we found E_a to vary little with the structure of the compound, we may assume that the force constants C and C' are also similar in the various compounds studied. Kramers' theory predicts then k_a^0 values to be inversely proportional to $I^{1/2}$ unless the processes are characterized by different ΔS^\ddagger . The αk_a^0 values for the three ethers listed in Table III carrying phenyl, 1-naphthyl, and 4-biphenyl substituents, respectively, are in the ratio of 1:0.12:0.08, falling off much more rapidly with increasing size of the chromophore than would be expected from the change in the moment of inertia. Part of the discrepancy may be accounted for by a change in ΔS^\ddagger . In the

case of the 1-naphthyl group, rotation around the X-CH₂ bond may lead to a parallel or antiparallel orientation of the chromophores, but only the parallel one leads to excimer formation. In the case of the biphenyl derivative, the two phenyl rings are not restricted to coplanarity in the ground state; the excited chromophore is coplanar²⁷ and the second biphenyl must become coplanar, with a loss of entropy, when the excimer is formed.

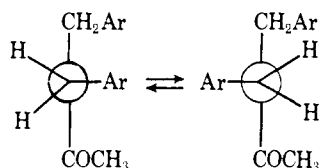
Values of η^* should be according to eq 8 proportional to $m_i \eta / f_i I^{1/2}$. For the ethers carrying phenyl, 1-naphthyl, and 4-biphenyl substituents Table III lists η^* in the ratio of 1:0.38:0.13, which appears to be reasonable considering the structure of these compounds. We may note that $\eta^* = 0.021$, characterizing the biphenyl derivative, is close to 0.018 for ethanol at 0 °C. We see then that even solvents of relatively low viscosity may reduce substantially the rate of internal rotations required for excimer formation if the transition involves motions of bulky groups.

The substantial increase in the αk_a^0 value (by a factor of 3-4) when X = -CH₂- is replaced by an ether linkage is surprising since the E_a values in Table I show no trend toward a lower energy barrier in the ethers. In addition, the energy difference between the gauche and the trans conformations in a -CH₂OCH₂CH₂- sequence is, if anything, somewhat higher than in paraffin hydrocarbons,²⁸ so that α would be expected to be lower for the ethers.

There may be several factors which contribute to the high value of αk_a^0 for *N,N*-dibenzylacetamide as compared to the dibenzylammonium ion. In the amide derivative the CH₂-Ar bond will tend to lie in a plane perpendicular to that of the coplanar grouping



allowing for each aryl group only two orientations:



Thus, there are for this substance no conformations which require more than a single hindered rotation for excimer formation, i.e., $\alpha = 1$. By comparison, the dibenzylammonium ion is not only characterized by a lower value of α , but k_a^0 should also be reduced owing to the mutual repulsion of the dipoles induced in the phenyl rings by the cationic charge.²⁰

Let us now consider the experimental data comparing the temperature dependence of I_d/I_m in ethanol and in ethylene glycol. As stated above, experimental difficulties allow us to make such a comparison only at relatively high temperatures, introducing uncertainties into the interpretation of the data, since the temperature dependence of k_{id} will make a contribution of unknown magnitude to the temperature dependence of the excimer emission. The apparent activation energies $E_a^{\text{gly}} = 6.9$ kcal/mol, $E_a^{\text{eth}} = 3.3$ kcal/mol for dibenzyl ether, $E_a^{\text{gly}} = 6.7$ kcal/mol, $E_a^{\text{eth}} = 3.6$ kcal/mol for bis(4-biphenylmethyl) ether, are therefore not subject to a reliable interpretation. However, whatever the temperature dependence of k_{id} , the difference in the apparent activation energies $E_a^{\text{gly}} - E_a^{\text{eth}}$ should be, by eq 11, $E_a^{\text{gly}} - E_a^{\text{eth}} = \beta^{\text{gly}} E_{\eta^{\text{gly}}} - \beta^{\text{eth}} E_{\eta^{\text{eth}}}$. The activation energies for viscous flow are 2.9 kcal/mol for ethanol and 7.1 kcal/mol for glycol.²⁹ Using eq 7 and 11 with the η^* data in Table III leads to $\beta^{\text{eth}} = 0.13$, $\beta^{\text{gly}} = 0.97$ for dibenzyl ether and $\beta^{\text{eth}} = 0.40$, $\beta^{\text{gly}} = 0.997$ for bis(4-biphenylmethyl) ether. This yields for these compounds $E_a^{\text{gly}} - E_a^{\text{eth}}$

values of 6.4 and 6.7 kcal/mol, very different from the experimental values of 3.4 and 3.2 kcal/mol.

While Kramers' theory fails to give a correct prediction of the dependence of E_a on the viscosity of the medium, this dependence is in good agreement with the theories of Christiansen, Marcus, and Noyes which lead to eq 14. For instance, in the case of dibenzyl ether E_a should be close to ΔU^\ddagger in ethanol but close to ΔE_{η^\ddagger} in glycol solution. Using for ΔU^\ddagger the value $E_a = 3.7$ kcal/mol obtained at low temperature, this leads to a prediction of $E_a^{\text{gly}} - E_a^{\text{eth}} = 3.4$ kcal/mol, equal to the experimental $E_a = 3.4$ kcal/mol.

Treatments similar to those suggested by the theories of Christiansen, Marcus, and Noyes have previously been used to interpret the viscosity dependence of rates of conformational transitions. Biddle and Nordstrom³⁰ used such a procedure for data on the conformational mobility of polystyrene studied by the depolarization of fluorescence of a chromophore attached to the polymer chain. An analogous treatment was used by Peterlin³¹ for the resistance of a flexible chain to conformational transitions in response to a mechanical force applied to the chain ends. In analogy to our parameter η^* , Peterlin concluded that this resistance will be doubled if the frictional coefficient of the chain residue which has to move in a hindered rotation assumes a value $f^* = (h/l^2) \exp(\Delta U^\ddagger/RT)$ where h is Planck's constant and l is a length characteristic of the conformational transition. It is instructive to estimate the viscosity dependence of the conformational transition of dibenzyl ether predicted from this formulation. Using the E_a value from Table I for ΔU^\ddagger and assuming $l = 0.5$ nm, we obtain $f^* = 2.3 \times 10^{-9}$ g s⁻¹. If the hydrodynamic behavior of the phenyl group is approximated as equal to a sphere with a radius of 0.3 nm, we obtain $\eta^* = 4 \times 10^{-3}$ P, i.e., the effect of viscosity is overestimated by about an order of magnitude. This is not surprising since hydrodynamic interactions between the phenyl group and the rest of the molecule would be expected to reduce substantially the viscous resistance to the internal rotation.

Concluding Remarks. We believe that the present study constitutes a first attempt to determine the dependence of the rate of a conformational transition on the bulk of the group which has to be moved through a viscous medium during that process. The use of Kramers' theory seemed attractive since hindered rotation involves the passage from a potential energy well over a potential energy barrier. On the other hand, this theory is predicated on the assumption of a Maxwell distribution of particles in the well, so that it is limited to relatively high energy barriers. The model of Christiansen, Marcus, and Noyes involves no potential energy well but it is applicable no matter how low the potential energy barrier may be. While the initial upward curvature in plots of $1/k_a$ against η appears to favor Kramers' theory, we should perhaps not attach too much weight to this feature of our results, particularly in view of uncertainties concerning the relation of the microscopic viscosity governing molecular motion and the macroscopic viscosity in a mixed solvent. By comparison, the failure of Kramers' theory to account correctly for the viscosity dependence of the activation energy seems a much more important piece of evidence and it leads us to give preference to the Christiansen-Marcus-Noyes analysis for the interpretation of the viscosity dependence of rates of conformational transitions.

Experimental Section

Fluorescence Measurements. Fluorescence spectra were taken on an Hitachi Perkin-Elmer MPF-2A spectrophotometer equipped with a thermostated sample cell compartment and are uncorrected. Concentrations of the fluorescing species were 2×10^{-3} M for the phenyl derivatives and less than 10^{-4} M for the other compounds. Excitation

wavelengths of 258 nm for phenyl, 270 nm for naphthyl, and 292 nm for biphenyl derivatives were chosen to give maximum intensity and minimum interference from the scattering band. All samples were degassed by passing prepurified nitrogen (Airco, 99.995%) through the solution for 25 min. I_m/I_d values were obtained from the relative peak heights of the monomer and excimer bands and were corrected for contributions of the monomer emission at the excimer λ_{\max} and excimer emission at the monomer λ_{\max} .

The temperature was regulated by an FTS Flexicool system with precooled, dry nitrogen passing over the cell to prevent condensation. The temperature was monitored with a YSI thermistor/tele-thermometer system (Models 427/42SL-SC) immersed in a separate cuvette. Temperature regulation was better than $\pm 0.3^\circ\text{C}$.

Lifetime measurements were carried out at 0°C using an SLM phase-modulation subnanosecond spectrofluorometer equipped with a thermostated sample cell compartment and excitation and emission monochromators.³² Measurements were made at 90° excitation using 10-MHz excitation frequency. For each measurement of sample and scattering standard an average of ten readings was taken. At least eight alternating measurements of the scattering and sample solutions were made to compensate for drifts in the phase and modulation of the exciting light.

Materials. Solvents. Absolute ethanol was distilled over magnesium turnings and only the fluorescence-free fractions were used. Ethylene glycol and glycerol (spectrograde) were purified by stirring with activated carbon and subsequent centrifugation until the extraneous fluorescence was negligible. Heptane (Fisher) was fluorescence-free and used directly.

Compounds (Excimer Forming). Dibenzyl ether was purchased from Pfaltz and Bauer and doubly distilled under reduced pressure to use. The other bis(arylmethyl) ethers were prepared by Me_2SO -mediated dehydration of the corresponding alcohols as previously described.³³

Bis(α -naphthylmethyl) ether, mp 119–120 $^\circ\text{C}$ (absolute ethanol, then sublimed).

Anal. Calcd for $\text{C}_{22}\text{H}_{30}\text{O}$: C, 85.16; H, 9.68. Found: C, 84.93; H, 9.49.

Bis(4-biphenylmethyl) ether, mp 87–89 $^\circ\text{C}$ (absolute ethanol).

Anal. Calcd for $\text{C}_{26}\text{H}_{22}\text{O}$: C, 89.14; H, 6.28. Found: C, 89.11; H, 6.34.

Dibenzylamine (Pfaltz and Bauer) was doubly distilled under reduced pressure and converted to the hydrochloride salt with HCl gas in ether. The salt was recrystallized twice from absolute ethanol, mp 261–264 $^\circ\text{C}$ dec (lit.³⁴ 260–261 $^\circ\text{C}$ dec). *N*-Acetyldibenzylamine, bp 182–184 $^\circ\text{C}$ (0.9–1.1 mm) (lit.³⁵ 153 $^\circ\text{C}$ (0.15 mm)), *N,N*-dimethyldibenzylammonium chloride, mp 91–94 $^\circ\text{C}$ (lit.³⁶ 94–95 $^\circ\text{C}$ (absolute ethanol/ethyl acetate)), and bis(α -naphthylmethyl)ammonium chloride,³⁷ mp 230–234 $^\circ\text{C}$ (ethanol, dec) (lit.³⁸ 239 $^\circ\text{C}$), were prepared as described in the literature.

1,3-Diphenylpropane was purchased from API Standard Reference Materials (Carnegie-Mellon University). 1,3-Dinaphthylpropane was a gift from Dr. E. A. Chandross.

Compounds (Analogue Single Chromophore). The following compounds were used as the model compounds in lifetime determinations: 4-diphenylmethanol (Pfaltz and Bauer), 1-naphthalenemethanol (Aldrich, recrystallized from absolute ethanol), benzyl alcohol (Matheson Coleman and Bell), toluene (chromatoquality, Matheson Coleman and Bell), acetylbenezylamine (Aldrich), benzylmethylamine (Aldrich, converted to hydrochloride salt (HCl gas/ether) recrystallized from absolute ethanol) and 1-methylnaphthalene (Aldrich, vacuum distilled).

All compounds exhibited only one spot by TLC (Merck silica gel F-254, ethanol/ether eluant).

Viscosity Measurements. Viscosity and density measurements were carried out at 0°C using a Cannon LC viscometer and pycnometer using the average of two determinations. Activation energies of viscous flow were calculated from literature data²⁹ using the range 0–20 $^\circ\text{C}$ for ethanol and heptane and 20–40 $^\circ\text{C}$ for ethylene glycol.

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