the gas phase to the solid thus explaining the structure difference in this case.

Force field calculations predict the structures of **11, 12, 13, 14,** and **15** astonishingly well. Both the bond angle Φ and the twist angle θ are predicted in such a way that the resulting geometries are in full agreement with what we inferred from the UP and electronic spectra. This finding contrasts with previous observations for *trans*-stilbene in which the force field calculations were not able to describe the nonplanar structure of the free molecule in the gas phase. The force field methods also fail to predict the nonplanar structure of the larger monophenylcycloalkenes. As in the case of *trans*-stilbene the nonplanarity of these monophenylcycloalkenes seems to be caused by improper balancing of the weak hydrogen/hydrogen interactions and the resonance interactions. These compounds provide a substantial test for the balance of these forces. Presently available force-field methods seem not to be optimized properly for this balance.

Semiempirical quantum chemical methods like MNDO, MINDO, and even MNDOC (including second-order Møller–Plesset corrections) all overestimate the twist angles in these loosely coupled π systems, either by overestimating the repulsive forces

or by underestimating the stabilization resulting from π-electron delocalization.

Rate Constants for Reactions in Viscous Media: Correlation between the Viscosity of the Solvent and the Rate Constant of the Diffusion-Controlled Reactions[1]

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Abstract: The kinetics of the quenching of excited pyrene by several molecules in a variety of hydrocarbon solvents and in a diol are reported. The rate constants for reaction of the excited pyrene are, for the most part, diffusion-controlled and considerably faster than those calculated by use of the Smoluchowski and Stokes–Einstein equations. Measurements of the diffusion constants of the reactants and direct use of the Smoluchowski equation does predict rate constants that are in agreement with those measured. Application of the Stokes–Einstein equation shows that this equation does not calculate the correct diffusion constant for the reactants in the media studied. A free volume theory with transition-state concepts suggests that the diffusion constants of reactants in the liquids used vary as the increase of the square root of the bulk viscosity. This is in very good agreement with the experimental findings. A discussion of what the data mean for diffusion-controlled reactions involving electron transfer and complex formation is included, and also hinted at is the implication of the data for reactions in micelles and vesicles.

A diffusion-controlled reaction is defined as one occurring at each encounter of the reactants. The theory of such reactions has been developed by Smoluchowski,[2] Collins and Kimball,[3] Noyes,[4] and others, and the subject has been reviewed by Noyes,[4] Birks et al.,[5] and recently by Rice.[6]

The smoluchowski equation in its simplest form, i.e. when transient terms are disregarded, is given below:

$$k = 4\pi N'RD \qquad (1)$$

where k is the rate constant of the bimolecular process in units $M^{-1} s^{-1}$, N' is Avogadro's number per millimole, R represents the encounter distance taken as the sum of the molecular radii, and D is the relative diffusion coefficient ($D = D_A + D_B$).

For a particle moving in a continuous medium the diffusion coefficient is given by

$$D = kT/f \qquad (2)$$

where k is the Boltzmann constant and f is the friction coefficient.

The friction coefficient has been calculated by Stokes, for a sphere of radius r, moving in a continuum of viscosity η and is given by[7]

$$f = 6\pi\eta r \frac{1 + 2\eta/\beta r}{1 + 3\eta/\beta r} \qquad (3)$$

where β is the coefficient of sliding friction between the diffusing molecule and its surroundings. If the dimensions of the moving molecule are large compared with those of the solvent molecules, then $\beta = \infty$ and no slipping occurs. In such a case, $f = 6\pi\eta r$ and the diffusion coefficient is given by the known Stokes–Einstein equation:

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$$D = kT/6\pi\eta r \tag{4}$$

The other limit, $\beta = 0$, is supposed to apply when the moving particle is smaller than the solvent molecules. In this case

$$D = kT/4\pi\eta r \tag{5}$$

Thus, the theories of diffusion predict an inverse relation between the diffusion coefficient and the viscosity of the solvent. In addition, for a given solvent and temperature, D is determined exclusively by the radius of the moving molecule, which is supposed to be spherical.

Experimental diffusion coefficients often are larger than those predicted by the Stokes-Einstein relation, the discrepancy being greater in more viscous solvents.[8] There have been attempts to explain these deviations by using the microfriction theory of Grierer and Wirtz.[9] This theory introduces a correction factor that depends upon the ratio of the radii of the solute to solvent. Several other empirical and semiempirical relations have been proposed,[10] and the most recent is due to Davis, Tominaga, and Evans;[11] recently this subject has been reviewed by Tyrrell and Harris.[8]

Thus, the principal problem that arises in treating diffusion-controlled reactions is not in the theory itself, but in the values used for the diffusion coefficients. Attention has been drawn to this by Ware.[12a] This fact is particularly important when one attempts to extract structural information about the mechanism of a reaction by comparing theoretical and experimental rate constants.[12b] Indeed, for several reactions both between neutral molecules and between charged molecules, the Smoluchowski equation, or that corrected for electrostatic effects by Debye, has been useful in explaining results quantitatively.[13,14] For the most part, the reactions studied have been in liquids of roughly 1 cP, such as water, small alcohols, and light hydrocarbons;[5,15] however, some abnormality exists for more viscous media.[16-18] In viscous media the diffusion coefficients (and rate constants) do not obey the Stokes-Einstein relationship and do not follow the empirical relation:[8,18]

$$K\eta/T = a + b\eta^x \tag{6}$$

which has been used to fit experimental results for a great variety of diffusion-controlled reactions.[5]

In spite of these facts, recent studies of diffusion-controlled reactions initiated in organized media such as micelles and membranes have been used to portray microproperties of these media.[19-21] It is tacitly assumed in these studies that the Stokes-Einstein relationship between the diffusion constant and viscosity is correct, so that some statement may be made about the microviscosity of the medium. However, in view of the earlier work in viscous liquids illustrating an unusual dependence between the diffusion coefficient and the viscosity of the medium, it is important to fully investigate the Stokes-Einstein relationship in more viscous media. In particular, media that relate to micelles and vesicles are of some concern. Hence, in this paper we have studied the quenching of excited pyrene by several molecules under conditions where the reactions are diffusion-controlled in a series of different solvents, viz various hydrocarbons from heptane to squalane, i.e. increasing the viscosity by some 400-fold, and also in a dihydric alcohol 2-methylpentane-2,4-diol. In all these systems the diffusion coefficients were determined by using the Taylor dispersion technique.[23,24] Using the data obtained, we comment on the applicability of the Stokes-Einstein and empirical relationships and in some instances explore the nature of the diffusion-controlled reactions.

Experimental Section

The experimental equipment has been described previously.[22] Basically, a short-pulsed laser, typically a small PRA nitrogen laser, pulse length 0.3 ns, is directed onto a sample that contains a 10^{-5} M pyrene solution. The pyrene fluorescence is then detected at 400 nm by an optical system and a fast photomultiplier circuit, the electrical signal is captured on a 7912AD Tektronix multitransient digitizer; the data is then processed by a Tektronix 4052AD computer. The quenching rate constants of excited pyrene, k_q, were determined by measuring the increased rate of decay on addition of the quencher. The lifetime, τ, is related to τ_0 and k_q by the relationship $\tau^{-1} = \tau_0^{-1} + k_q[Q]$ where [Q] is the concentration of quencher and τ_0 is the lifetime in absence of quencher. The slope of τ_0/τ vs [Q] gives the quenching rate constant, which was measured under a variety of conditions such as different temperature and media. Fluorescence spectra were measured on a Perkin-Elmer 55B spectrofluorimeter, and absorption spectra were measured on a Perkin-Elmer Model 44 instrument. Solutions were deaerated by bubbling with nitrogen for 5 min prior to use.

The diffusion coefficients were measured by using the Taylor diffusion method, which monitors the dispersion of a small sample of solute that is injected into a solvent passing in laminar flow through a capillary tube. The apparatus used is similar in design to that developed by Pratt and Wakeham,[23] Grushka and Kikta,[24] and others. Basically, solvent is pumped at a steady flow (0.1 mL/min) through 15 m of coiled stainless steel tubing (0.0762 cm i.d.) by using a Waters 501 HPLC pump. The tubing is immersed in a thermostated bath where the temperature is controlled by a Haake A 80 bath. Injection is made with a Waters U6K injector, and detection of the dispersed solute is accomplished by a Waters Lambda-Max 481 spectrophotometer. The signal was recorded on a BBC Goerz Metrawatt 5E120 recorder. The diffusion coefficients were calculated by using the following equation:

$$D = \frac{0.2310 r^2 t_R^2}{W_{1/2}^2} \tag{7}$$

where r is the radius of the tube, t_R is the retention time of the solute in the tube, and $W_{1/2}$ is the eluted peak width at half its height. The applicability of this method and a comparison of results obtained by different techniques has been discussed by Tyrrell[8] and Wakeham et al.[25] The smallest diffusion coefficient that could be measured accurately and analyzed by eq 7 is 3×10^{-8} cm^2 s^{-1}.

Heptane, octane, decane, dodecane, hexadecane, and 2-methylpentane-2,4-diol were purchased from Aldrich and used as received. Squalane (Aldrich) was purified by chromatography on an alumina column. Nitromethane, nitrobenzene, diiodomethane, nitrohexane, and nitrododecane were used without further purification.

The viscosity values for squalane were taken from Leone and Hammill,[26] and for 2-methylpentane-2,4-diol (MPD), the values were calculated by using the equations given by Tyrrell and Watkins.[17]

Results and Discussion

The solvents used in this study were chosen in such a way that a change in the viscosity of the medium did not alter other medium properties that might affect both the kinetics of the quenching reaction and the diffusion process. Hence, a family of saturated hydrocarbons were selected ranging from heptane to squalane, also a diol for comparison. With squalane and 2-methyl-

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Table I. Diffusion Coefficients Determined by Taylor Dispersion Technique

In Viscous Solvents ($\times 10^{-7}$ cm^2 s^{-1})

	MPD			squalane					
T, K	pyrene	CH_2I_2	$NO_2C_6H_5$	pyrene	CH_2I_2	NO_2CH_3	$NO_2C_6H_{13}$	$NO_2C_{12}H_{25}$	$NO_2C_6H_5$
268	0.79	1.90	1.63	1.60	3.73	8.31	3.55	2.38	3.73
273	1.10	2.59	2.30	1.92	5.05	10.90	4.34	3.17	4.57
278	1.44	3.47	2.79	2.79	6.80	12.69	5.64	4.48	6.28
283	2.00	4.42	3.90	3.37	8.03	15.86	7.33	3.54	8.03
288	2.47	5.83	5.18	4.28	10.62	20.37	8.66	5.85	10.62
293	3.19	8.02	6.53	5.23	13.11	31.82	14.14	8.66	11.77
298	4.15	10.62	8.24	6.48	14.70	31.82	13.39	7.96	14.70
303	5.62	11.77	10.90	8.02	18.88	37.87	17.90	11.46	18.88
308	6.80	15.60	14.23	9.66	22.16	41.57	19.07	10.90	22.16
313	8.78	18.88	17.03	12.41	25.13	50.78	23.38	13.39	27.18

In Normal Hydrocarbons ($\times 10^{-5}$ cm^2 s^{-1})

	pyrene	CH_2I_2	NO_2CH_3	$NO_2C_6H_{13}$	$NO_2C_6H_5$
n-heptane	1.48	2.21	2.94	1.79	2.02
n-octane	1.18	1.72	2.42	1.47	1.72
n-decane	0.87	1.22	1.84	1.10	1.26
n-dodecane	0.62	0.97	1.48	0.91	0.91
n-hexadecane	0.31	0.52	0.76	0.52	0.63

Table II. Experimental and Theoretical Parameters for the Studied Systems

	pyrene	CH_2I_2	NO_2CH_3	$NO_2C_6H_{13}$	$NO_2C_{12}H_{25}$	$NO_2C_6H_5$
r_{vw},[a] Å	3.46	2.68	2.29	3.19	3.84	2.92
a^{Kin}[b]		0.55	0.55	0.50	0.40	0.56
a^{D}[b]	0.57	0.50	0.50	0.53		0.53
a^{emp}[c]	0.79	0.68	0.60	0.76	0.83	0.72
E_{act}^{kin} (kcal/mol)		8.4 (7.5)	8.0	6.5	5.3	7.4 (9.7)
E_{act}^{D} (kcal/mol)	7.4 (9.0)[d]	7.2 (8.5)	6.6	7.1	6.6	7.2 (8.5)

[a] Calculated by using Bondi and Edward's method (ref 16 and 27). [b] a^{Kin} and a^{D} correspond to the experimental slopes of a plot ln k_q (ln D) vs ln $T/\eta\sigma$ respectively. [c] Empirical value of the parameter a according to the relation proposed by Evans et al. in Evans, D. F.; Tominaga, T.; Chan C. *J. Solution Chem.* **1979**, *8*, 461. [d] The values between parentheses correspond to 2-methylpentane-1,4-diol as solvent.

pentane-2,4-diol (MPD), a change of temperature (0–40 °C) produced a total viscosity variation of some 400-fold.

Diffusion Coefficients. The diffusion coefficients of pyrene and the quencher molecules were determined by using the chromatographic broadening method described in the Experimental Section. Table I shows the measured diffusion coefficients in squalane and MPD at different temperatures and in hydrocarbons at 293 K for all the molecules used in the quenching reactions.

Figure 1A shows the effect of changing the viscosity, via temperature change, on the diffusion coefficient of various molecules in squalane. The data plotted as $-\ln D$ vs ln T/η exhbit a slope of approximately 0.53, thus indicating that in squalane the diffusion coefficient varies inversely with the square root of the viscosity and is independent of the nature of the solute, i.e. its size and shape. This is in contrast to the prediction of the Stokes–Einstein equation, where D should vary inversely with the viscosity. Figure 1B shows the same type of plots in various hydrocarbons and with different solutes. Again the slopes are considerably less than unity, indicating that the Stokes–Einstein relationship is not applicable in these systems. With the diol, shown in Figure 1C, two slopes are given for the plot of ln D vs ln T/η, the break occurring at the transition temperature in this liquid.[17] The slopes obtained are 0.67 and 0.94, and indicate that in the more viscous medium, at lower temperatures, that the diffusion coefficients vary as η raised to a power less than unity.

Figure 2, parts A and B, show ln D plotted vs $1/T$ for various solutes in squalane. The plots are linear, and the activation energy for diffusion can be derived from the Eyring equation[33] given below

$$D = D_0 e^{-E_a^{D}/RT} \tag{8}$$

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Table III. Comparison of the Experimental Diffusion Coefficients of CH_2I_2 with Those Predicted by the Stokes–Einstein Equation and Some Empirical Relationships

solvent	D_{exp}	D_{Stokes}[a]	D_{SW}[b]	D_{DTE}[c]
n-heptane	2.21×10^{-5}	1.96×10^{-5}	3.92×10^{-5}	2.81×10^{-5}
n-octane	1.72×10^{-5}	1.48×10^{-5}	3.02×10^{-5}	2.32×10^{-5}
n-decane	1.22×10^{-5}	0.87×10^{-5}	1.89×10^{-5}	1.62×10^{-5}
n-dedecane	0.97×10^{-5}	0.59×10^{-5}	1.31×10^{-5}	1.25×10^{-5}
n-hexadecane	0.52×10^{-5}	0.24×10^{-5}	0.57×10^{-5}	0.67×10^{-5}
squalane (40 °C)	2.5×10^{-6}	1.06×10^{-6}	2.8×10^{-6}	4.0×10^{-6}
squalane (30 °C)	1.9×10^{-6}	0.50×10^{-6}	1.3×10^{-6}	2.4×10^{-6}
squalane (20 °C)	1.3×10^{-6}	0.23×10^{-6}	0.60×10^{-6}	1.4×10^{-6}
squalane (10 °C)	0.8×10^{-6}	0.10×10^{-6}	0.26×10^{-6}	0.8×10^{-6}
squalane (0 °C)	0.5×10^{-6}	0.04×10^{-6}	0.10×10^{-6}	0.4×10^{-6}

[a] Calculated by using $D = KT/6\pi\eta r$ with r equal to van der Waal's radius according to Bondi[26] and Edward.[27] [b] Values obtained by using Spernol and Wirtz equation $D = KT/6\pi\eta r f$ where f is the microfriction factor (eq 23, ref 15). [c] Values predicted by the Davis, Tominaga, and Evans relationship.

a form which is similar to the Arrhenius equation. Similar plots are shown in Figure 2C for MPD. The activation energies for diffusion and the slopes of the plots ln D vs ln (T/η) are given in Table II.

The activation energies for diffusion in squalane are about 7 kcal/mol for pyrene and all the quenchers used. A comparison of this value with the activation energy for the solvent viscous motion, which is approximately 13 kcal/mol,[26] indicates that a square-root relationship is obeyed for the dependence of the diffusion coefficient on the viscosity of the medium.

Table III shows a comparison of the values of the experimental diffusion coefficients, obtained for diiodomethane, compared to those calculated by using the Stokes–Einstein; Spernol and Wirtz; and the Davis, Tominaga, and Evans equations. This later empirical relation gives the best fit to the experimental data, but the

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Table IV. Quenching Rate Constants

In Viscous Solvents at Different Temperatures ($\times 10^8$ M^{-1} s^{-1})

	MPD		squalane				
T, K	CH_2I_2	$NO_2C_6H_5$	CH_2I_2	NO_2CH_3	$NO_2C_6H_{13}$	$NO_2C_{12}H_2$	$NO_2C_6H_5$
268	1.5	1.6	3.4	1.3	3.1	2.8	5.3
273	1.9	2.4	4.4	1.5	3.6	3.3	6.7
278	2.8	3.0	6.7	2.1	4.3	4.2	8.5
283	3.6	5.2	6.6	2.4	5.3	4.9	9.5
288	4.8	6.2	9.4	2.8	6.4	5.8	10.4
293	7.2	8.7	12.8	4.5	7.8	6.4	18.0
298	10.4	8.7	14.7	5.3	9.3	7.6	21.0
303	11.2	12.8	19.9	6.8	11.8	8.7	24.3
308	13.2	19.1				10.5	
313	16.6	22.1	34.7	9.0		11.7	40.2

In Normal Hydrocarbons at 293 K ($\times 10^{10}$ M^{-1} s^{-1})

	CH_2I_2	NO_2CH_3	$NO_2C_6H_{13}$	$NO_2C_{12}H_{25}$	$NO_2C_6H_5$
n-heptane	1.20	0.22	0.25	0.21	2.22
n-octane	0.97	0.26	0.22	0.21	1.90
n-decane	0.83	0.25	0.21	0.17	1.35
n-dodecane	0.62	0.21	0.21	0.18	0.95
n-hexadecane	0.45	0.12	0.16	0.14	0.60

Table V. Theoretical Rate Constants for Diffusion-Controlled Reactions

In Viscous Solvents ($\times 10^8$ M^{-1} s^{-1})

	MPD			squalane					
T, K	CH_2I_2	$NO_2C_6H_5$	k_{SE}	CH_2I_2	NO_2CH_3	$NO_2C_6H_{13}$	$NO_2C_{12}H_{25}$	$NO_2C_6H_5$	k_{SE}
268	1.25	1.17	0.22	2.48	4.31	2.59	2.19	2.57	0.20
273	1.71	1.64	0.36	3.24	5.58	3.15	2.81	3.13	0.33
278	2.27	2.04	0.57	4.45	6.73	4.24	4.01	4.38	0.50
283	2.97	2.85	0.87	5.30	8.36	5.38	3.82	5.50	0.78
288	3.89	3.69	1.26	6.92	10.72	6.51	5.59	7.19	1.21
293	5.19	4.69	1.80	8.52	16.12	9.74	7.67	8.20	1.83
298	6.84	5.98	2.45	9.84	16.66	10.00	7.70	10.22	2.74
303	8.05	7.97	3.27	12.49	19.96	13.04	10.76	12.98	4.04
308	10.37	10.15	4.32	14.78	22.28	14.45	11.35	15.36	
313	12.80	12.45	5.49	17.44	27.49	18.00	14.25	19.11	8.56

In Normal Hydrocarbons ($\times 10^{10}$ M^{-1} s^{-1})

	CH_2I_2	NO_2CH_3	$NO_2C_6H_{13}$	$NO_2C_6H_5$	k_{SE}
n-heptane	1.71	1.92	1.64	1.69	1.62
n-octane	1.35	1.57	1.33	1.40	1.22
n-decane	0.97	1.18	0.99	1.02	0.72
n-dodecane	0.74	0.91	0.77	0.74	0.49
n-hexadecane	0.39	0.47	0.42	0.45	0.20

slopes predicted for the plot ln *D* vs ln (T/η) are greater than the experimental values. (These data are summarized in Table II). The Stokes–Einstein relation is a poor approximation in viscous solvents, and the inclusion of the microfriction factor of Spernol and Wirtz does not improve the results, as has been found in other work with less viscous solvents.[10,15]

Rate Constants. The quenching rate constants were determined from a Stern–Volmer type plot:

$$\tau_0/\tau = 1 + k_q \tau_0 [Q] \qquad (9)$$

where τ_0 and τ are the lifetime of the singlet excited pyrene in the absence and presence of a quencher at concentration, [Q]. Typical plots are shown in Figure 3. The actual values for the rate constants are conveniently collected in Table IV for all the solvents and temperatures used.

Figure 4, parts A and B, show plots of the logarithm of the quenching rate constant as a function of the viscosity and are plotted as the logarithm of the temperature divided by the viscosity. Quenching data for excited pyrene in two media are shown in Figure 4A for squalane at different temperatures and for the normal hydrocarbons (heptane to hexadecane) at 293 K; Figure 4B shows data for 2-methylpentane-2,4-diol (MPD), a viscous alcohol. The quenchers used are diiodomethane, nitrobenzene, nitromethane, nitrohexane, and nitrododecane. Plots of ln k_q vs ln T/η were linear over the full range of viscosities studied. In

the case of nitrobenzene and diiodomethane, the same slope was obtained over the full viscosity range. However, for the other quenchers, nitromethane, nitrohexane, and nitrododecane, an initial low slope (or plateau) was obtained at lower viscosity followed by a sharper slope at higher viscosities. These data are shown in Figure 4A.

The data in MPD, Figure 4B, indicate that two slopes are also obtained in this solvent and exhibit a break at the transition temperature, a well-defined parameter for this particular alcohol, at 293 K.[17]

Figure 5 shows an Arrhenius plot for the rate constant k_q for deactivation of singlet excited pyrene by nitrobenzene both in squalane and MPD. These systems gave linear plots, the slopes of which gave activation energies for the quenching process of approximately 5–9 kcal/mol.

The activation energies and the slopes of the plot ln K_q vs ln (T/η) are shown in the Table II.

Theoretical Rate Constants. In the calculation of the rate constants for a diffusion-controlled process, the Smoluchowski equation as given in (1) was used. The encounter distance, R, has been taken as the sum of van der Waal's radii of pyrene and the quencher. These radii appear in Table II and have been calculated according to the method proposed by Bondi[27] and Edwards.[28] The relative diffusion coefficient, $D = D_A + D_B$, was calculated from the experimental diffusion coefficients.
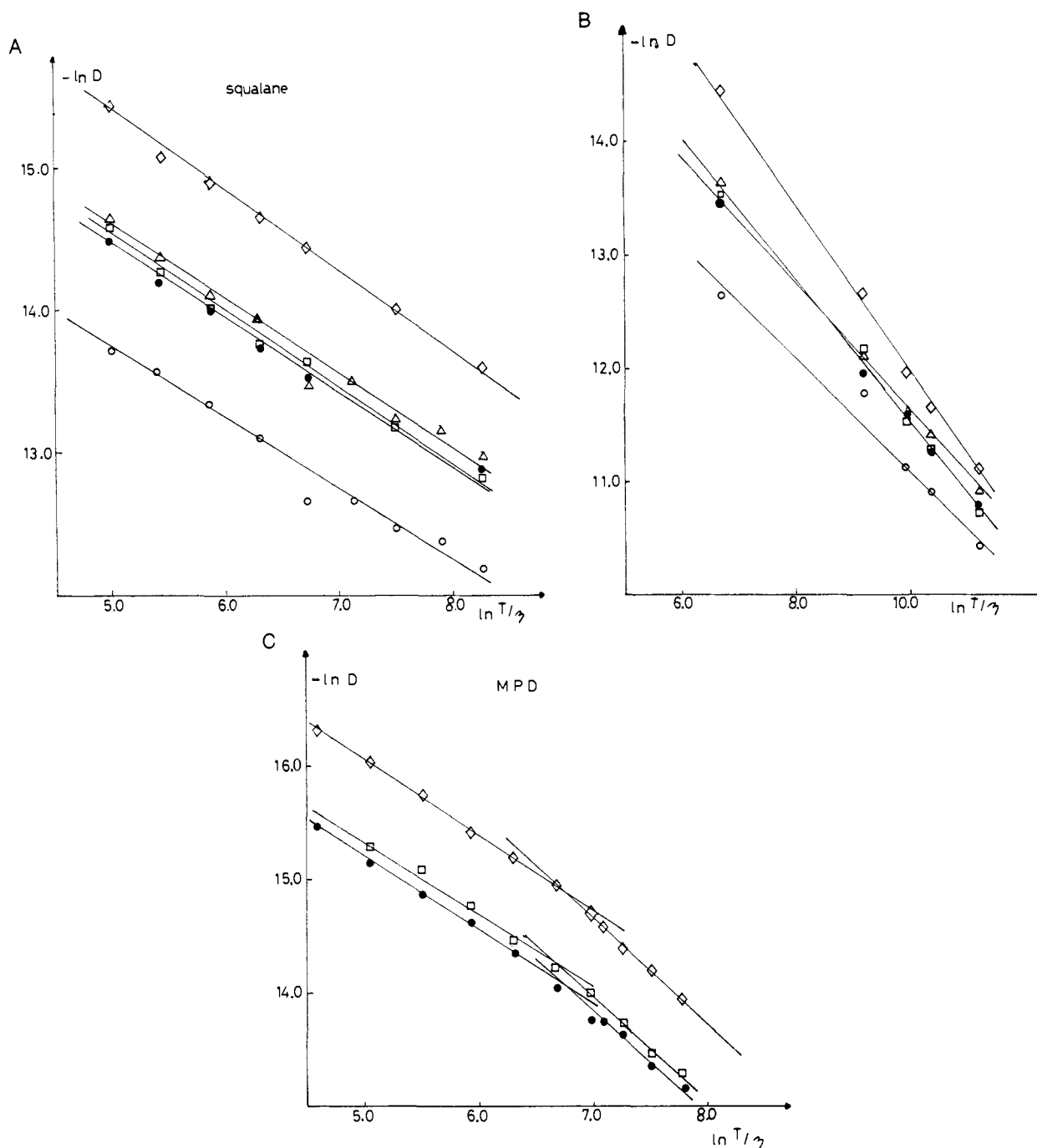
Figure 1. Dependence of the diffusion coefficients with the viscosity, plotted as $\ln D$ vs $\ln T/\eta$, ($\bullet$) diiodomethane, ($\square$) nitrobenzene, ($\bigcirc$) nitromethane, ($\triangle$) nitrohexane, ($\diamond$) pyrene. (A) In squalane. (B) In a series of hydrocarbons. (c) In 2-methylpentane-2,4-diol.

Table V lists the theoretical rate constants for diffusion-controlled reactions obtained for each particular liquid. It can be noted in Table VI that the measured rate constant in some cases is larger than that calculated whereas in other cases it is lower. In particular for nitrobenzene the measured rate constant tends to be 1.5–2 times greater than that calculated. In contrast for nitromethane the rate constant is less than half that calculated. This situation exists for all the liquids studied. It is inherent in our thinking that the Smoluchowski equation does define the reaction rate in these systems, whereas the Stokes–Einstein equation, as has been discussed above, does not describe correctly the diffusion coefficient.

It is pertinent to inquire into the lack of agreement between the calculated and measured rate constants. In the case of nitrobenzene, earlier studies[29] showed that the reaction between pyrene and nitrobenzene, in a viscous medium such as a polymerized microemulsion particle, was via electron tunnelling. Hence, for nitrobenzene it is suggested that the interaction radius is larger

than that calculated for the sum of the radii of the two reactants, because of the electron-tunnelling reaction that occurs on close proximity of the reactants. Pilling and Rice[30] have resolved the diffusion equation, including electron transfer as a long-range effect. In this model the rate constant is given by

$$k_T = 4\pi N' R_{eff} D \qquad (10)$$

where

$$R_{eff} = R + \frac{1}{B}\left[2\gamma + \ln \frac{W_0^2}{4} \right] \qquad (11)$$

and $W_0^2 = 4\alpha/\beta^2 D$. α and β are parameters with typical values of $\sim 10^{14}$ s^{-1} and 15 nm^{-1}, respectively,[38] and γ is Euler's constant

(34) Turley, W. D.; Offen, H. W. *J. Phys. Chem.* **1985**, *89*, 2933. Turley, W. D.; Offen, H. W. *J. Phys. Chem.* **1986**, *90*, 1967.
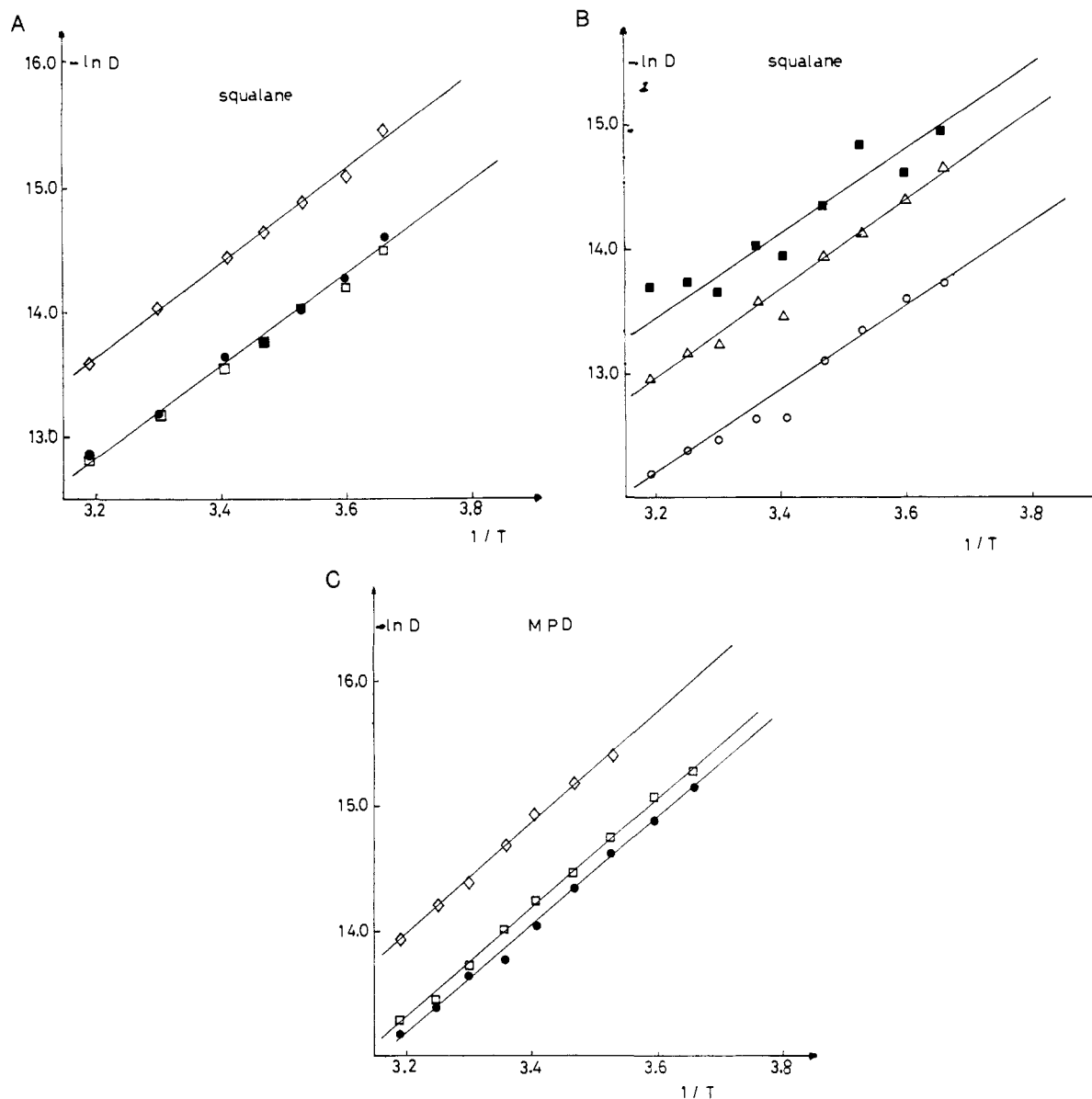(35) Atik, S.; Thomas, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 3550.

Figure 2. Plots of ln D vs $1/T$, (●) diiomethane, (□) nitrobenzene, (O) nitromethane, (△) nitrohexane, (■) nitrododecane, (◇) pyrene. (A and B) In squalane. (C) In 2-methylpentane-2,4-diol.
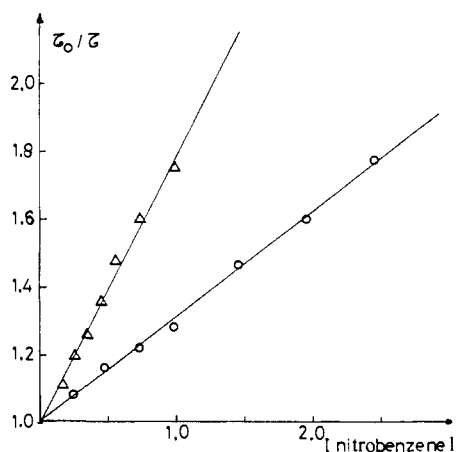

Figure 3. Stern–Volmer plot (eq 8) for nitrobenzene at 20 °C, (O) 2-methylpentane-2,4-diol (△) squalane.

(0.57721). With the measured diffusion coefficients, we have calculated the rate constant k_T for the couple pyrene–nitrobenzene

in viscous solvents. The results are shown in Figure 6 where the experimental vs the tunnelling constants are plotted. The line corresponds to unit slope. The broken line is a best fit of the experimental data when compared with the Smoluchowski equation.

In the cases of systems exhibiting lower rate constants such as nitromethane, nitrohexane, and nitrododecane, we conclude that the experimental values are lower than the theoretical due to the fact that the reactions are activation controlled. However, as seen in Figure 4A when the liquids become more viscous, the reaction rates show a similar dependence on T and η as that for a diffusion-controlled reaction, such as nitrobenzene. For nitromethane the absolute rate constant is still smaller than that predicted by the Smoluchowski equation. This kind of behavior has been reported for some radical recombination reactions and has been called "pseudo-diffusion-controlled."[31] The low rate constant was completely ascribed to the high stereospecificity of these reactions, as the phenomenon appears most commonly when the radicals involved have their reaction sites screened by substituents. For the system pyrene–nitromethane, this condition of stereospecificity

(36) Tram, C. D.; Klahn, P. K.; Romero, A.; Fendler, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 1622.

(37) Murtagh, J.; Thomas, J. K. *Faraday Discuss. Chem. Soc.* **1986**, *81*, 127.

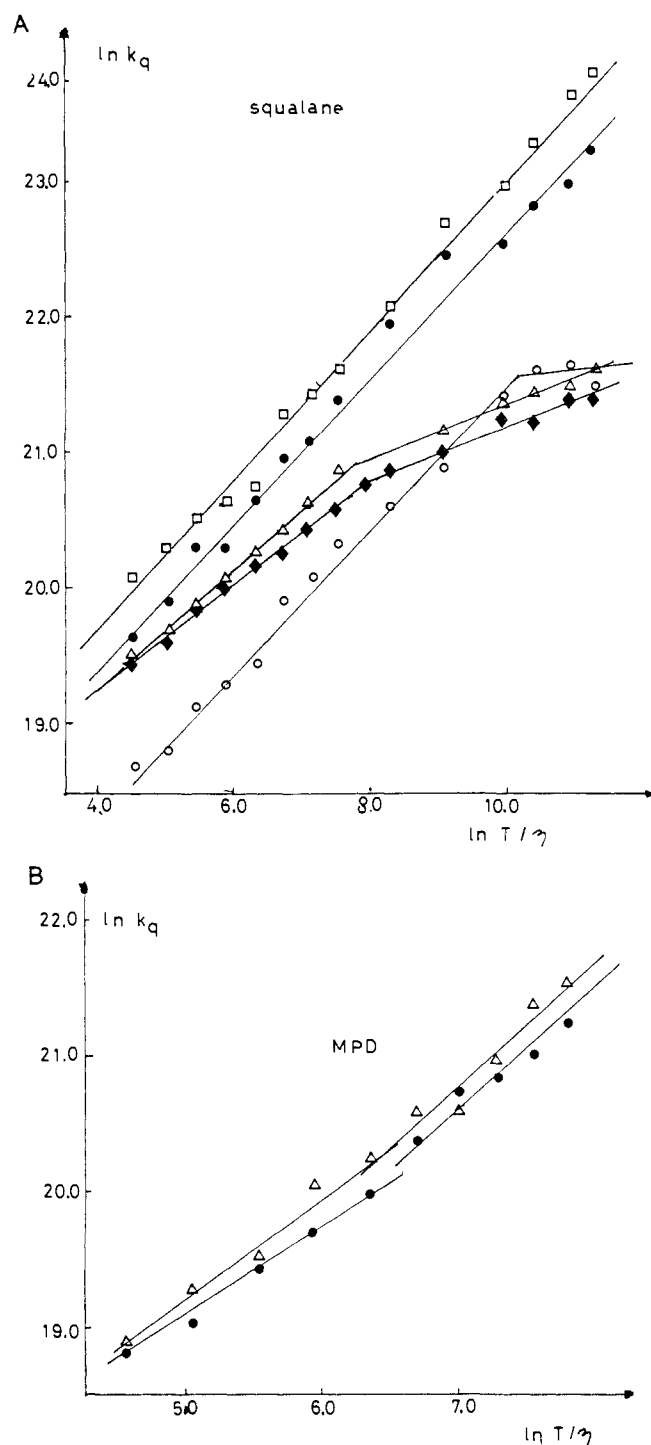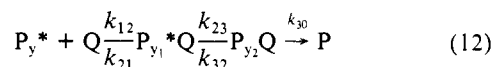(38) Miller, J. R.; Peeples, J. A.; Schmitt, M. J.; Closs, G. L. *J. Am. Chem. Soc.* **1982**, *104*, 6488.

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A

B

Figure 4. (A) Plot of ln k_q against ln T/η for the deactivation of singlet excited pyrene by different quenchers in squalane and several hydrocarbons, (●) diiodomethane, (□) nitrobenzene, (O) nitromethane, (△) nitrohexane, (■) nitrododecane. (B) Same as in Figure 1A with 2-methylpentane-2,4-diol as solvent, (●) diiodomethane, (△) nitrobenzene.
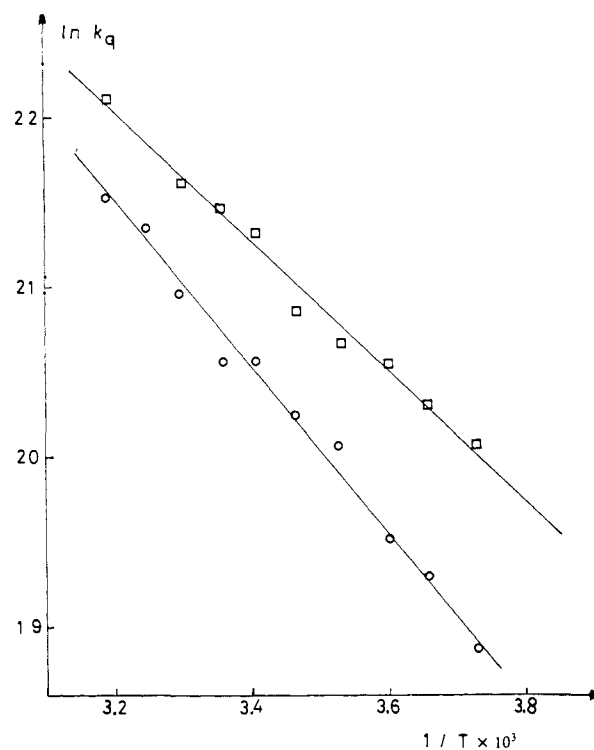

Figure 5. Typical Arrhenius plot for nitrobenzene, (□) squalane, (O) 2-methylpentane-2,4-diol.
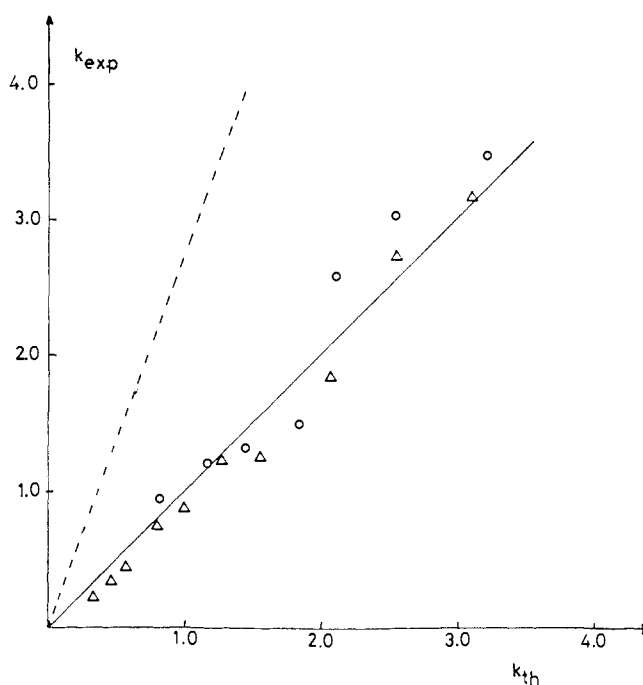

Figure 6. Reaction rate constants for the quenching by nitrobenzene in (●) squalane and (△) 2-methylpentane-2,4-diol, plotted against the Pilling and Rice rate constant (eq 9). The solid line is of unit slope. The broken line corresponds to the best fit of experimental data when it is compared to the Smoluchowski equation (1).

is not operative, and the lower rate constant is explained by using the following mechanism for the reaction, namely that the reaction consists of two states. The reactants first diffuse together to form an encounter pair followed by collisions in the solvent cage, leading to formation of a "complex" (radical pair or exiplex). Escape from the cage of these complexes may lead to separation of the products or a return to reactants in the cage. This mechanism may be represented by

$$P_y^* + Q \xrightarrow{k_{12}}_{k_{21}} P_{y_1}^* Q \xrightarrow{k_{23}}_{k_{32}} P_{y_2} Q \xrightarrow{k_{30}} P \qquad (12)$$

where 1 represents an encounter complex, and 2 is a radical pair

or an exciplex. This approach has been used previously[32] to rationalize both electron and energy-transfer quenching mechanisms.

At higher temperatures or in less viscous media nitromethane, nitrohexane and nitrododecane escape efficiently from the solvent cage, and the reaction is not diffusion controlled. However, when the medium becomes more viscous, escape from the cage is less probable, and ultimate reaction is more efficient due to a longer cage lifetime; at this stage the rate constant for nitrohexane and nitrododecane approaches the diffusion limit. The rate constant

Table VI. Ratio between the Experimental and Theoretical Rate Constants ($\text{Å} = k_q/k_{th}$)

In Viscous Solvents

	MPD		squalane				
T, K	CH_2I_2	$NO_2C_6H_5$	CH_2I_2	NO_2CH_3	$NO_2C_6H_{13}$	$NO_2C_{12}H_{25}$	$NO_2C_6H_5$
268	1.22	1.37	1.37	0.30	1.21	1.27	2.08
273	1.14	1.43	1.37	0.26	1.14	1.16	2.15
278	1.25	1.50	1.50	0.32	1.01	1.04	1.93
283	1.21	1.83	1.24	0.28	0.98	1.29	1.73
288	1.10	1.67	1.37	0.26	0.99	1.05	1.45
293	1.39	1.86	1.50	0.28	0.78	0.83	2.20
298	1.52	1.45	1.49	0.32	0.93	0.98	2.05
303	1.39	1.60	1.59	0.34	0.90	0.81	1.87
308	1.27	1.86				0.93	
313	1.30	1.77	1.99	0.33		0.82	2.11

In Normal Hydrocarbons

	CH_2I_2	NO_2CH_3	$NO_2C_6H_{13}$	$NO_2C_6H_5$
n-heptane	0.69	0.12	0.15	1.31
n-octane	0.72	0.16	0.16	1.36
n-decane	0.86	0.21	0.21	1.32
n-dodecane	0.85	0.23	0.26	1.28
n-hexadecane	1.16	0.26	0.38	1.33

for nitromethane is still lower than that for a diffusion-controlled reaction, due to the greater mobility of this small molecule.

In the scheme shown in eq 12, the experimental rate constant is given by

$$k_q = \frac{k_{12}k_{23}k_{30}}{(k_{23}k_{30} + k_{21}k_{30} + k_{32}k_{23} + k_{32}k_{21})} \quad (13)$$

and the value of k_q is determined by the relative magnitudes of k_{30} and k_{32}. Thus, if $k_{30}/k_{32} = 0.1$, as expected in viscous media, then $k_{23} > k_{21}$, and the $k_q \sim 0.1k_{12}$. Hence, a second equilibrium in the kinetic scheme predicts that the experimental rate constant should be lower than that calculated by diffusion theory, but at the same time both rate constants show a similar dependence on the viscosity.

Noyes[4] has pointed out that the diffusion-controlled rate constant may be defined as the sum of two parts. Namely, a contribution to the rate constant k_a from the activation process required to initiate the reaction, the k_d, which is the diffusion part. This can be written as

$$\frac{1}{k} = \frac{1}{k_d} + \frac{1}{k_a} \quad (14)$$

Now, the rearrangement of equation 13 gives

$$\frac{1}{k_q} = \frac{1}{k_{12}} + \frac{1}{k_{23}}\left[\frac{k_{21}}{k_{12}}\left(1 + \frac{k_{32}}{k_{30}}\right)\right]$$

or

$$\frac{1}{k_q} = \frac{1}{k_{12}} + \frac{1}{k_{23}p} = \frac{1}{k_d} + \frac{1}{pk_a} \quad (15)$$

where p is determined by the ratio k_{32}/k_{30}. The process defined by k_{32} does not depend on η as it occurs in the solvent cage. On the other hand, the process defined by k_{30}, the separation of the products formed in k_{23}, depends on η. A factor is introduced that decreases the efficiency of k_{23} (k_a in eq 14) on a purely kinetic basis and agrees with the concept of enhanced cage lifetime. Such a concept has been utilized previously[31] for modifying Noye's equation and takes into account the "effectiveness" of the contact, i.e. the probability that the reaction occurs in the time the reactants are in contact. As seen in Figure 7 a plot of $1/k_q$ vs $1/k_d$ is indeed linear and agrees with this simple concept.

In the previous section, we have indicated that in the quenching of excited pyrene by nitrobenzene or diiodomethane, the rate constant k does not follow the Stokes–Einstein relationship, i.e. vary with the inverse of the viscosity η of the medium. The relationship between k and η is closer to that of the square root of viscosity. Measurements of the diffusion coefficient show that the problem lies entirely in the diffusion coefficient, which does
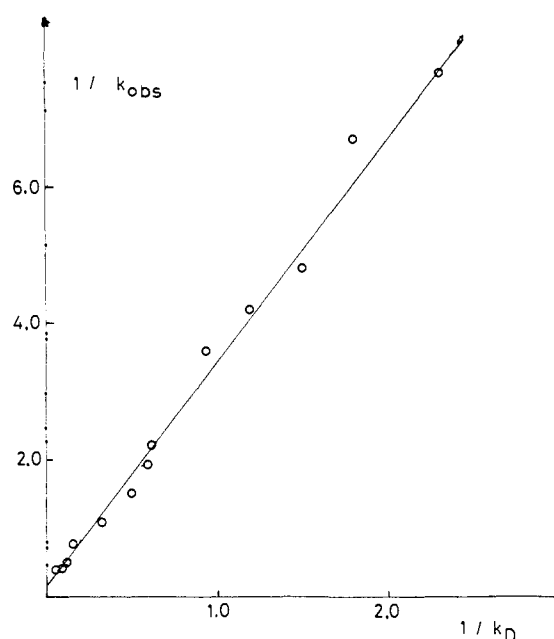

Figure 7. Plot of the observed rate constant against the theoretical rate constant, according to modified Noye's equation (15) for nitromethane in squalane and a series of hydrocarbons.

not follow the Stokes–Einstein relationship. If the measured diffusion coefficients are taken, then reasonable estimates of the diffusion-controlled rate constants can be obtained, which agree with those measured experimentally. In the case of activation-controlled reactions, such as quenching of excited pyrene by nitromethane, nitrododecane, and nitrohexane, these reactions become diffusion-controlled at higher viscosities due to the simple concept of the increased reaction due to an enhanced cage lifetime of the reactants. A simple formulation involving an equilibrium between the quencher and reactive excited state gives an excellent fit between calculated and experimental data.

It is pertinent at this stage to inquire into the nature of the process whereby the diffusion constant does not exactly follow the Stokes–Einstein model. In the Stokes–Einstein model the molecule is considered to be significantly larger than the solvent molecules in which it moves. Hence, in order for movement to occur the solvent molecules have to move out of the path of diffusion of the molecule in order to make space into which the solute can diffuse. In other words, the solvent molecules move against the bulk solvent, a process similar to that applying to viscosity, hence the derivation of the Stokes–Einstein relationship.

If, on the other hand, the diffusing molecules are smaller than or comparable to the size of the solvent molecules, then it is not always necessary for the solvent molecules to move completely out of the pathway of the diffusing solvent molecule. The solvent molecules could exhibit some minor motion whereby a "defect" is created in the liquid that aids in the diffusion process. Then the diffusion can be faster than that predicted by a simple Stokes–Einstein viscosity concept. In the extreme limit, that of a long-chain hydrocarbon as might be the case with squalane, the solvent deformation aiding solute diffusion could be the elasticity of the liquid. In other words, the solvent molecules reside in a coiled position with some overlap of coils and surround the solute. Stretching of the solvent molecules gives rise to a vacancy in the solvent in which the solute can move, and diffusion may occur without an overall gross movement of the solvent as required for the Stokes–Einstein model. Small molecules or molecules that are planar or flat in nature such as the molecules used in the present study will tend to benefit more from this effect than large nonplanar molecules.

In the transition-state theory of viscosity and diffusion developed by Eyring,[33] the fluidity of the medium (inverse of viscosity) is proportional to the number of holes in the liquid where the viscous motion is taking place, i.e.

$$\phi = c \frac{V - V_s}{V_s} = 1/\eta \tag{16}$$

where V and V_s are the molar volumes of the liquid and the solid, respectively.

The phenomena of diffusion may be treated in a similar manner to viscosity, where the diffusion coefficient D is also proportional to the number of holes. Thus, D is given by

$$D = c_1 \frac{V - V_s}{V_s} \tag{17}$$

With a long chain hydrocarbon liquid, the unit flow of viscous motion is a segment of the chain rather than the whole molecule. The fluidity of the hydrocarbon depends on the number of holes and on the probability that all the segmental motions are in the direction that permits the whole molecule to move. If the volume associated with the unit of flow is V_1 and the volume of the molecule is V_2, then it has been shown that the probability that the segmental motion is unsuccessful is given by[33]

$$k = \frac{V_1}{V_1 + V_2} \tag{18}$$

With this factor the fluidity of a long-chain hydrocarbon is decreased to

$$\phi = c \left(\frac{V - V_s}{V_s} \right) \left(\frac{V_1}{V_1 + V_2} \right) \tag{19}$$

If it is assumed that the volume of the hydrocarbon, V_2, is equal to the molar volume of the solid, V_s, and that the volume of the unit of flow, V_1, is similar to the hole volume [i.e. $V_1 = a(V - V_s)$], then the fluidity may be written as

$$\phi = c \left(\frac{V - V_s}{V_s} \right) \left(\frac{V_1}{V_1 + V_2} \right) = c' \frac{(V - V_s)^2}{V_s V}$$

$$\phi \simeq c_2 \left(\frac{V - V_s}{V_s} \right)^2 = 1/\eta \text{ as } V_s \simeq V \tag{20}$$

On the other hand, the diffusion of a solute according to this kind of motion will follow the same relation with the number of holes as in a normal solvent (eq 17). Use of eq 17 and 20 gives

$$\phi = C_3 D^2 = 1/\eta \tag{21}$$

This indicates that, to a degree of approximation, the diffusion coefficient of a solute in long-chain liquids varies with the inverse of the square root of the solvent viscosity. This agrees well with the experimental data.
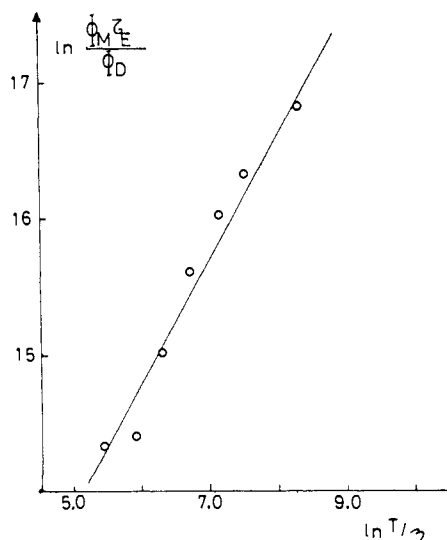

Figure 8. Plot of ln $(\phi_m \tau_E / \phi_E)$ vs ln T/η for 1,3-dipyrenylpropane in squalane at different temperatures.

Stokes Motion. Contrary to the above argument for planar molecules, if planar molecules are restricted in their movement by a structural constraint, as occurs in 1,3-dipyrenylpropane, then the above effect is lost. In this kind of molecule, the conformational motion that gives rise to the intramolecular excimer must involve the solvent molecule. As a consequence, the rate constant for the excimer formation varies inversely in the viscosity as indicated by the Stokes–Einstein relationship. In the mechanism of excimer formation proposed by Birks, the rate constant is proportional to the ratio of monomer/isomer emission quantum yield multiplied by the excimer lifetime. Figure 8 shows a plot of ln $[(\frac{\phi_m}{\phi_E})\tau_E]$ vs ln T/η for 1,2-dipyrenylpropane in squalane at different temperatures. The data are linear with a slope of –0.95, which corroborates the above concepts of the Stokes-like motion of this molecule in squalane.

Micelles and Vesicles. It has been customary in micellar and vesicular chemistry to use photophysical measurements in order to define properties of the microsystem. In particular, the measured rate constant for a diffusion-controlled reaction in a microsystem compared to that established in a simple homogeneous solvent of known viscosity can be used to estimate the microviscosity of the microsystem. This is a direct consequence of the fact that the rate constant k varies as the inverse of the viscosity, η^{-1}. It is paramount in such extrapolations that the Stokes–Einstein equation is valid. The following simple considerations throw some light onto the situation.

The microviscosity of a CTAB micelle has been measured to be 39 cP at 15 °C by the dipyrenylpropane probe.[34] Quenching studies of excited pyrene by quenchers such as dimethylaniline, pyridinium derivatives, etc., give a k_q of 2.0 × 10^7 s^{-1};[35] the k_q refers to the first-order decay of one excited pyrene and one quencher–micelle. If the quenchers are confined to the "skin" of the micelle defined by two radii of 7.5 and 17.5 Å, then the second-order rate constant for quenching is 3 × 10^8 M^{-1} s^{-1}. This is $1/33$ that measured in water or alcohol where $\eta = 1$ and the microviscosity of the micelle is calculated as 33 cP, in good agreement with that measured by the dipyrenylpropane probe.

Similar measurements in dioctadecyldimethylammonium bromide (DODAB) vesicles at 30 °C give a microviscosity of 144 cp by the dipyrenylpropane-probe method.[36] Quenching studies of excited pyrene by cetylpyridinium in DODAB give a second-order rate constant by quenching in the vesicle of 7.6 × 10^7 M^{-1} s^{-1}. This indicates a microviscosity of 132 cP.[37]

These data in micellar and vesicular systems indicate that the motions of reactants in these systems follow Stokes type behavior, i.e. the solvent (surfactant molecule) diffuses or moves to create a vacancy for diffusion of the reactant. Early estimates of microviscosities in these systems still seem to be valid.