

Kinetics of Diffusion-Controlled Reactions. An Experimental Test of the Theory as Applied to Fluorescence Quenching

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An experimental test of the theory of diffusion-controlled reactions as applied to fluorescence quenching is described. Both steady-state fluorescence quenching measurements and fluorescence lifetime studies with a nanosecond flash have been made. It was found that departures from Stern–Volmer kinetics are satisfactorily accounted for by the theory based on Fick's laws, including transient term, for the system of anthracene quenched by carbon tetrabromide. The sum of the collision radii was taken as an adjustable parameter and it was found that the steady-state quenching data could be explained with values falling between 6 and 7.5 Å. Radii in this range were also consistent with the lifetime measurements. The possibility of static quenching is also discussed.

Introduction

The problem of diffusion-controlled reactions has received considerable theoretical attention in the past several decades.¹ Theoretical treatments of the problem may be divided into two categories, one involving a consideration of the concentration gradients in the system^{2–6} and the other involving an analysis of the behavior of a pair of diffusing molecules.^{1,7} This latter approach, which utilizes the probability of reencounter derived from the theory of random walks, has been developed over the past 10 years by Noyes, whereas the development based on concentration gradients had its origin in the work of Smoluchowski, who applied Fick's laws to the problem of the rate of coagulation of colloidal particles. Smoluchowski² solved Fick's second law

$$\partial C / \partial t = D \nabla^2 C \quad (1)$$

subject to the boundary conditions

$$\begin{aligned} C(r, 0) &= C_0 \\ C(\infty, t) &= C_0 \\ C(R, t) &= 0 \end{aligned} \quad (2)$$

where R is the sum of the collision radii and C_0 is the initial concentration of the diffusing species. The problem of the relative motion of the particles in question was taken into account by adding the individual dif-

fusion coefficients, i.e., $D = D_A + D_B$. The solution to eq 1 is

$$C(r, t) = C_0 \left[1 - \frac{R}{r} \operatorname{erfc} \left(\frac{r - R}{2\sqrt{Dt}} \right) \right] \quad (3)$$

where

$$\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-\lambda^2} d\lambda$$

Equation 3 yields for the flux at R

$$\Phi = 4\pi R D N' C_0 (1 + R/\sqrt{\pi D t}) \quad (4)$$

which leads to the familiar equation

$$\Phi/C_0 = 4\pi R D N' \quad (5)$$

for the rate constant for a diffusion-controlled reaction in the absence of transient effects. N' is the number of molecules in 1 mmole.

The boundary condition, $C(R, t) = 0$, has been the

- (1) R. M. Noyes *Progr. Reaction Kinetics*, **1**, 131 (1961).
- (2) M. v. Smoluchowski, *Z. Physik. Chem.*, **92**, 129 (1917).
- (3) E. W. Montroll, *J. Chem. Phys.*, **14**, 202 (1946).
- (4) T. R. Waite, *ibid.*, **28**, 103 (1958); **32**, 21 (1960).
- (5) A. Weller, *Z. Physik. Chem. (Frankfurt)*, **13**, 335 (1957).
- (6) J. Yguerabide, M. A. Dillon, and M. Burton, *J. Chem. Phys.*, **40**, 3040 (1964).
- (7) R. M. Noyes, *J. Phys. Chem.*, **65**, 763 (1961).

subject of much discussion,^{1,8,9} and it is now generally recognized that one must use instead

$$\Phi = kC_R \quad (6)$$

or its equivalent

$$C_R = \frac{D}{k} \left(\frac{\partial C}{\partial r} \right)_R \quad (7)$$

where k is the rate constant that would pertain if the equilibrium concentration of encounter pairs were maintained. The subscript R refers to evaluation at a distance R from the species considered fixed.

The flux now becomes

$$\Phi = \frac{4\pi RDC_0N'}{1 + \frac{4\pi RD}{k}} \left[1 + \frac{k}{4\pi RD} \exp(x^2) \operatorname{erfc}(x) \right] \quad (8)$$

where

$$x = (\sqrt{Dt}/R)(1 + k/4\pi RD) \quad (9)$$

At times greater than 10^{-11} sec for ordinary values of D and R , $\exp(x^2)\operatorname{erfc}(x)$ may be expanded in a series with retention only of the first term, giving¹

$$k(t) = \Phi/C_0 = 4\pi R'DN' \left(1 + \frac{R'}{\sqrt{\pi Dt}} \right) \quad (10)$$

where

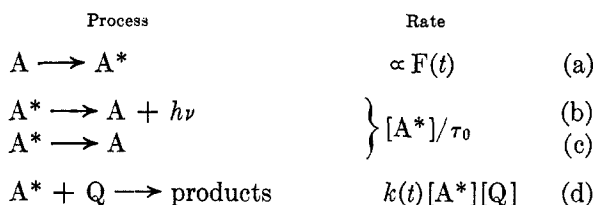
$$R' = R/(1 + 4\pi RD/k) \quad (11)$$

Collins,⁹ using random-walk considerations, has obtained a similar relationship for R'

$$R' = \alpha R^2/(\alpha R + \rho) \quad (12)$$

where α is the reaction probability and ρ is related to the average diffusive displacement. Equation 10 is of the form of Smoluchowski's solution and approaches it as $k \gg 4\pi RD$.

The application of eq 10 to fluorescence quenching is straightforward.^{3,5,6} For the mechanism



one obtains the decay law from eq 10 for instantaneous excitation. This is given by the expression

$$I(t) = I_0 \exp \left\{ -\frac{t}{\tau_0} - 4\pi R'DN'[Q]t \left[1 + \frac{2R'}{\sqrt{\pi Dt}} \right] \right\} \quad (13)$$

The application of eq 13 to experimental results requires the evaluation of a superposition integral of $F(t)$, the excitation function, and $G(t)$, the decay function of A^* for instantaneous excitation, *i.e.*

$$J(t) = \int_0^t F(t)G(t - \lambda)d\lambda \quad (14)$$

$J(t)$ gives the time dependence of the fluorescence intensity anticipated experimentally. The steady-state solution is obtained by considering the response to excitation by a step function. The result is

$$(I_0/I)_{ss} = (1 + 4\pi R'DN'[Q]\tau_0)Y^{-1} \quad (15)$$

where

$$Y = 1 - (b/a^{1/2})\pi^{1/2} \exp(b^2/a) \operatorname{erfc}(b/a^{1/2})$$

and

$$a = 1/\tau_0 + 4\pi R'DN'[Q]$$

$$b = 4R'^2\sqrt{\pi DN'[Q]}$$

This development, based on the questionable application of a continuum theory to the diffusion of two species through a solvent composed of molecules of similar size, remains essentially unverified experimentally. The recently reported results of Noyes^{10,11} on the rate of recombination of iodine atoms in carbon tetrachloride are encouraging, but the test suffers somewhat from a lack of accurate diffusion coefficients.

This paper reports an attempt to test experimentally the theory (including transient term) as outlined above. Steady-state and transient measurements have been made on a fluorescence quenching system of high efficiency, the quenching of anthracene fluorescence by carbon tetrabromide. This system has been reported by Bowen and Metcalf¹² to depart significantly from Stern-Volmer kinetics. Bowen and Metcalf attributed this behavior to static quenching, but Noyes¹³ adopted the view that the observed concentration dependence of the Stern-Volmer constant was due to transient effects in the diffusion-controlled kinetics. However, Noyes had no transient studies available to use in reinterpreting the data.

Experimental Section

Fluorescence decay measurements were made with a photocurrent-sampling apparatus similar to that de-

(8) F. C. Collins and G. E. Kimball, *J. Colloid Sci.*, **4**, 425 (1949).

(9) F. C. Collins, *ibid.*, **5**, 499 (1950).

(10) R. M. Noyes, *J. Am. Chem. Soc.*, **86**, 4529 (1964).

(11) R. M. Noyes, *J. Phys. Chem.*, **69**, 3182 (1965).

(12) E. J. Bowen and W. S. Metcalf, *Proc. Roy. Soc. (London)*, **A206**, 437 (1951).

(13) R. M. Noyes, *J. Am. Chem. Soc.*, **79**, 551 (1957).

scribed by Bennett.¹⁴⁻¹⁵ Fluorescence was excited with a nanosecond flash lamp operated at a repetition rate of 5-7 kc. The flashing gas was air, the emission originating primarily from the $C^3\pi_u \rightarrow B^3\pi_g$ fluorescence of nitrogen quenched by oxygen. The time base was set by a variable delay line, which determined the time interval between the pulsing of the lamp and the pulsing of the photomultiplier tube. This variable-delay line was calibrated against the speed of light and was found to be linear and accurate to better than 2.5%.

In the past decade a number of investigators have made fluorescence lifetime measurements, and there is some overlap regarding the compounds measured and the solvent used. If one compares the measurements of Ware,¹⁶ Ware and Baldwin,¹⁵ Birks and Dyson,¹⁷ Metcalf,¹⁸ and Lumry, Kokubun, and Müller¹⁹ on compounds such as acridone, quinine bisulfate, fluorescein, anthracene, perylene, and 9,10-diphenylanthracene, one finds that the agreement between investigators is on the average within 2.5% for a given compound. This comparison includes measurements made with both the phase-shift technique and the direct-observation nanosecond-flash method. Thus we have apparently reached the point where considerable confidence may be placed in such measurements.

Steady-state measurements of fluorescence intensity ratios were accomplished with the apparatus illustrated in Figure 1. The instrument utilizes the double-beam method described by Bowen and Metcalf¹² and is quite insensitive to variations in lamp intensity. Measurements were made in 1-cm cells. Oxygen was carefully removed from all solutions. In obtaining $(I_0/I)_{ss}$, corrections were made for dark current and scattered light. Care was exercised to limit the exposure time in the steady-state measurements in order to prevent the photochemical disappearance of anthracene from introducing an error.

Zone-refined anthracene was used for all experiments. The carbon tetrabromide (Matheson Scientific Co.) was vacuum sublimed until white crystals were obtained. Carbon and bromine microanalyses indicated better than 99% purity. The solvents heptane and acetonitrile were spectroscopic grade. Isobutyl alcohol was distilled prior to use.

Representative solutions containing anthracene and carbon tetrabromide were examined with a Cary 14 spectrophotometer and the resultant spectra compared with spectra of the individual components. No evidence was obtained to suggest ground-state complex formation.

Results and Discussion

The comparison of experimental results with the

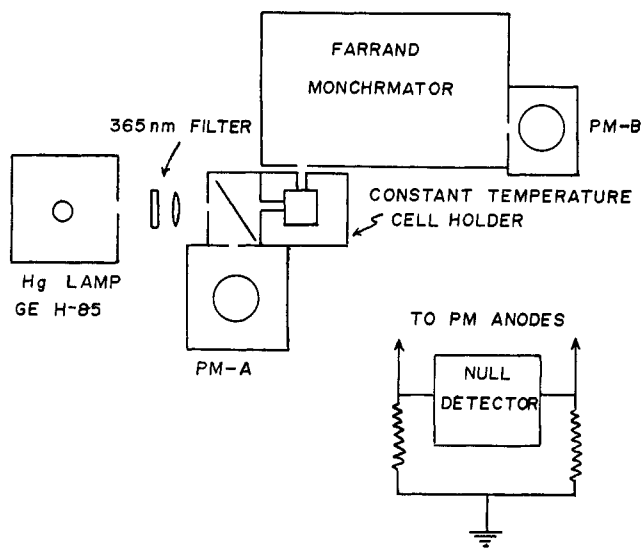


Figure 1. Steady-state fluorescence apparatus.

theory of diffusion-controlled reactions involved two different approaches. The first, which will be referred to as method A, was as follows. Equation 15 was fit to the $(I_0/I)_{ss}$ data, using R' as an adjustable parameter. The value of R' which gave the best fit for each solvent was then used in the analysis of the fluorescence decay data to produce a comparison between $(\Delta(1/\tau)/\Delta[Q])_{obsd}$ and the theory.

In method B, the results of the fluorescence lifetime measurements were also used directly to interpret the steady-state results by making the following modifications of eq. 15

$$(I_0/I)_{ss} = (1 + k'[Q]\tau_0)Y^{-1} \quad (16)$$

with

$$a = 1/\tau_0 + k'[Q]$$

$$b = k'[Q]R'/\sqrt{\pi D}$$

The value of k' was obtained from the superposition integral calculations; *i.e.*, the decay law was taken to be

$$I(t) = I_0 \exp\{-t/\tau_0 - k'[Q]t[1 + 2R'/\sqrt{\pi Dt}]\} \quad (17)$$

and k' was varied until agreement with the measured variation of the lifetime with concentrations was ob-

(14) R. G. Bennett, *Rev. Sci. Instr.*, **31**, 1275 (1960).

(15) W. R. Ware and B. A. Baldwin, *J. Chem. Phys.*, **40**, 1703 (1964).

(16) W. Ware, *J. Am. Chem. Soc.*, **83**, 4374 (1961).

(17) J. B. Birks and D. J. Dyson, *Proc. Roy. Soc. (London)*, **A275**, 135 (1963).

(18) W. S. Metcalf, *J. Sci. Instr.*, **42**, 603 (1965).

(19) A. Müller, R. Lumry, and H. Kokubun, *Rev. Sci. Instr.*, **36**, 1214 (1965).

tained. This fit was not particularly sensitive to the value of R' , and k' was thus easily found. R' in eq 16 was then varied to obtain a fit with the steady-state data. The decay law calculations were then checked to see if the new R' caused a significant change in k' .

These two methods will now be discussed in detail. Steady-state measurements produced values of $(I_0/I)_{ss}$ and K_{sv} , where

$$K_{sv} = \frac{1}{[Q]} \left(\frac{I_0}{I} - 1 \right)_{ss} \quad (18)$$

To compare the results with eq 15, values for the diffusion coefficients of anthracene and carbon tetrabromide were required. Diffusion coefficients were estimated from values of $D\eta/T$, where η is the solvent viscosity, reported in the literature for phenanthrene and carbon tetrabromide²⁰ in benzene. To obtain values of the diffusion coefficient in heptane and acetonitrile, it was assumed that $D\eta/T = C$. For isobutyl alcohol, account was taken of the fact that the value of C is different from that appropriate to benzene or heptane, and a correction was applied based on the diffusion coefficient for bromoform in various alcohols.²⁰ The resultant diffusion coefficients listed in Table I were within 20% of the values predicted from the nomographs of Othmer and Thaker²¹ and are in fair agreement with the tracer measurements recently reported,²² although these latter measurements appear to give somewhat high results.

Examples of the degree to which eq 15 fits the experimental data are shown in Figures 2-4, and the results for all systems studied are contained in Table I. Equation 15 is clearly quite sensitive to the value of R' , as is indicated by the ranges given on the theoretical curves.

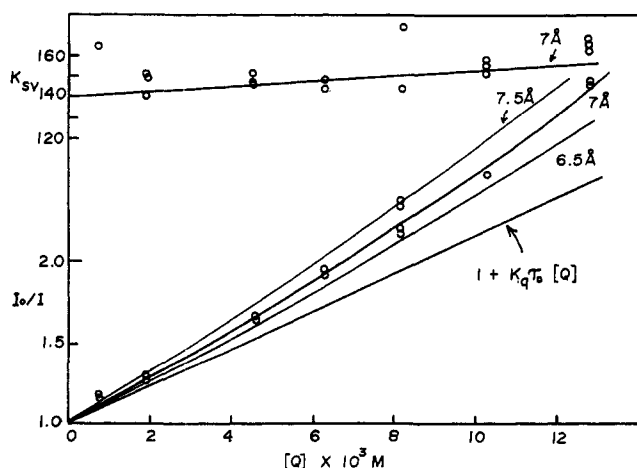


Figure 2. Steady-state results in heptane at 25°C

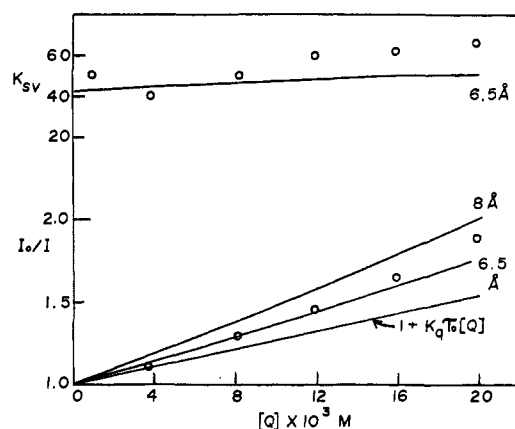


Figure 3. Steady-state results in isobutyl alcohol (low concentration) at 25°C.

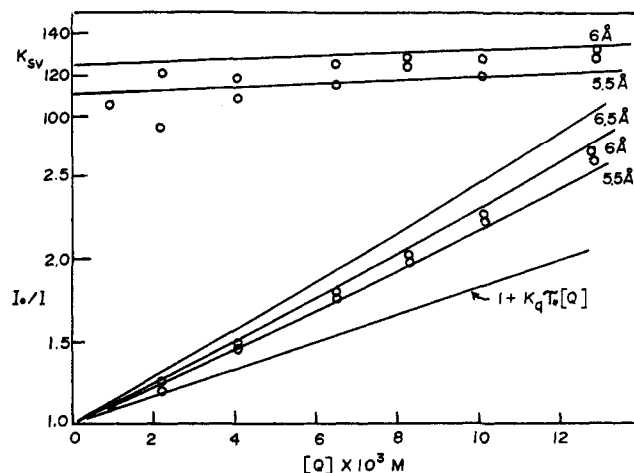


Figure 4. Steady-state results in acetonitrile at 25°C.

The values of R' found to produce a fit with the steady-state data were then used to calculate the fluorescence decay behavior, $J(t)$, anticipated theoretically. The superposition integral

$$J(t) = \int_0^t \exp \left\{ -\frac{\lambda}{\tau_0} - 4\pi R' D N' [Q] \lambda \left[1 + \frac{2R}{\sqrt{\pi D \lambda}} \right] \right\} F(t - \lambda) d\lambda \quad (19)$$

where $F(t)$ is the empirical lamp intensity function, was calculated numerically. The lamp function had a rise time (10-90%) of about 2 nsec, a width at half-

(20) A. E. Stearn, E. M. Irish, and H. Eyring, *J. Phys. Chem.*, **44**, 981 (1940).

(21) D. F. Othmer and M. S. Thakar, *Ind. Eng. Chem.*, **45**, 589 (1953).

(22) T. A. Miller, *et al.*, *J. Am. Chem. Soc.*, **87**, 121 (1965).

Table I: Results of Analysis of Data by Method A^a

Solvent	T, °C	10 ⁶ D, cm ² sec ⁻¹	10 ⁻⁸ /τ ₀ , sec ⁻¹	R', Å	10 ⁻¹⁰ Δ(1/τ)/Δ[Q], M ⁻¹ sec ⁻¹		K _{sv} ⁰ , M ⁻¹	
					Theoret	Exptl	Theoret	Exptl
Heptane	10	3.59	1.79 (±0.009)	7.0	1.99	1.74 (±0.013)	125	118 (±3)
Heptane	25	4.35	1.81 (±0.007)	7.0	2.38	2.13 (±0.023)	140	140 (±2)
Heptane	40	5.36	1.82 (±0.011)	7.0	2.97	2.37 (±0.037)	170	160 (±20)
Aceto- nitrile	25	5.07	2.07 (±0.17)	6.0	2.33	1.76 (±0.36)	120	107 (±2)
Isobutyl alcohol	25	1.10	1.95 (±0.018)	6.5	0.59	0.54 (±0.023)	35	25 ^b (±1)

^a Experimental errors listed are probable errors from least-squares analysis. ^b Low-concentration value.

maximum of 4.4 nsec, and a decay time given by $\exp(-5.55 \times 10^8 t)$. $J(t)$ was calculated from $t = 0$ to $t = 30$ nsec with values of $[Q]$ from 3.00×10^{-3} to 1.10×10^{-2} M. The decay portion of $J(t)$ became exponential soon after the maximum was passed and was exponential for 4–6 half-lives. It was thus possible to associate with each $[Q]$ value a value of the apparent lifetime, τ_{app} . The range over which $\Delta \log J(t)/\Delta t$ was computed corresponded to the range used in the analysis of the experimental decay curves. Plots of $1/\tau_{app}$ vs. $[Q]$ were linear below 7×10^{-3} M and this slope was used to obtain a theoretical value for $\Delta(1/\tau)/\Delta[Q]$. The exponential decay predicted theoretically was observed experimentally in all cases. The results of the lifetime measurements are given in Table I, along with the theoretical predictions.

From the experimental value of $\Delta(1/\tau)/\Delta[Q]$ it was possible to construct a Stern-Volmer line on the I_0/I plots from

$$(I_0/I)_{ss} = 1 + (\Delta(1/\tau)/\Delta[Q])_{\text{exptl}} \tau_0 [Q] \quad (20)$$

The results are shown in Figures 2–5 to emphasize the magnitude of the departures from the anticipated behavior if Stern-Volmer kinetics had been obeyed in both the transient and steady-state studies.

The results of the calculations following method B are given in Table II. It should be noted that in method B, k' is held constant while R' is varied in order to fit the steady-state data. This is, of course, not strictly valid since k' is a function of R' , but one can argue that this approach makes maximum use of the experimental data and leaves only part of the R' dependence of the correction factor b to be determined. It can be seen that method B produces results that are not significantly different from those of method A.

Table II: Analysis of Data by Method B^a

Solvent	T, °C	10 ⁻¹⁰ k', M ⁻¹ sec ⁻¹	R', Å	K _{sv} ⁰ , M ⁻¹	
				Theoret	Exptl
Heptane	10	1.68	8.0	139	118 (±3)
Heptane	25	2.05	7.0	143	140 (±2)
Heptane	40	2.30	7.0	173	160 (±20)
Aceto- nitrile	25	1.70	6.0	120	107 (±2)
Isobutyl alcohol	25	0.50	6.0	32	28 ^b (±1)

^a Experimental errors listed are probable errors from least-squares analysis. ^b Low-concentration value.

The values of R' obtained are reasonable since the sum of the collision radii must fall somewhere between 6 and 8 Å. In addition, since according to eq 11, $R' < R_A + R_B$, it is encouraging that the values of R' are found to be in the range of 6–7 Å. For example, if one calculates k from the kinetic theory of gases, then eq 11 gives $R' \cong R/1.2$ for low-viscosity solvents.

The agreement between $\Delta(1/\tau)/\Delta[Q]$ obtained by method A and the experimental results of the lifetime measurements given in Table I would appear to be satisfactory when one considers that, once the value of R' is fixed by the fit to the steady-state data, there are no adjustable parameters. The agreement between the value of K_{sv} obtained by extrapolating the theoretical calculations to zero concentration

$$K_{sv}^0 = \lim_{[Q] \rightarrow 0} K_{sv} = 4\pi R' D N' \tau_0 \left(1 + \frac{R'}{\sqrt{D \tau_0}} \right) \quad (21)$$

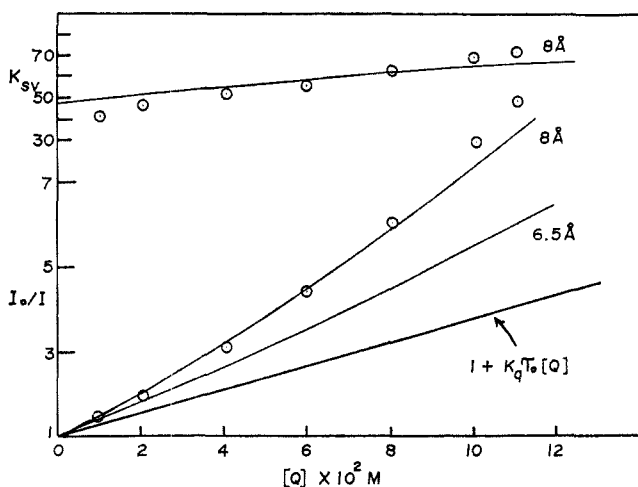


Figure 5. Steady-state results in isobutyl alcohol (high concentration) at 25°.

and the experimental least-squares intercepts of plots of K_{sv} vs. $[Q]$ is also satisfactory, as can be seen in Table I.

It can be seen from Figures 4 and 5 that the R' value found to fit the steady-state data at low concentration fails to fit the data at high concentration for the solvent isobutyl alcohol. The reason for this is not clear, but it is possible that this represents a genuine failure of the theory, which, strictly speaking, is valid only for very dilute solutions where the correlated motion of the A's and B's may be ignored.²³

Plots of $\log \Delta(1/\tau)/\Delta[Q]$ vs. $1/T$ for the heptane solutions and $\Delta(1/\tau)/\Delta[Q]$ vs. D for all of the solvents studied are presented in Figure 6. The corrections for transient effects are small enough to be ignored in these plots (see Table I). The slope of the plot of $\Delta(1/\tau)/\Delta[Q]$ vs. $1/T$ yielded an activation energy of 1910 cal, whereas for heptane the activation energy associated with viscosity is 1840 cal. The behavior is of course what one would expect for a diffusion-controlled reaction. The dependence on the diffusion coefficient is likewise as expected.

Bowen and Metcalf,¹² whose steady-state studies on the quenching of anthracene fluorescence by carbon tetrabromide prompted the present study, explained the concentration dependence of K_{sv} by static quenching. If one modifies the mechanism given above, *i.e.*

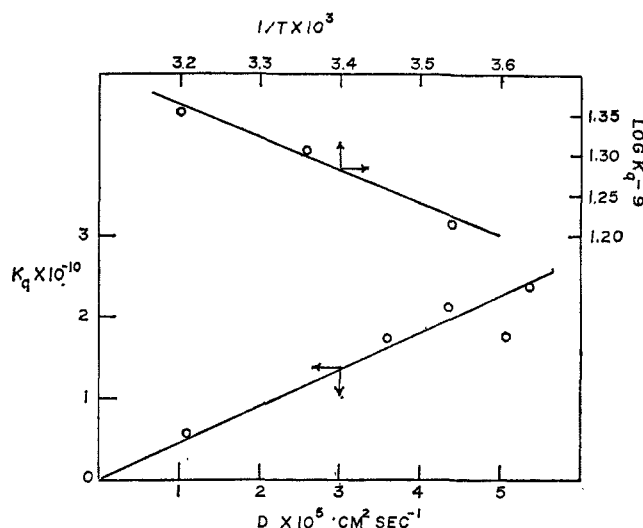
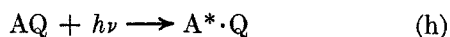
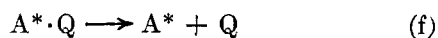
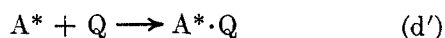


Figure 6. Dependence of the rate constant for quenching on temperature and on the diffusion coefficient.

steady-state analysis ignoring *all* effects of diffusion-controlled reactions yields²⁴

$$\left(\frac{I}{I_0}\right)_{ss} = \frac{1 - \gamma\alpha}{1 + \gamma k_q \tau_0 [Q]} \quad (22)$$

where k_q is the steady-state rate constant for process d' and γ is the probability for reaction e . α is the fraction of directly excited AQ complexes and is given by

$$1/\alpha = \left(1 + \frac{\epsilon_A}{\epsilon_{AQ} K [Q]}\right) \quad (23)$$

where

$$K = [AQ]/[A][Q] \quad (24)$$

In the system under study it is reasonable to assume that $\gamma \cong 1$ and one then obtains

$$K_{sv} = (K' + k_q \tau_0) + (K' k_q \tau_0) [Q] \quad (25)$$

where

$$K' = \epsilon_{AQ} [AQ]/(\epsilon_A [A][Q]) \quad (26)$$

Bowen and Metcalf¹² found that when the quenching of anthracene fluorescence by oxygen and by sulfur dioxide was analyzed by application of eq 25, one was led to the implausible conclusion that the association of A and Q increased with increasing temperature.

Our attempts to explain the steady-state behavior in terms of eq 25 have not been successful. If one takes $k_q = (\Delta(1/\tau)/\Delta[Q])_{\text{exptl}}$, then K' may be calcu-

(23) R. A. Reck and S. Prager, *J. Chem. Phys.*, **42**, 3027 (1965).

(24) A. Weller, *Progr. Reaction Kinetics*, **1**, 193 (1961).

lated directly from the concentration dependence of K_{sv} . However, the slope and intercept of plots of K_{sv} vs. $[Q]$ together provide sufficient information to permit calculation of both $k_q\tau_0$ and K' . It was found that the two methods are not consistent and that K' is not a constant at 25°. For isobutyl alcohol, the calculation was done only for the high concentration results since in the low-concentration range, $k_q\tau_0 \cong K_{sv}$. The results are listed in Table III.

Table III: Analysis of the Data According to Eq 22

Solvent	T , °C	K_{sv}^a , M^{-1}	$\Delta K_{sv}/$ $\Delta[Q]$, M^{-2}	K'^a	K'^b	K'^c
		(exptl)	(exptl)			
Heptane	10	118	2570	29	21	26
Heptane	25	140	1770	14	23	16
Heptane	40	160	2200	16	30	17
Aceto- nitrile	25	107	1830	21	23	17
Isobutyl alcohol	25	39 ^d	300	11	11	8.6

^a From slope and intercept. ^b From assumed $k_q\tau_0$ and intercept. ^c From assumed $k_q\tau_0$ and slope. ^d High-concentration intercept.

We have attempted to fit eq 15 to the data of Bowen and Metcalf, using the least-squares slopes and intercepts quoted by Noyes¹³ for the K_{sv} vs. $[Q]$ plots of Bowen and Metcalf. Diffusion coefficients were estimated from the diffusion coefficient of toluene reported for a series of hydrocarbon solvents ranging from heptane to tridecane.²⁰ It was assumed that the D vs. T/η plot for $D = D_A + D_Q$ would be similar in shape but displaced upward. The curve was made consistent with the values of D quoted in Table I. This was taken as valid over the range of T/η of 5.8×10^{-4} to 1.25×10^{-4} deg/poise. The I_0/I plots were reconstructed from Bowen and Metcalf's K_{sv} data. The value of the unquenched lifetime was taken to be 5.5 nsec, since the lifetime of anthracene does not appear to vary significantly from one saturated hydrocarbon solvent to the next. Values of R' required to cause eq 15 to fit the I_0/I data were determined and are given in Table IV. The results of fitting to the low-concentration (1 – 10×10^{-3} M) portions of Bowen and Metcalf's I_0/I curves are in reasonable agreement with our own results, as can be seen from Table IV. The R' values are somewhat higher, but this is perhaps due to the fact that this analysis involves linear extrapolation of data obtained at higher quencher concentrations than used in most of the

work reported above. Also listed in Table IV are the results of comparing the predicted slopes and intercepts of K_{sv} vs. $[Q]$ plots with those observed experimentally by Bowen and Metcalf. Since both τ_0 and D are somewhat uncertain, the agreement seen in the values listed in Table IV is considered within the uncertainty of the calculations and the experimental data used.

Table IV: Analysis of the Data of Bowen and Metcalf^a

$10^4 T/\eta$, deg/poise	$10^6 D$, cm^2 sec^{-1}	R' , A	K_{sv}^a , M^{-1}		$\Delta K_{sv}/\Delta[Q]$, M^{-2}	
			Exptl	Theoret	Exptl	Theoret
5.8	3.48	7.5	125	126	953	1000
4.8	2.96	7.5	110	109	785	950
3.5	2.20	8.0	93	91	857	700
2.4	1.50	8.0	76	64	468	350
1.25	0.85	8.5	49	48	355	300

^a See ref 12 and 13.

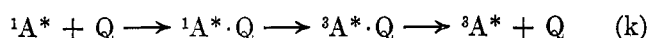
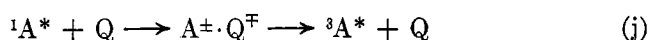
Since we have seen no spectral evidence to suggest the existence of a complex between anthracene and carbon tetrabromide, and since eq 15 appears to fit the existing data better than eq 22, it is more reasonable to view the concentration dependence of K_{sv} as a result of the transient effects in diffusion-controlled reactions rather than as a result of static quenching.

Summary and Conclusions

The magnitude of the departures from Stern-Volmer kinetics leaves little doubt as to the existence of an "effect," whatever its origin might be. The theory of diffusion-controlled reactions based on Fick's laws has been found to fit the experimental data using reasonable values for the sum of the collision radii, provided transient terms in the flux equation are retained. Noyes,^{10,11} using eq 10 (without the transient terms, which were unnecessary), was able to account within about 20% for the magnitude of the rate constant for iodine atom recombination in carbon tetrachloride. In the iodine system, the difference between the observed rate constant and $4\pi R'DN'$ again leaves little doubt as to the existence of an "effect" in spite of the uncertainty in the value of the diffusion coefficient. It would thus appear that a start has been made in the direction of providing experimental verification for the theory of diffusion controlled reactions. A variety of interesting experiments remains. For example, once quenching measurements with subnanosecond flash lamps become practical, it should be possible to test directly the validity of the decay law. In addition, a detailed steady-state and transient study should be made on an efficient

quenching system where static quenching is well characterized (ϵ_A/ϵ_{AQ} and K known independently from spectral studies), since this would eliminate one of the minor uncertainties associated with the present system. It would also be of interest to establish, through the study of several efficient quenching systems, whether or not the high-concentration failure is indeed a characteristic of diffusion-controlled reactions. Furthermore, the quantitative characteristics of this failure at high concentrations should be investigated.

There are three mechanisms that have been frequently invoked to explain the mechanism of fluorescence quenching,²⁵ *i.e.*



where $^1A^*$ and $^3A^*$ are the first excited singlet and lowest triplet states of the molecule, respectively. Wilkinson and Medinger²⁵ have recently presented experimental evidence that the triplet state is the product of the fluorescence quenching of anthracene by bromobenzene. They found no effect on the mechanism in going from a low to a moderate dielectric

constant solvent and no evidence for charged species following flash excitation. This led them to favor process k over process j. We also find no dielectric constant effect; the rate appears to be controlled entirely by diffusion. Recent²⁶ work in our laboratory with aromatic hydrocarbons quenched by amines suggests that when a charge-transfer complex is involved in a fluorescence-quenching mechanism, low dielectric constant solvents can cause a reversal of the quenching process with the regeneration of $^1A^*$ and thus a nonexponential fluorescence decay. On the other hand, in solvents of high dielectric constant, the decay becomes exponential and the rate follows the inverse of the viscosity and is independent of the dielectric constant. This type of behavior has not been found with anthracene quenched by carbon tetrabromide, suggesting perhaps that process k is correct.

Acknowledgment. This research was supported by a grant from the National Science Foundation (GP-1619). The authors also wish to acknowledge the assistance of Michael Richter, who made some of the preliminary measurements on this system.

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