

PHOTOPHYSICS OF EXCIPLEXES: SOME KINETIC ASPECTS†

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ABSTRACT

The characteristics of systems where fluorescence quenching does not follow simple kinetics are discussed and illustrated. The complicating effects discussed include ground-state complexing, transient effects in diffusion-controlled kinetics and feedback from an excited state complex or exciplex. Methods for differentiating these complicating effects are presented as well as methods for extracting rate parameters from systems where feedback is operating.

When the interaction between an excited molecule and some other molecule results in the disappearance of the excited state, quenching is said to have occurred. When this phenomenon involves short-lived species (nanosecond or sub-nanosecond) then the kinetics of disappearance of the excited molecule are generally followed by fluorescence quenching if fluorescence is present, or by the sensitized fluorescence of the quencher, if generated. Laser flash photolysis is also used.

In the typical fluorescent quenching experiment, one measures quantitatively the diminution of either the fluorescent intensity or the fluorescent lifetime of the fluorophor as a function of the quencher concentration. Ideally, both are measured. Frequently, one observes the same second-order rate constant for both the steady-state and transient measurements and is inclined to regard the quenching mechanism as simple. Not-so-simple systems may deviate from this norm in a number of subtle and fascinating ways which can yield insights into the kinetics, mechanism of quenching, and to some extent the nature of the interactions involved. Of special interest is the case where fluorescent quenching is accompanied by spectral changes in the absorption and/or emission spectrum of the system.

Unfortunately, the study of these three aspects, namely the spectroscopic behaviour of the system, the transient kinetics of fluorescence quenching and the steady-state kinetics, is seldom carried out in the course of an investigation of a fluorescence quenching mechanism.

It is the purpose of this paper to illustrate some of the departures from simple

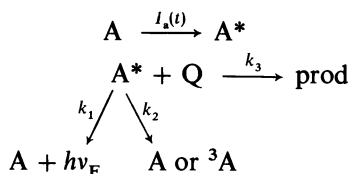
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kinetic behaviour and to discuss the interpretation of results as they pertain to mechanisms of fluorescence quenching.

During the last decade, there has been a significant improvement in the techniques available for fluorescence decay measurements^{1, 2, 3}. To a lesser extent, the same is true of fluorescence intensity ratio measurements such as are required for the construction for Stern-Volmer plots⁴. Laser techniques are now assuming more importance in fluorescence quenching studies^{5, 6} and the picosecond time range can be studied with mode-locked lasers⁷.

This paper will deal primarily with certain aspects of fluorescence quenching studied by conventional fluorescence decay and steady-state techniques in the nanosecond time range.

As a basis for considering the several interesting effects that complicate fluorescence quenching, the simple case is first given even though it is of course well known.



This gives (for δ -pulse optical excitation)

$$I_F(t) = I_F(0) \exp \{-t/\tau\} \quad (1)$$

where

$$1/\tau = k_1 + k_2 + k_3[Q] \quad (2)$$

The pertinent steady-state equation is

$$[I_F^0/I_F - 1] (1/[Q]) \equiv K_{sv} = k_3\tau_0 \quad (3)$$

where

$$1/\tau_0 = k_1 + k_2 \quad (4)$$

I_F is the intensity of fluorescence in the presence of quencher, I_F^0 that for $[Q] = 0$, and K_{sv} the Stern-Volmer constant. Thus k_3 can be determined either from $\Delta(1/\tau)/\Delta[Q]$ or from K_{sv}/τ_0 , and in this simple case they must agree within experimental error if this simple description is valid. Both the transient and steady-state measurements should give results that are independent of the wavelength at which the fluorescence is measured provided the quencher does not absorb in the wavelength region of emission of A. Likewise, if the quantum yield of fluorescence of A is independent of wavelength in the absence of the quencher, and if the quencher does not absorb a significant amount of light in the wavelength region where A absorbs, then the fluorescence quenching results should also be independent of the excitation wavelength. Corrections can be applied if the quencher competes with A for the incident light. Corrections for absorption of the fluorescence of A by the quencher are more difficult and in some cases, virtually impossible to make with the high precision and accuracy generally required for steady-state measurements. This for example, complicates considerably the study of dipole-dipole energy transfer⁸.

Some reasons why systems deviate from these simple kinetics are as follows:

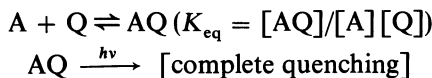
- (a) ground-state complex formation between A and Q;
- (b) so-called transient effects in the kinetics of diffusion-controlled reactions;
- (c) long-range Förster energy transfer from A* to Q;
- (d) feedback from an exciplex, excimer or excited-state complex;
- (e) competition between A and Q for the incident light;
- (f) polarization effects;
- (g) quenching of an exciplex, excimer or excited-state complex by either A or Q.

Case (e) is generally trivial and frequently can be avoided by the proper selection of excitation wavelength. Corrections can also be made provided the system is optically thin. Cases (a), (b), (d) and (g) will be discussed in detail because these represent instances which may be frequently observed when fluorescence quenching is studied in detail.

In case (a), the ground-state complex competes with A for the incident light^{9,10}. The fraction of light going into A is given by equation 5 where ϵ_A and ϵ_{AQ} are the extinction coefficients for the fluorophor and complex, respectively.

$$f_A = \epsilon_A[A] / \{\epsilon_{AQ}[AQ] + \epsilon_A[A]\} \quad (5)$$

We now add the following steps to the simple mechanism



It is obvious that the fluorescence decay is unaffected by the ground-state complex formation since the complex merely acts as a sink for photons. It is easily shown that the new steady-state equation is

$$K_{sv} = K' + k_3\tau_0 + K'k_3\tau_0[Q] \quad (6)$$

where

$$K' = K_{eq}(\epsilon_{AQ}/\epsilon_A) \quad (7)$$

Dramatic discrepancies between steady-state and fluorescence decay measurements are now possible^{10,11}.

For example, consider the quenching of 3-hydroxynaphthoic acid by a base such as pyridine in toluene¹¹. For this system at 298 K, K' is observed to be 970 M^{-1} whereas $k_3\tau_0$ was only 230 M^{-1} . At 278 K the discrepancy is even larger with $K' = 1770 \text{ M}^{-1}$ whereas $k_3\tau_0$ is 275 M^{-1} . A typical set of Stern-Volmer plots at three temperatures is shown in *Figure 1*. These plots illustrate strong concentration dependence of the Stern-Volmer constant and are linear as expected from equation 6. From slopes and intercepts of such plots one can obtain both K' and $k_3\tau_0$. As can be seen from *Figure 2*, the $1/\tau$ versus $[Q]$ plots are normal. If ground-state complexing is the only complicating feature of the kinetics, then the steady-state $k_3\tau_0$ should agree with $\Delta(1/\tau)/\Delta[Q]$. *Table 1* lists some representative data for the hydroxynaphthoic acid-pyridine system in toluene at several temperatures. Similar data are given in *Table 2* for the case where acetonitrile was the solvent.

One can also establish the enthalpy associated with the ground-state

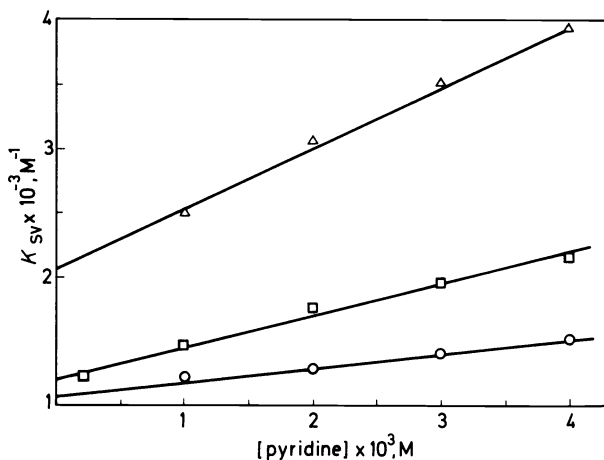


Figure 1. $[Q]$ dependence of K_{sv} for 3-hydroxy-2-naphthoic acid quenched by pyridine in toluene. ●, 60°C; ■, 25°C; ▲, 5°C.

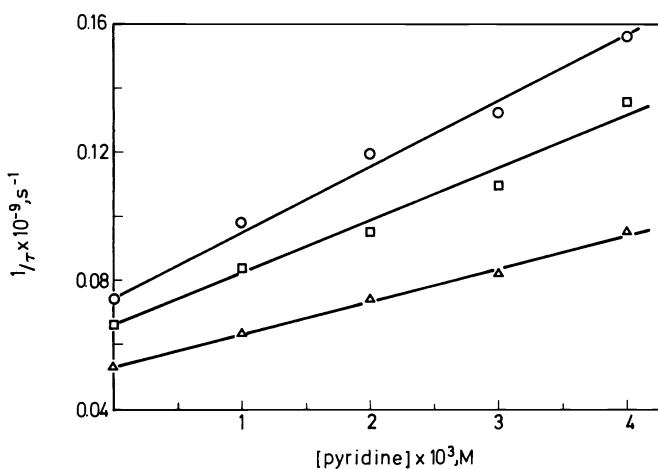


Figure 2. Lifetime versus quencher concentration plots for 3-hydroxy-2-naphthoic acid quenched by pyridine in toluene. ●, 60°C; ■, 25°C; ▲, 5°C.

Table 1. Fluorescence quenching via intramolecular proton transfer in 3-hydroxy-2-naphthoic acid (see ref. 11). Solvent: hexane.

t, K	Transient measurements			Steady-state measurements	
	$\tau_0 \times 10^9$ (s)	$k_3 \times 10^{-10}$ ($M^{-1} s^{-1}$)	$k_3 \tau_0 \times 10^{-2}$ (M^{-1})	K' (M^{-1})	$K_{sv} \times 10^{-2}$ (M^{-1})
330	13.5	2.0	2.7	670	3.3
298	15.8	1.65	2.6	970	2.3
278	20.0	1.10	2.2	1770	2.7

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Table 2. Fluorescence quenching via intramolecular proton transfer in 3-hydroxy-2-naphthoic acid (see ref. 11). Solvent: acetonitrile.

t K	Transient measurements			Steady-state measurements	
	$\tau_0 \times 10^9$ (s)	$k_3 \times 10^{-10}$ ($M^{-1} s^{-1}$)	$k_3 \tau_0 \times 10^{-2}$ (M^{-1})	K' (M^{-1})	K_{sv} (M^{-1})
278	22.1	3.9	86	—	—
298	19.3	0.90	18	148	23
313	17.5	0.25	04.4	—	—

complex formation reaction and the temperature coefficient of $k_3 \tau_0$ can also be obtained from such measurements as well as from fluorescent decay measurements. For example, the enthalpy of ground-state association of hydroxynaphthoic acid with pyridine is 3.2 kcal and the interaction is presumably of the H-bond type. Several other systems have been studied which exhibit ground-state complexing. These include anthracene quenched by carbon tetrachloride^{4, 12} and 1,2-benzanthracene quenched by carbon tetrabromide^{13, 14}. In addition, Weller¹⁰ described similar ground-state complexing with 3-hydroxypyrene quenched by pyridine and α -chloropyridine.

In systems where one can prepare the excited state of a complex both by direct excitation of a ground-state complex and through bimolecular interaction of its precursors, similar effects are predicted and will be important in the study of the photophysics of these systems.

In the presence of ground-state complexing, K_{sv} becomes in general a function of the extinction coefficients of both A and the complex and the possibility exists for wavelength effects in the steady-state quenching, even when there is no spectral evidence for the presence of the complex or only a suggestion of a spectral change on an absorption edge. The anthracene carbon tetrachloride system is a good example of this^{4, 12} where wavelength effects were originally interpreted to be due to a difference in the quenching properties of S_1 and S_3 but now appear in fact due to ground-state complexing.

Very weak interactions can¹⁵ still give one $K_{eq} = 0.5-2$ and if $\epsilon_{AQ}/\epsilon_A \cong 1$, then one might expect to see the effects of ground-state complexing rather frequently. However, for typical fluorophors $\tau_0 \cong 10^{-8}$ s, and $k_3 \cong 10^{10} M^{-1} s^{-1}$ for efficient quenching. Thus $k_3 \tau_0 \cong 100$ and the effect is difficult to detect if K' is between 0.5 and 2. As the interaction between A and Q approaches the normal non-specific van der Waals type interaction one must consider the influence of Q as the nearest neighbour to A when A undergoes excitation. This effect is presumably covered by the theory of diffusion-controlled reactions (*vide infra*). However, as will be discussed below, complexes with binding energies in excess of kT , as distinguished from encounter complexes with interaction energies less than kT , can be treated through the ground-state complexing formalism even in the presence of time-dependent concentration gradients associated with the diffusion-controlled kinetics. The transient effects of diffusion-controlled kinetics can be viewed as operating only for molecules which are not bound nearest neighbours at the instant of illumination. However, for such systems to be

easily treated it is necessary for the quenching reaction to be very efficient^{13, 14}.

Some aspects of the behaviour of systems which are complicated by the presence of ground-state complexing are summarized in *Table 3*. This can be subsequently compared with other effects to be discussed below.

Table 3. Characteristics of systems where fluorescence quenching does not follow simple kinetics

Complicating effect	Property	$K_{sv} = f([Q])$	$K_{sv} = f(\lambda_{ex})$	$I_F(t) \propto \exp\{-kt\}$	$K_{sv}/\tau_0 = \Delta(1/\tau)/\Delta[Q]$	Temp. coef. of K_{sv}
None (simple kinetics)		No	No	Yes	Yes	+
Ground-state complex		Yes	Yes	Yes	No	\pm
Transient effects in diffusion-controlled kinetics		Yes	No	(a)	No	+
Simple feedback (d)		No	No	(b)	No	\pm
Förster energy transfer		Yes	No	(c)	No	+

(a) 'yes' in non-viscous solvents; 'no' in viscous solvents.

(b) single exponential, sum or difference of exponentials, possible depending on rate constants, and wavelength of emission measurement.

(c) 'yes' in non-viscous solvents; 'no' in viscous solvents.

(d) (AQ)* not quenched by [Q].

The so-called *transient effects* of diffusion-controlled reactions, which have their origin in the time evolution of concentration gradients in a quenched system, affect both the steady-state and transient quenching kinetics. While the theory of such effects based on a continuum model has been thoroughly developed¹⁶⁻²⁵, relatively little experimental support for the validity of the model, even as applied to fluorescence quenching, is to be found in the literature^{27, 28, 29}. Some progress towards remedying this situation has recently been made by Nemzek and Ware who studied naphthalene and 1,2-benzanthracene quenched by carbon tetrabromide in 1,2-propanediol and mineral oil. The viscosity of these solvents is such that even at room temperature one sees significant deviations from simple single exponential decay due to these transient effects.

The continuum model¹⁶⁻²⁶ predicts the following transient and steady-state equations:

$$G(t) = G(0) \exp\{-t/\tau_0 - 4\pi R'DN'[Q]t[1 + 2R'/(\pi Dt)^{\frac{1}{2}}]\} \quad (8)$$

and

$$(I_0/I)_{ss} = (1 + 4\pi R'DN'[Q]\tau_0)Y \quad (9)$$

where

$$Y = 1 - (b/a^{\frac{1}{2}}) \pi^{\frac{1}{2}} \exp(b^2/a) \operatorname{erfc}(b/a^{\frac{1}{2}}) \quad (10)$$

$$a = 1/\tau_0 + 4\pi R'DN'[Q] \quad (11)$$

$$b = 4(R')^2 \{\pi D\}^{\frac{1}{2}} N'[Q] \quad (12)$$

$$\operatorname{erfc}(x) = (2/\pi^{\frac{1}{2}}) \int_x^{\infty} e^{-u^2} du \quad (13)$$

N' represents the number of molecules in a millimole, D the sum of the diffusion

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coefficients for A and Q, and R' is the effective quenching radius for the encountered pair²⁹.

From a detailed study of steady-state and fluorescence decay behaviour, Ware and Nemzek^{13, 14, 30} reached the following conclusions.

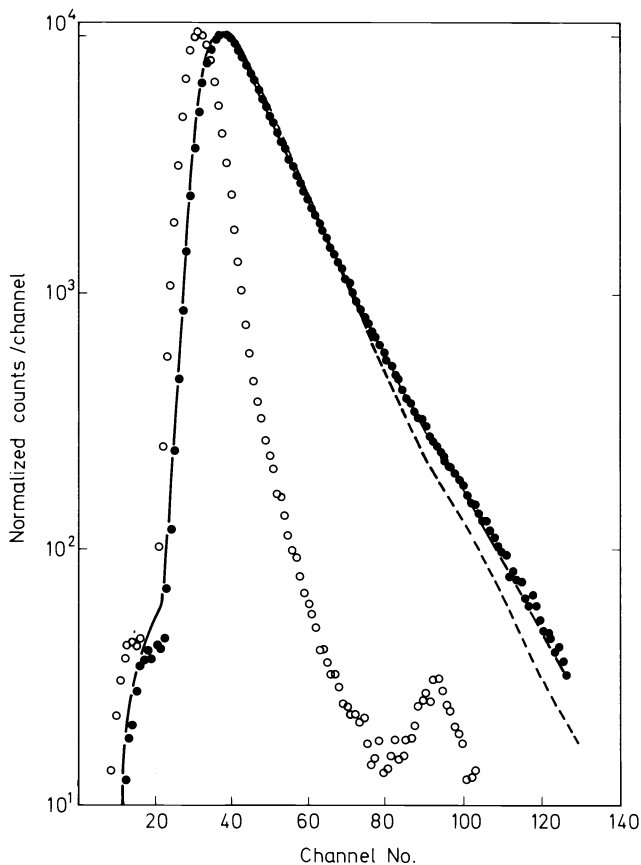


Figure 3(a). Decay curve for 1,2-benzanthracene quenched by carbon tetrabromide (0.29 M) in propane-1,2-diol at 30°C. O, flashlamp distorted by timing system; ●, experimental decay curve; dashed line, attempt to fit to $\exp\{-kt\}$. Solid line, fit to $\exp\{-At - Bt^3\}$. The best-fit A and B gave $R' = 7.5 \text{ \AA}$ and $D = 7.9 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ (338 ps/channel).

The decay law accurately follows $\exp\{-(at + bt^3)\}$, i.e. equation 8. This is illustrated in Figure 3. For example, from a series of measurements of the quenching of 1,2-benzanthracene by carbon tetrabromide in propanediol solvent as a function of both temperature and concentration, one can derive unique values for D and R' in equation 8. Plots of $\log D$ versus $1/T$ gave the expected activation energy for diffusion in propanediol (50 kJ/mole)^{31, 32} and the values of R' are approximately $9 \pm 1 \text{ \AA}$. This rather large radius is interpreted to be the distance of separation, on the average, when an actual encounter is inevitable. Its magnitude is presumably dictated by the solvent and solute size and the free volume.

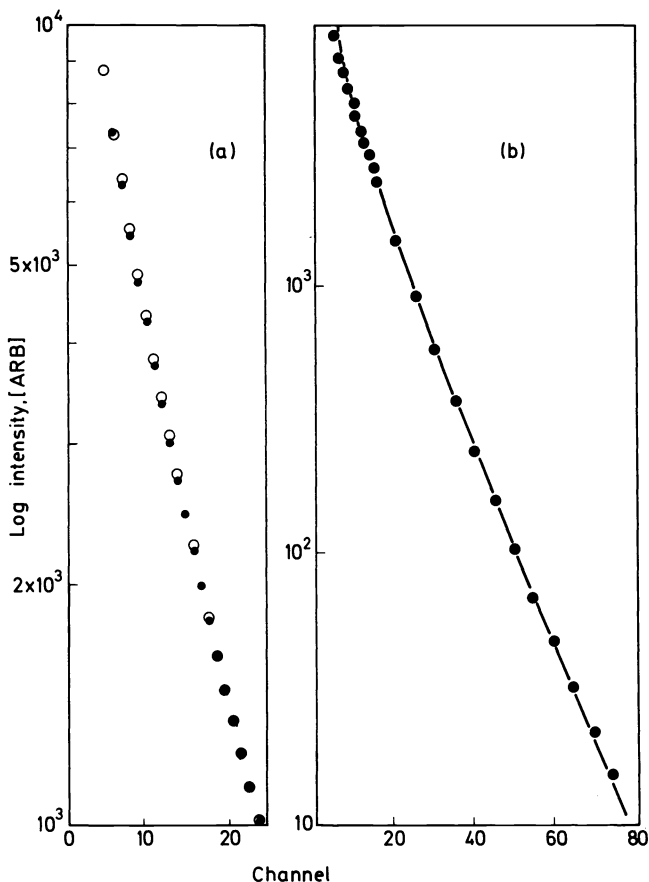


Figure 3(b). Deconvolution of a typical decay curve by the method of Ware, Doemeny and Nemzek³. (a): ●, deconvoluted points; ○, $\exp\{-At - Bt^2\}$ function. (b): all three decades; ●, deconvoluted points; line $\exp\{-At - Bt^2\}$. This illustrates that the decay law appropriate to a diffusion-controlled reaction can be recovered without making the *a priori* assumption as to the form of the law.

The mutual diffusion coefficient D in propanediol was observed to be 20–30 per cent larger than expected, based on measurements by Tyrrell^{31,32} but about the same as expected from the measurements by Nickel³³. In the latter case, it is necessary to extrapolate from measurements in glycerol assuming constant $D\eta/T$, when η is the viscosity. Only more measurements will resolve this problem.

In Figure 4 are illustrated typical steady-state data for this same quenching system. The dashed line is that predicted from the values of R' and D obtained with fluorescence decay measurements (using equation 8).

The large discrepancy between theory and experiment can be remedied by adding a ground-state quenching step. Then the steady-state equation becomes

$$(I_0/I)_{\text{corr}} = (1 + K'[Q])(I_0/I)_{\text{ss}} \quad (14)$$

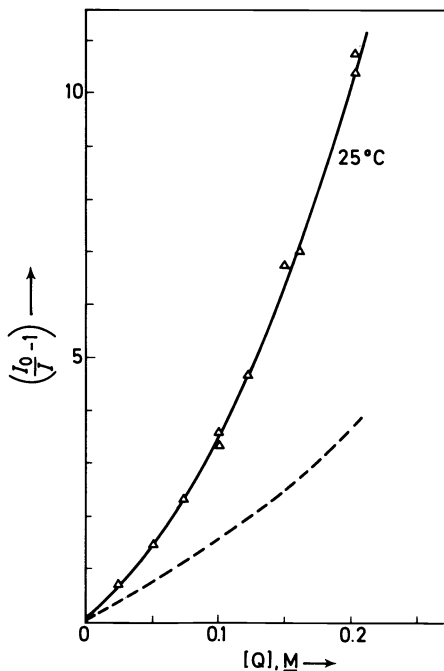


Figure 4. Stern-Volmer plot for 1,2-benzanthracene quenched by carbon tetrabromide at 25°C in propane-1,2-diol. Points: experimental. Dashed line—theoretical without ground-state complexing (parameters from A and B of $\exp\{-At - Bt^{\frac{1}{2}}\}$). Solid line—theoretical including ground-state complexing (same parameters).

where K' is defined above (equation 7) and $(I_0/I)_{ss}$ is given by equation 9. Equation 14 fits the steady-state data perfectly with $K' = 3.2 \text{ M}^{-1}$ at 25°C. This is indicated by the solid line in Figure 4. Similar results are obtained at other temperatures in propanediol and in mineral oil. These results are taken to indicate that ground-state complexing can be successfully separated from the effects treated by the theory of diffusion-controlled reactions in that we can view separately the weakly bound complex and the time evolution of concentration gradients associated with unbound species.

These results when added to the earlier results of Ware and Nouros²⁹, provide considerable support for the belief that the continuum model is valid for microscopic diffusion of the type encountered where the solvents and solutes are approximately the same size. Furthermore, it gives one considerable confidence in making corrections to kinetic data for these transient effects. One can, for example, proceed as follows:

From equation 9 it is easily shown that

$$\lim_{[Q] \rightarrow 0} (K_{sv}/\tau_0) = 4\pi R'DN' (1 + R'/\{\tau_0 D\}^{\frac{1}{2}}) \quad (15)$$

This is to be compared with the equation that pertains to the absence of

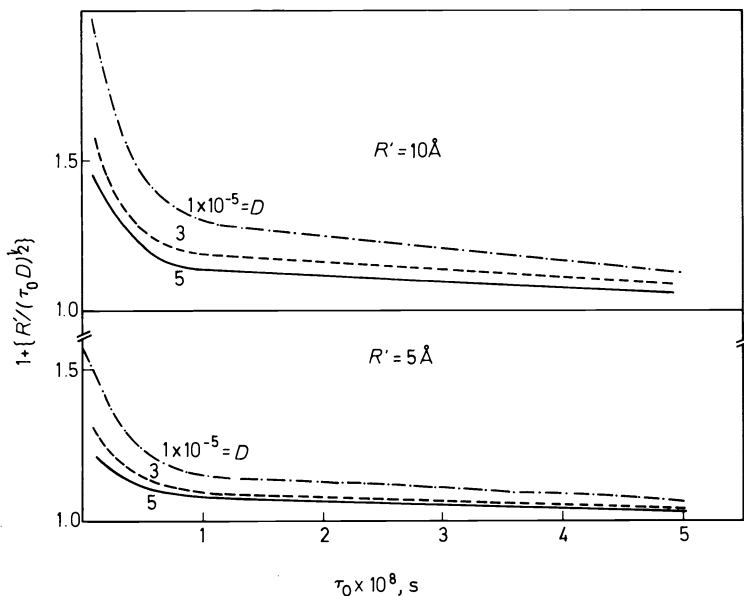


Figure 5. The correction term $[1 + (R'/\tau_0 D)^{1/2}]$ as a function of R' , τ_0 and D .

transient effects from diffusion-controlled kinetics, where

$$K_{sv}/\tau_0 = 4\pi R' D N' \quad (16)$$

Figure 5 shows plots of $(1 + R'/\{\tau_0 D\}^{1/2})$ for various τ_0 , D and R' values. It is clear from these figures that the corrections can be quite significant. In non-viscous systems such as benzene or hexane, it can be shown that these transient diffusion gradients have a much more pronounced influence on the steady-state behaviour than on the fluorescence decay kinetics of the system²⁹. Thus

$$\Delta(1/\tau)/\Delta[Q] \cong 4\pi R' D N' \quad (17)$$

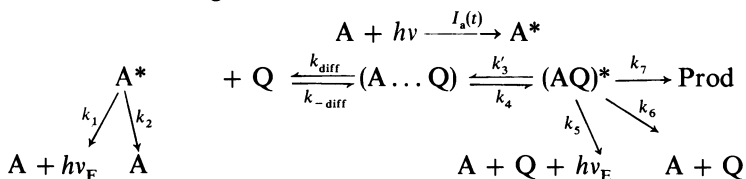
whereas as $(I_0/I)_{ss}$ is given by equation 9. Thus there arises a discrepancy of $(1 + R'/\{\tau_0 D\}^{1/2})$ between the steady-state and the decay-time measurements. The correction factor can be established once an estimate for D has been made since R' can be calculated to a good approximation from fluorescence decay-time measurements. While this approach is not exact, it is nevertheless a very satisfactory starting point for estimating the effects of diffusion-controlled kinetics. If the efficiency of quenching is considerably less than that predicted by the diffusion-controlled limit, this is reflected to a first approximation in a small value for R' , and the correction term $(1 + R'/\{\tau_0 D\}^{1/2})$ rapidly approaches unity.

Equation 9 predicts that K_{sv} is a function of the quencher concentration. This has now been verified experimentally for two cases as described above^{13, 14, 29, 30}. However, even when the concentration dependence of the Stern-Volmer constant is small, the intercept K_{sv}^0 can still differ from $4\pi R' D N'$ if R' , D' and τ_0 are of the right order of magnitude. In fact quenching experi-

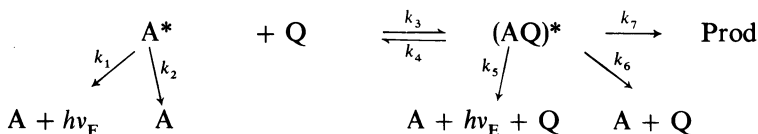
ments are frequently not carried to high enough concentration to enable one to see the curvature predicted by equation 9.

An example of such curvature is shown in *Figure 4*. Corrections for diffusion-controlled kinetics can be important in connection with another type of discrepancy between steady-state and decay measurements caused by feedback. This will be discussed below. The characteristic features of these transient effects of diffusion-controlled kinetics are summarized in *Table 3*.

There are numerous examples of fluorescence quenching where any possible energy transfer process is strongly endothermic, a good example being aromatic hydrocarbons quenched by olefins^{35,36}. To explain the occurrence of quenching it is common to invoke the presence of an exciplex or heteroexcimer as an intermediate. If this exciplex has binding energy excess of kT , then it becomes meaningful to write the following mechanism, which will be recognized as classical excimer kinetics³⁷.



The number of rate constants in the above mechanism can be reduced by assuming that the forward reaction to give $(\text{AQ})^*$ has a probability p and that the rate of formation of $(\text{AQ})^*$ is pk_{diff} . Then the mechanism can be simplified to



and $k_3 = pk_{diff}$. If the loose encounter $(\text{A} \dots \text{Q})$ has products other than A , Q and $(\text{AQ})^*$, this should not alter the basic kinetics as they pertain to A^* and $(\text{AQ})^*$, although there would be an effect on the product formation kinetics if the same product arose from $(\text{AQ})^*$ and $(\text{A} \dots \text{Q})$.

The above photokinetic scheme is described by a pair of coupled ordinary differential equations:

$$d[\text{A}^*]/dt = k_4[(\text{AQ})^*] - (k_1 + k_2 + k_3[\text{Q}])[\text{A}^*] + I_a(t) \quad (18)$$

$$d[(\text{AQ})^*]/dt = k_3[\text{Q}][\text{A}^*] - (k_4 + k_p)[(\text{AQ})^*] \quad (19)$$

where

$$k_p = k_5 + k_6 + k_7 \quad (20)$$

The driving function $I_a(t)$ can be either time-dependent as in transient studies (a pulse of light) or time-independent as in steady-state experiments.

Steady-state analysis of equations 18 and 19 yields the familiar Stern-Volmer type equation

$$K_{sv} \equiv [I_F^0/I_F - 1] (1/[Q]) = k_3 k_p \tau_0 / (k_4 + k_p) \quad (21)$$

where

$$\tau_0^{-1} = k_1 + k_2 = \lambda_0 \quad (22)$$

In addition, if Φ_E is defined as the exciplex fluorescence intensity integrated over the exciplex band, and if I_F is similarly integrated to yield Φ_F , then

$$\Phi_E/\Phi_F[Q] = (k_3/(k_4 + k_p))(k_5/k_1) \quad (23)$$

These steady-state equations are important because, when combined with the equations that describe the transient behaviour, in theory they provide a method for obtaining individual rate constants.

The description of the transient behaviour of I_F depends on the nature of the time-dependence of $I_a(t)$, and the temporal response characteristics of the fluorescence decay apparatus. The most straightforward analysis involves considering the response of the system to a δ -pulse of light followed by the use of the convolution theorem³⁸ to deduce the behaviour in the presence of the driving function $I_a(t)$ and instrumental distortions.

For δ -pulse excitation one has the boundary conditions $[A^*] = [A^*]_0$ and $[(AQ^*)] = [(AQ^*)]_0 = 0$ at $t = 0$. With $I_a(t) = 0$, the coupled first-order differential equations may be solved simultaneously to yield a linear, homogeneous second-order differential equation with constant coefficients having the following auxiliary equation

$$m^2 + (\lambda_0 + k_3[Q] + k_4 + k_5)m + (k_4\lambda_0 + k_5\lambda_0 + k_3k_5[Q]) = 0 \quad (24)$$

and solutions

$$[A^*] = C_1 e^{-\lambda_1 t} + C_2 e^{-\lambda_2 t} \quad (25)$$

$$[(AQ^*)] = C_3 (e^{-\lambda_1 t} - e^{-\lambda_2 t}) \quad (26)$$

where

$$2\lambda_{1,2} = [\{k_1 + k_2 + k_3[Q] + k_4 + k_p\} \{(k_4 + k_p - k_1 - l_2 - k_3[Q])^2 + 4k_3k_4[Q]\}^{\frac{1}{2}}] \quad (27)$$

$$C_1 = [(\lambda_2 - X)/(\lambda_2 - \lambda_1)] [A^*]_0 \quad (28)$$

$$C_2 = [(X - \lambda_1)/(\lambda_2 - \lambda_1)] [A^*]_0 \quad (29)$$

$$C_3 = k_3[Q][A^*]_0/(\lambda_2 - \lambda_1) \quad (30)$$

and

$$X = k_1 + k_2 + k_3[Q] \quad (31)$$

The rate constants k_1 and k_5 relate excited state concentrations to fluorescence intensities, i.e.

$$I_F(t) \propto k_1[A^*] \quad (32)$$

$$I_E(t) \propto k_5[(AQ^*)] \quad (33)$$

Thus one obtains a simple two-component decay for $I_F(t)$ and a growth and

decay for $I_E(t)$, with $I_E(t)$ showing a maximum at

$$t_{\max} = \{1/(\lambda_2 - \lambda_1)\} \ln (\lambda_2/\lambda_1) \quad (34)$$

From equation 27 one has the important relationship of $(\lambda_1 + \lambda_2)$ to $[Q]$,

$$\lambda_1 + \lambda_2 = k_1 + k_2 + k_3[Q] + k_4 + k_p \quad (35)$$

Since one knows the unquenched lifetime $1/(k_1 + k_2)$, equation 35 gives k_3 and $(k_4 + k_p)$ from a plot of $(\lambda_1 + \lambda_2)$ versus $[Q]$. There are two important sets of limits. As $[Q]$ approaches zero, one has the limits:

$$\begin{aligned} \lambda_1 &\rightarrow k_1 + k_2 \\ \lambda_2 &\rightarrow k_4 + k_p \end{aligned} \quad (36)$$

As $1/[Q]$ approaches zero, one has the limits:

$$\begin{aligned} \lambda_2 &\rightarrow k_p \\ \lambda_1 &\rightarrow k_1 + k_2 + k_3[Q] + k_4 \end{aligned} \quad (37)$$

This provides a method for obtaining k_4 and k_p . If the mechanism is correct, steady-state measurements must provide rate constants or ratios thereof which are consistent with the above transient measurements.

Since

$$K_{sv}/\tau_0 \equiv (k_q)_{ss} = k_3k_p/(k_4 + k_p) \quad (38)$$

it follows that measurements of k_3 and $(k_4 + k_p)$ from $(\lambda_1 + \lambda_2)$ versus $[Q]$ when combined with equation 21 immediately yield k_p and thus k_4 . These values should agree with the values obtained from equations 35, 36 and 37.

We can obtain k_1/k_5 from the knowledge of k_3 , k_4 and k_p through the use of equation 23. Since k_1 can then be calculated from the quantum yield of fluorescence of the fluorophor and its unquenched lifetime, one thus obtains k_5 , the radiative transition probability of the exciplex. One can then calculate Φ_E , where

$$\Phi_E = k_5/(k_4 + k_p) \quad (39)$$

The above approach can be used at a series of temperatures to obtain temperature coefficients of rate constants. This needs to be done for a number of exciplexes to determine if $k_5 = f(T)$.

One cannot in general ignore the finite width and decay of $I_a(t)$. From the convolution theorem³⁸ and the δ -pulse response functions it is easily shown that

$$I_E^{\text{obs}}(t) = \int_0^t (C_1 e^{-\lambda_1 t'} + C_2 e^{-\lambda_2 t'}) I_L(t - t') dt' \quad (40)$$

$$I_E^{\text{obs}}(t) = \int_0^t C_3 (e^{-\lambda_1 t'} - e^{-\lambda_2 t'}) I_L(t - t') dt' \quad (41)$$

where $I_L(t)$ is $I_a(t)$ distorted by the measuring instrument^{2,3}. The derivation of these equations has been discussed elsewhere^{2,3} as have deconvolution

techniques for recovering the parameters λ_1 and λ_2 in equations 40 and 41 from the observed fluorescence decay measurements.

It will be assumed that the δ -pulse response of the luminescence system can be recovered by numerical methods or the parameters in an assumed decay law determined by iterative calculations^{2,3}.

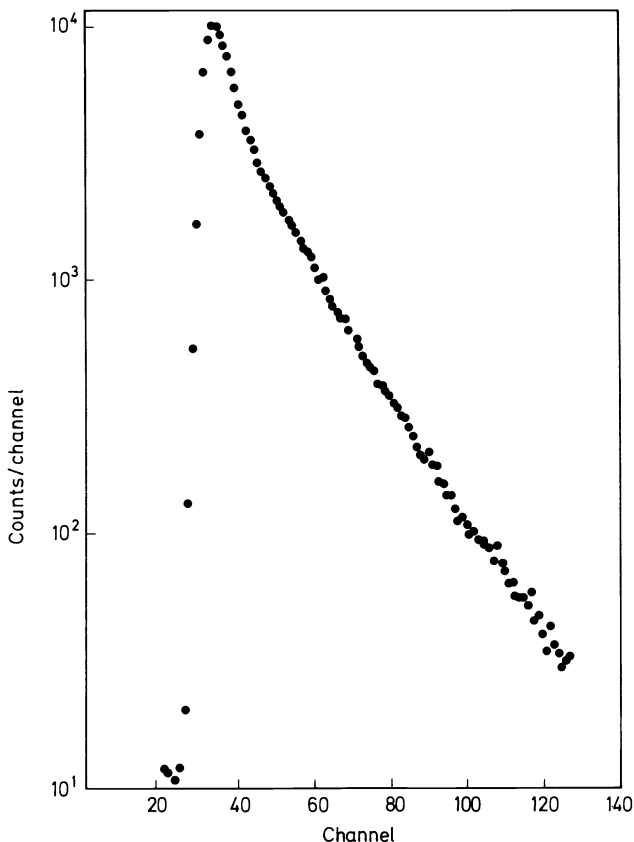


Figure 6. Two-component decay of 9,10-dicyanoanthracene quenched by 4,4'-dimethyl-1,1-diphenylethylene in hexane at 25°C. Emission from the blue edge of the cyanoanthracene emission band.

Consider for example the quenching of 9,10-dicyanoanthracene by 4,4'-dimethyl-1,1-diphenylethylene in benzene at room temperature³⁹. In Figure 6 a typical decay curve for the cyanoanthracene is illustrated and in Figure 7 the deconvolution of this curve by the method of Ware, Doemeny and Nemzek³ is shown. The resultant two-component decay curve is then further resolved to yield λ_1 and λ_2 , as illustrated. With equations 35, 36 and 21 one immediately obtains the following rate constants:

$$k_1 + k_2 = 8.05 \times 10^7 \text{ s}^{-1}$$

$$k_3 = 9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

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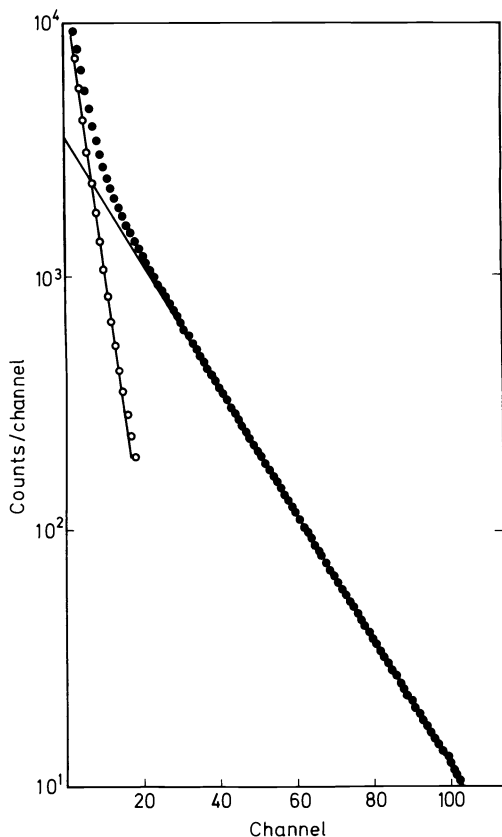


Figure 7. Resolution of the decay curve in Figure 6 into two components using the deconvolution method of Ware, Doemeny and Nemzek³ followed by curve subtraction. The two lifetimes are 9.0 and 2.6 ns.

$$k_A = 4 \times 10^7 \text{ s}^{-1}$$

$$k_P = 4 \times 10^7 \text{ s}^{-1}$$

This type of analysis can obviously be extended to yield much additional information. Other examples where this type of analysis has been applied to exciplexes are due to Ware and Richter⁴⁰ and Okada *et al.*⁴¹. It is clear that a detailed description of the photophysics of a system in terms of the rate constants and their temperature coefficients in general involves a rather extensive set of measurements.

It is somewhat rare, unfortunately, to see two components in the fluorescence decay of the fluorophor, even when the emission spectrum clearly indicates emission from both A* and (AQ)*. Measurements in the region in which the decay is predominantly due to the exciplex are frequently found to give similar decay curves as obtained from measurements of the decay of A* itself. The decay is very close to a single exponential with a single decay

constant λ , and frequently λ is found to be a rather strong function of $[Q]$. It is not unusual to find for the exciplex that λ follows the equation

$$\lambda = (\lambda_0 + B[Q]) / (1 + C[Q]) \quad (42)$$

If the following approximation is valid

$$\begin{aligned} & [(k_4 + k_3[Q])^2 + 2(k_4 - k_3[Q])(k_p - k_1 - k_2)]^{\frac{1}{2}} \\ & \cong k_4 + k_3[Q] + \frac{2(k_4 - k_3[Q])(k_p - k_1 - k_2)}{k_4 + k_3[Q]} \end{aligned} \quad (43)$$

equation 26 can be reduced to equation 42. This is related to the condition quoted by Birks³⁷, i.e.

$$k_4, k_3[Q] \gg k_1, k_2, k_p$$

to which must be added, the more restrictive condition⁴²

$$k_4 + k_3[Q] > 2(k_4 - k_3[Q])(k_p - k_1 - k_2) \quad (44)$$

The conditions quoted in equations 43 and 44 thus yield from equation 42 the exciplex decay constant equation

$$\lambda = \frac{\lambda_0 + (k_3 k_p / k_4)[Q]}{1 + (k_3 / k_4)[Q]} \quad (45)$$

A plot of $(\lambda - \lambda_0)^{-1}$ versus $1/[Q]$ should yield a straight line with slope S given and intercept I given by

$$S^{-1} = (k_p - \lambda_0)(k_3 / k_4) \quad (46)$$

$$I^{-1} = k_p - \lambda_0 \quad (47)$$

Thus, $S/I = k_4/k_3$ and $I^{-1} + \lambda_0 = k_p$. The $[Q]$ dependence alone of λ (along with λ_0) fails to yield the complete set of rate constants, but rather yields only k_p and the ratio k_3/k_4 . However, from the steady-state quenching measurements, we have

$$1/k_3 = 1/(k_q)_{ss} - k_4/k_3 k_p \quad (48)$$

where

$$(k_q)_{ss} = K_{sv}/\tau_0$$

When this equation is used with values of k_3/k_4 and k_p , one obtains k_3 , and thus k_4 can be deduced. These results then yield k_5 from equation 23. It is important to recognize that the success of this approach in the analysis of the so-called *rapid equilibrium* case depends critically upon being able to obtain a significant number from the subtraction of $1/k_q$ and $k_4/k_3 k_p$. It is not uncommon that the two terms in equation 48 are nearly identical and the analysis fails.

The relative $[Q]$ dependence of the numerator and denominator in equation 31 can be estimated by examining the function on the LHS of

equation 49

$$\left[\frac{\lambda}{\lambda_0} - 1 \right] \frac{1}{[Q]} = \frac{(k_3 k_p / k_4 \lambda_0) - (k_3 / k_4)}{1 + (k_3 / k_4)[Q]} \quad (49)$$

Absence of $[Q]$ dependence over a given range of $[Q]$ implies that $(k_3/k_4)[Q] \ll 1$, indicating the magnitude of k_3/k_4 .

The parameters in equation 45 can also be recovered by non-linear least squares using a Taylor's series development:

$$\lambda_i^{\text{cal}} = \lambda_i^{\text{est}} + \left(\frac{\partial \lambda}{\partial \lambda_0} \right)_{\text{est}} \Delta \lambda_0 + \left(\frac{\partial \lambda}{\partial B} \right)_{\text{est}} \Delta B + \left(\frac{\partial \lambda}{\partial C} \right)_{\text{est}} \Delta C \quad (50)$$

The residual ρ_i is

$$\rho_i \equiv \lambda_i^{\text{calc}} - \lambda_i^{\text{obs}} \quad (51)$$

and one uses least-squares techniques to find $\Delta \lambda_0$, ΔB and ΔC , i.e.

$$\begin{aligned} \frac{\partial}{\partial \Delta \lambda_0} (\sum \rho_i^2) &= 0 \\ \frac{\partial}{\partial \Delta B} (\sum \rho_i^2) &= 0 \\ \frac{\partial}{\partial \Delta C} (\sum \rho_i^2) &= 0 \end{aligned} \quad (52)$$

The estimated λ is then corrected and its derivatives with respect to λ_0 , B and C recalculated. The calculation is then repeated until a satisfactory convergence is obtained. Grid search methods are also quite satisfactory for this type of analysis. Other methods have been described by Bevington⁴³ that are more powerful than the Taylor's series expansion.

Another approach⁴² to the analysis of the rapid equilibrium case involves starting with

$${}^2\lambda_{1,2} = [\lambda_0 + k_3[Q] + k_4 + k_p \pm \{(k_p + k_4 - \lambda_0 - k_3[Q])^2 + 4k_3k_4[Q]\}^{\frac{1}{2}}] \quad (53)$$

Let

$$\gamma = \lambda_0 - k_4 - k_p \quad (54)$$

$$\xi = 2\lambda - \lambda_0 - (k_4 + k_p) \quad (55)$$

Then from equation 53

$$\xi^2 - 2\xi k_3[Q] - \gamma^2 = (2\gamma k_3 + 4k_3k_4)[Q] \quad (56)$$

From an estimate of k_p , one can then calculate k_3/k_4 from the slope of $(\lambda - \lambda_0)^{-1}$ versus $[Q]$. Then from $k_q = (k_3 k_p)/(k_4 + k_p)$ one obtains k_3 and k_4 . This uses only the slope of the $(\lambda - \lambda_0)^{-1}$ versus $[Q]^{-1}$ plot and not the more uncertain intercept. One can then calculate the LHS of equation 56 and plot against $[Q]$. If k_5 has been correctly estimated one should get a straight line with a slope $2\gamma k_3 + 4k_3k_4$. One now varies k_5 until this situation

is obtained. Once a value is found for k_5 , the other rate constants are determined.

Another method⁴² uses the auxiliary equation (equation 24). From equation 24, since $m = \lambda$, we have

$$\lambda^2 + (\lambda_0 + k_3[Q] + k_4 + k_p)\lambda + (k_4\lambda_0 + k_p\lambda_0 + k_3k_p[Q]) = 0 \quad (57)$$

λ is known as a function of $[Q]$ and one can for each concentration obtain the coefficients to equation 58 which is merely a rearrangement of equation 57.

$$C_{j3}k_3 + C_{j4}k_4 + C_{j5}k_p + C_{j6} = 0, j = 1, 2, 3 \dots \quad (58)$$

This set of simultaneous equations can then be solved for k_3 , k_4 and k_p .

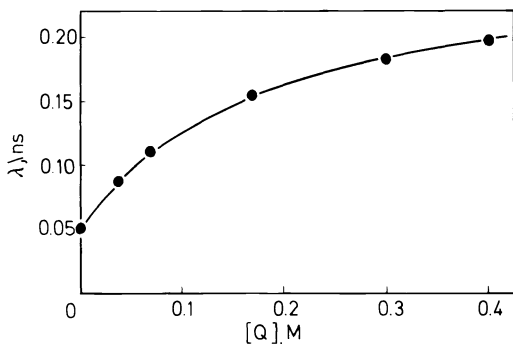


Figure 8. Decay constant of α -cyanonaphthalene in hexane at 17°C as a function of tetramethylethylene concentration. Points, experimental; Line, equation 45.

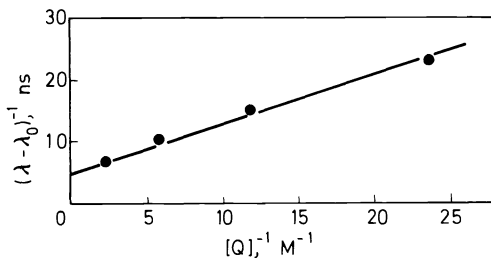


Figure 9. Linearization of Figure 8.

The quenching of α -cyanonaphthalene by tetramethylethylene provides a good example^{42,44} of the rapid equilibrium case. A plot of λ versus $[Q]$ for this system at 25°C is shown in Figure 8 and these data are linearized by plotting $(\lambda - \lambda_0)^{-1}$ versus $1/[Q]$, as shown in Figure 9. Experiments of this type have been performed for several olefins as a function of temperature⁴². Through the use of the various methods described above for the analysis of steady-state and fluorescence decay data, values for k_3 , k_4 and k_p were obtained. Values at 17°C for three olefins are shown in Table 4 and typical

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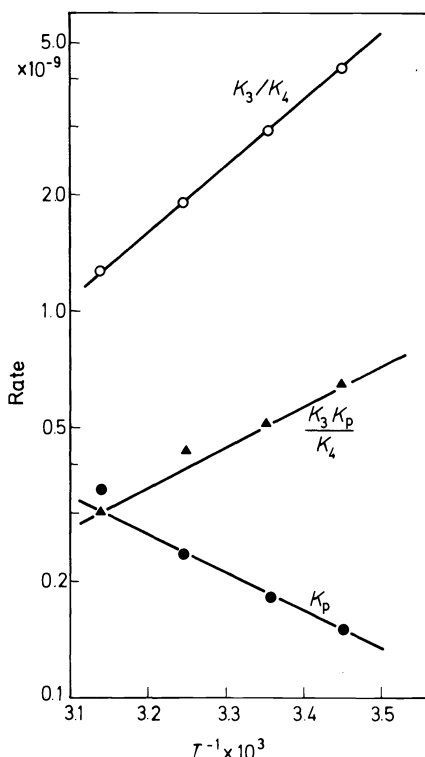


Figure 10. Arrhenius plots of several rate parameters for α -cyanonaphthalene quenched by 1,2-dimethylcyclohexene.

Table 4. Quenching of α -cyanonaphthalene by various olefins in hexane at 17°C. Values of k_3 , k_4 and k_p calculated⁴² from the plots such as shown in Figure 8 and Figure 9.

Quencher	$k_3 \times 10^{-10}$ $M^{-1} s^{-1}$	$k_4 \times 10^{-9}$ s^{-1}	$k_p \times 10^{-9}$ s^{-1}	IP eV
1,2-Dimethyl-cyclopentene	1.2	0.4	0.14	7.84
Tetramethyl-ethylene	1.1	1.8	0.25	8.05
1,2-Dimethyl-cyclohexene	0.24	0.58	0.15	8.04

Arrhenius plots are given in Figures 10 and 11 for α -cyanonaphthalene quenched by 1,2-dimethylcyclohexane in hexane⁴². From such temperature studies both the binding energy and the ground-state repulsion energy were obtained. Some representative values are shown in Table 5. Application of these techniques to a number of systems will hopefully ultimately result in some understanding of the correlation between the physical properties of the pair of molecules that form an exciplex and the properties of the exciplex itself. From studies completed thus far in the author's laboratory^{39, 42} it appears that for α -cyanonaphthalene quenched by various olefins, the quench-

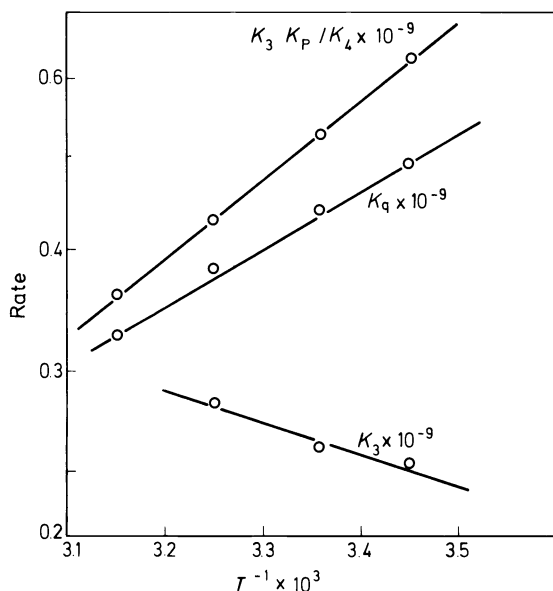


Figure 11. Arrhenius plots for several rate parameters for α -cyanonaphthalene quenched by 1,2-dimethylcyclohexene, k_3 determined with equation 48.

Table 5. Ground-state repulsion energies and enthalpies of formation for three exciplexes of olefins with α -cyanonaphthalene in hexane⁴².

Quencher	ΔH_R kcal Note 1	$-\Delta H$ kcal	IP eV
Tetramethyl-ethylene	3.8	11.2	8.05
1,2-Dimethyl-cyclohexene	5.3	8.7	8.04
1,2-Dimethyl-cyclopentene	3.2	9.0	7.84

Note 1. Assuming $\Delta E_{\infty} = 3.87$ eV.

ing efficiency ($k_{q,ss}$) as a function of the olefin ionization potential (IP) is in fact due mostly to a variation of k_4 with IP . Olefins with high IP have values of k_4 that are large (10^{10} – 10^9 s⁻¹) whereas olefins with low IP have values of k_4 that are low (10^7 – 10^8 s⁻¹ or lower). These are merely illustrative figures, but this appears to be the trend. The values of k_p appear to be much less sensitive to the nature of the olefin, and k_3 is not always equal to the diffusion-controlled rate.

Two interesting special cases of the above 'excimer kinetics' are important in connection with exciplexes and fluorescence quenching. In one case (Case A) one observes the following:

- (a) exponential decay of A^* ;
- (b) no exciplex emission;
- (c) $K_{sv} \neq f([Q])$;

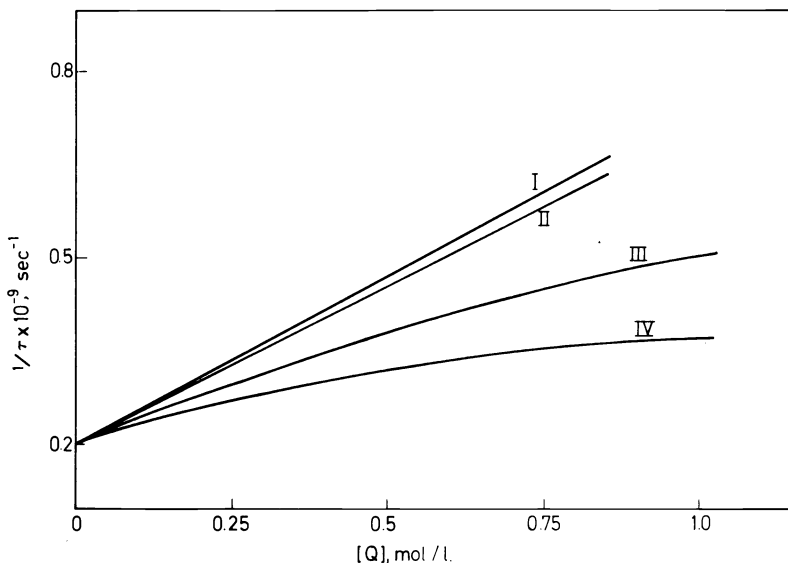


Figure 12. Theoretical quenching plots for $k_p/(k_p + k_4) = 0.091$, $\tau_0 = 5$ ns:

$$\begin{aligned}
 \text{I } K_{sv}/\tau_0 &= \Delta(1/\tau)/\Delta[Q] = 5.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}; \\
 k_4 &= 10^{12} \text{ s}^{-1}; k_5 = 10^{11} \text{ s}^{-1}. \\
 \text{II } k_4 &= 10^{11} \text{ s}^{-1}; k_5 = 10^{10} \text{ s}^{-1}. \\
 \text{III } k_4 &= 10^{10} \text{ s}^{-1}; k_5 = 10^9 \text{ s}^{-1}. \\
 \text{IV } k_4 &= 5 \times 10^9 \text{ s}^{-1}; k_5 = 5 \times 10^8 \text{ s}^{-1}.
 \end{aligned}$$

(d) $1/\tau$ versus $[Q]$ may or may not be a linear function of $[Q]$;

(e) $d(1/\tau)/d[Q] < K_{sv}/\tau_0$ for all $[Q]$.

Equation 45 actually represents an extreme example of this case where $d(1/\tau)/d[Q]$ is a function of $[Q]$ and is always less than K_{sv}/τ_0 and in fact can show extreme curvature with λ , approaching k_p asymptotically at high $[Q]$.

It is also possible to have all degrees behaviour intermediate between Case A described above and the limiting behaviour where $K_{sv}/\tau_0 = d(1/\tau)/d[Q]$. An interesting aspect of Case A is where $d(1/\tau)/d[Q]$ is constant over the concentration range investigated and is less than K_{sv}/τ_0 . Using equations 21 and 25 one can calculate values of k_4 and k_p required to explain such so-called *discrepancies* for any assumed value of k_3 and the measured Stern–Volmer constant. A number of cases have been calculated and reported elsewhere⁴⁵.

Several are shown in Figure 12 and Figure 13. These figures reveal that as the exciplex lifetime gets longer the discrepancy becomes greater and eventually curvature develops in λ versus $[Q]$. These same calculations allow the analysis of the absence of such discrepancies between decay measurements and the steady-state kinetic behaviour. The absence of discrepancies places severe restrictions on the lifetimes of the exciplex that are allowed. Consistent with a given discrepancy there exists a range of exciplex lifetimes corresponding to finite exciplex binding with $k_4 \neq k_{-diff}$. However, the range of binding energies is not large⁴⁵. It is worth emphasizing that the limit of Case A where

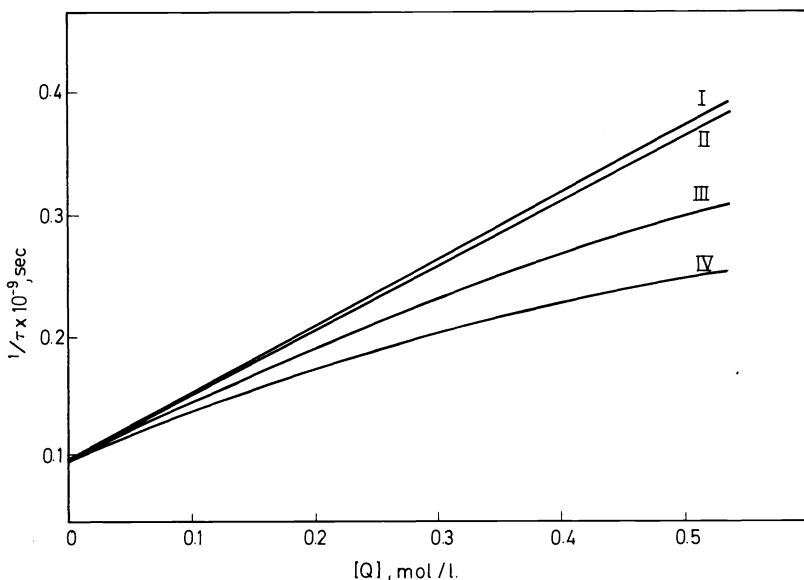


Figure 13. Theoretical quenching plots for $k_p/(k_p + k_4) = 0.091$, $\tau_0 = 10$ ns:

- I $K_{sv}/\tau_0 = \Delta(1/\tau)/\Delta[Q] = 5.4 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$;
 $k_4 = 10^{12}$; $k_3 = 10^{11}$.
 II $k_4 = 10^{11} \text{ s}^{-1}$; $k_5 = 10^{10} \text{ s}^{-1}$.
 III $k_4 = 10^{10} \text{ s}^{-1}$; $k_5 = 10^9 \text{ s}^{-1}$.
 IV $k_4 = 5 \times 10^9 \text{ s}^{-1}$; $k_5 = 5 \times 10^8 \text{ s}^{-1}$.

$d(1/\tau)/d[Q] = K_{sv}/\tau_0$ has very important applications. If one can for example calculate that the lifetime of the exciplex must be $< 10^{-10} \text{ s}$ for a given K_{sv} and assumed k_3 , then one has a constraint on $k_p + k_4$ which must in this example be in excess of 10^{10} s^{-1} . Such constraints can be calculated for various assumed values of k_3 . If, for example, one thinks that $k_4 \gg k_p$ and $k_4 + k_p > 10^{10} \text{ s}^{-1}$, this means that k_4 itself must be greater than 10^{10} s^{-1} . This can be a useful deduction in the analysis of the behaviour of an exciplex quenching system⁴⁵.

The other special case (Case B) occurs as a sub-case of the rapid equilibrium situation where $k_4 \gg k_3$, but where the conditions still exist which make equation 45 valid^{39, 42}. Then

$$\lambda \cong \lambda_0 + (k_3 k_p / k_4) [Q] \quad (59)$$

whereas

$$K_{sv}/\tau_0 = k_3 k_p / (k_4 + k_p) \quad (60)$$

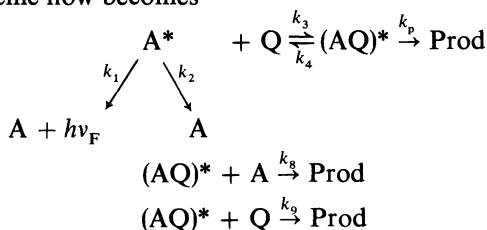
and thus

$$K_{sv}/\tau_0 < k_3 k_p / k_4 = \frac{\Delta(1/\tau)}{\Delta[Q]} \quad (61)$$

In this case the line for $1/\tau$ versus $[Q]$ lies above a line constructed with slope

K_{sv}/τ_0 and intercept λ_0 . This may be compared with Case A, where the opposite relationship of the two lines is observed, with discrepancies placing the $1/\tau$ line below the line constructed from the steady-state slope.

Another interesting complication can arise if either A or Q quenches (AQ)*. The kinetic scheme now becomes



Steady-state analysis yields

$$\frac{K_{sv}}{\tau_0} = \frac{k_3(k_p + k_8[A] + k_9[Q])}{k_4 + k_p + k_8[A] + k_9[Q]} \quad (62)$$

which has the form at constant [A] of

$$K_{sv}/\tau_0 = \{\alpha + \beta[Q]\}/\{\gamma + \delta[Q]\} \quad (63)$$

Roots of the auxiliary equation for the transient case now become

$$\begin{aligned}
 \lambda_{1,2} = & \frac{1}{2}[k_1 + k_2 + (k_3 + k_9)[Q] + k_p + k_8[A] \\
 & \pm \{(k_4 + k_p + k_8[A] + k_9[Q] - k_1 - k_2 - k_3[Q])^2 + k_3k_4[Q]\}^{\frac{1}{2}} \quad (64)
 \end{aligned}$$

In other words, the k_p of the earlier mechanism becomes dependent upon [A] and [Q]. The [Q] dependence of K_{sv} is unfortunate because its absence was a distinguishing characteristic of simple feedback systems (see Table 3). The new equation for the rapid equilibrium case becomes

$$\lambda = \frac{\lambda_0 + (k_3/k_4)(k_p + k_8[A] + k_9[Q])[Q]}{1 + (k_3/k_4)[Q]} \quad (65)$$

or

$$\lambda = \frac{\lambda_0 + C_1[Q] + C_2[Q]^2}{1 + C_3[Q]} \quad (66)$$

The $[Q]^2$ dependence of λ on [Q] may be diagnostic of this phenomenon and likewise, if λ is found to be a function of [A], and in particular if the functional dependence is linear, one might expect that the exciplex was quenched by [A]. The author is not aware of any examples of this type of quenching that have been studied quantitatively.

Feedback⁴⁵, as a complication to kinetics of fluorescence quenching, is included in the cases listed in Table 3, and is compared with the other effects described above. In addition, the complications introduced by Förster dipole-dipole energy transfer³⁷ are included for the sake of comparison.

If Förster energy transfer is possible, then the critical transfer distance should be computed³⁷ from the donor fluorescence spectrum and the

acceptor absorption spectrum. This should be followed by a calculation of the predicted characteristics of the steady-state and transient behaviour³⁷. For some of the characteristic properties listed in *Table 3*, quantitative comparison of decay laws and steady-state quenching behaviour may be necessary to differentiate the effects of Förster transfer from other complicating effects. Solvent viscosity is also critical.

This discussion has emphasized various special effects as well as the general problem of recovering kinetic parameters from the exciplex feedback mechanism. The approach discussed above can be summarized by listing what might be called the minimum set of essential experiments needed to sort out the fundamental photophysics of a fluorescence quenching system:

- Fluorescence decay as a function of quencher concentration, wavelength and temperature.
- (I_F^0/I_F) as a function of concentration, wavelength and temperature.
- Fluorescence spectra as a function of concentration and temperature.

In addition, one should obtain the best estimates possible for the diffusion coefficients appropriate to the system. These experiments can then be evaluated with the aid of *Table 3*. The steady-state data should first be corrected for the possible effects of transient diffusion gradients by estimating R' from the fluorescence decay studies (if $\Delta(1/\tau)/\Delta[Q] \neq f[Q]$). Any residual discrepancy can then be interpreted on the basis of the effects listed in *Table 3*.

Variation of the temperature is more important than generally appreciated. It can reveal negative temperature coefficients which implicate feedback-type kinetics. For example⁴², in the quenching of α -cyanonaphthalene by 1,2-dimethylcyclopentene in hexane values of K_{sv}/τ_0 at 17, 25, 35 and 45°C were found to be 3.0, 2.8, 2.2 and $1.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, indicating a significant negative temperature coefficient for K_{sv} , consistent with the exciplex feedback mechanism.

In laboratories where serious studies of fluorescence quenching are undertaken, both the steady-state and fluorescence decay instruments as well as the fluorescence spectrometer should be equipped to operate over a wide range of temperature (-70°C to $+70^\circ\text{C}$). It is not uncommon to find exciplex emission at low temperature that is not present even at 0°C ⁴⁶. Special cell holders are required for quantitative measurements at low temperatures, unless special cell clamps are made for optical Dewar flasks that permit precise reproduction of cell position. Also, serious problems can arise from fluorescence of coolant liquids and for this purpose cold gases or a cooled cell block are preferable. This is critical for Stern-Volmer measurements.

The measurements outlined above will not necessarily produce a definitive description of a quenching system. For example, in the general exciplex quenching mechanism there are a number of rate constants ($k_1, k_2, k_3, k_4, k_5, k_6$ and k_p). While the first two are trivially measured if the system is fluorescent, the rest will in general remain a problem. Obviously, transient and steady-state measurements must present a number of measurable features if one is to obtain values for *five* additional rate constants. Even the hope of obtaining k_3, k_4 and k_p or even k_3/k_4 and k_p is frequently frustrated by lack of analysable features or by numbers that fall in an awkward range. It is in this area that the picosecond laser will be of great assistance in the study of quenching mechanisms.

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