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Exciplex Photophysics. I. The α -Cyanonaphthalene-Olefin System

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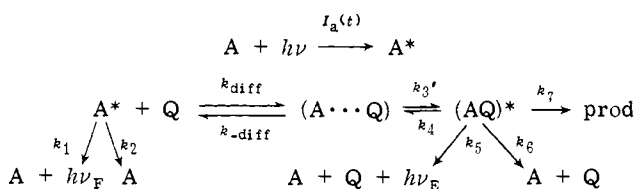
Abstract: A study of the photokinetics of the quenching of α -cyanonaphthalene by four olefins is reported and for three of these olefins a set of rate constants has been obtained on the basis of the standard exciplex kinetic scheme. In addition, heats of formation and ground-state repulsion energy have been determined for three exciplexes. In order to obtain individual rate constants, both steady-state and transient fluorescence measurements were employed and a general discussion of the approximations and numerical techniques appropriate to the so-called rapid equilibrium limit are discussed. The rate constant for exciplex dissociation to regenerate its precursors was observed in general to be related to the ionization potential of the olefin for a set of quenchers covering a range of ionization potential of about 1 eV.

It is well established that the exciplex is an intermediate in some fluorescence quenching processes.¹⁻⁵ It is also quite likely that the exciplex is an intermediate in many bimolecular photochemical transformations. In particular its presence is implicated in systems that exhibit radical anion-cation chemistry subsequent to illumination. The importance of exciplexes is sufficiently great that their properties merit detailed thermochemical and kinetic studies.

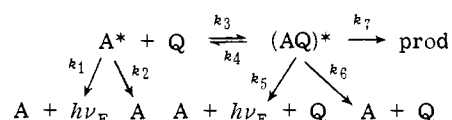
Considerable progress has been reported in the area of equilibrium thermodynamic properties of exciplexes,¹⁻⁵ such as heats of formation. However, detailed kinetic studies aimed not only at mechanistic tests but also at the acquisition of individual rate constants and their temperature coefficients have been of limited number.^{6,7} This series represents an attempt to remedy this situation through the use of modern photophysical techniques.

I. The Postulated Kinetic Scheme

A frequently postulated kinetic scheme for exciplex formation and decay is as follows.



This scheme can be simplified by assuming that the forward reaction to give $(AQ)^*$ has a probability p and that the rate is simply pk_{diff} . Then



with $k_3 = pk_{diff}$. $A \cdots Q$ is considered to be simply the encounter pair before exciplex formation (finite bonding or interaction) takes place. Although the definition of an exciplex is not universally agreed upon, it is operationally useful to consider the complete range of interaction energies down to the limit of thermal energy. This would in the limit include the contact complex. If the loose encounter ($A \cdots Q$) has products other than A , Q , and $(AQ)^*$, this should not alter the basic kinetics as they pertain to A^* and $(AQ)^*$, although of course there would be an effect on the product formation kinetics if the same product arose from $(AQ)^*$ and $(A \cdots Q)$. For the present, any effects of this complication will be ignored since the initial area of interest involves the properties of the exciplex itself.

The initial experimental challenge is to examine the validity of the proposed kinetic scheme, measure k_1 through k_7 , and establish the temperature coefficient of each rate constant. This must ultimately be done for many systems in order that there emerge an understanding of the relationship between the properties of the constituent partners in the exciplex and the kinetics of the formation and disappearance of the exciplex itself.

In the first paper of this series, we consider the case where both the exciplex and its precursor A^* are fluorescent. If both species emit, a number of useful relationships exist pertaining to the steady-state and transient be-

havior of fluorescence intensities. Some of these will now be examined in order to introduce the methods of analysis of the data obtained for such a system, namely α -cyanonaphthalene quenched by several olefins.

For the above photokinetic scheme, one has a pair of coupled ordinary differential equations.

$$\frac{d[A^*]}{dt} = I_a(t) + k_4[(AQ)^*] - (k_1 + k_2 + k_3[Q])[A^*] \quad (1)$$

$$\frac{d[(AQ)^*]}{dt} = k_3[Q][A^*] - (k_4 + k_p)[(AQ)^*] \quad (2)$$

where

$$k_p = k_5 + k_6 + k_7 \quad (3)$$

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

Steady-state analysis of eq 1 and 2 yields

$$K_{sv} \equiv \left[\frac{I_F^0}{I_F} - 1 \right] \frac{1}{[Q]} = \frac{k_3 k_p \tau_0}{k_4 + k_p} \quad (4)$$

where

$$\tau_0^{-1} = k_1 + k_2 = \lambda_0 \quad (5)$$

I_F^0 is the fluorophor fluorescence intensity in the absence of quencher; I_F the intensity in its presence. In addition if ϕ_E is the exciplex fluorescence intensity integrated over the exciplex band, and if I_F is similarly integrated to yield ϕ_F , then

$$\frac{\phi_E}{\phi_F[Q]} = \left(\frac{k_5}{k_1} \right) \frac{k_3}{k_4 + k_p} \quad (6)$$

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

$$\phi_F^0 \equiv \frac{k_1}{k_1 + k_2} \quad (7)$$

$$\phi_E^0 \equiv \frac{k_5}{k_4 + k_5 + k_6 + k_7} = \frac{k_5}{k_p + k_4} \quad (8)$$

The appropriate description of the transient behavior depends on the nature of the time dependence of $I_a(t)$, which now of course is not constant. The most straightforward analysis involves considering the response of the system to a δ pulse followed by the use of the convolution theorem⁸ to deduce the behavior in the presence of the driving function $I_a(t)$. A solution to the system of eq 1 and 2 with Laplace transform techniques for an arbitrary function $I_a(t)$ is equally straightforward and yields the same results as are obtained with the convolution theorem.

For δ -pulse excitation one has at $t = 0$, $[A^*] = [A^*]_0$ and $[(AQ)^*] = [(AQ)^*]_0 = 0$.

The coupled first-order differential equations may be combined to yield a second-order differential equation having the following auxiliary or "m" equation

$$m^2 + (\lambda_0 + k_3[Q] + k_4 + k_5)m + (k_4\lambda_0 + k_5\lambda_0 + k_3k_5[Q]) = 0 \quad (9)$$

and solutions

$$[A^*] = c_1 e^{-\lambda_1 t} + c_2 e^{-\lambda_2 t} \quad (10)$$

$$[(AQ)^*] = c_3 (e^{-\lambda_1 t} - e^{-\lambda_2 t}) \quad (11)$$

where

$$\lambda_{1,2} = \frac{1}{2} [k_1 + k_2 + k_3[Q] + k_4 + k_p \mp \{(k_4 + k_p - k_1 - k_2 - k_3[Q])^2 + 4k_3k_4[Q]\}^{1/2}] \quad (12)$$

$$c_1 = [(\lambda_2 - X)/(\lambda_2 - \lambda_1)][A^*]_0 \quad (13)$$

$$c_2 = [(X - \lambda_1)/(\lambda_2 - \lambda_1)][A^*]_0 \quad (14)$$

$$c_3 = k_3[Q][A^*]_0/(\lambda_2 - \lambda_1) \quad (15)$$

$$X = k_1 + k_2 + k_3[Q] \quad (16)$$

Also

$$I_F(t) \propto k_1[A^*] \quad (17)$$

$$I_E(t) \propto k_5[(AQ)^*] \quad (18)$$

Thus one predicts a simple two-component decay for $[A^*]$ and a growth and decay for $[(AQ)^*]$. $[(AQ)^*]$ should show a maximum at

$$t_{\max} = \frac{1}{\lambda_2 - \lambda_1} \ln \frac{\lambda_2}{\lambda_1} \quad (19)$$

From eq 12 one has

$$\lambda_1 + \lambda_2 = k_1 + k_2 + k_3[Q] + k_4 + k_p \quad (20)$$

This gives k_3 and $(k_4 + k_p)$ from a plot of $(\lambda_1 + \lambda_2)$ vs. $[Q]$, since one knows the unquenched lifetime $1/(k_1 + k_2)$. As $[Q] \rightarrow 0$

$$\begin{aligned} \lambda_1 &\rightarrow k_1 + k_2 \\ \lambda_2 &\rightarrow k_4 + k_p \end{aligned} \quad (21)$$

and as $1/[Q] \rightarrow 0$

$$\begin{aligned} \lambda_1 &\rightarrow k_4 + k_p \\ \lambda_2 &\rightarrow k_1 + k_2 + k_3[Q] + k_4 \end{aligned} \quad (22)$$

Thus one obtains k_4 and k_p . These results do not depend upon steady-state measurements, which, if the mechanism is correct, must provide consistent rate constants or ratios thereof, introducing a redundancy into the deduction of rate constants.

From steady-state data

$$K_{sv}/\tau_0 = k_q = k_3k_p/(k_4 + k_p) \quad (23)$$

It follows that measurements of k_3 and $(k_4 + k_p)$ from $(\lambda_1 + \lambda_2)$ vs. $[Q]$ when combined with eq 23 immediately yield k_p and thus k_4 . These values should agree with the values obtained from eq 20, 21, and 22. We can obtain k_1/k_5 from the knowledge of k_3 , k_4 , and k_p through the use of eq 6. Since k_1 then can be calculated from the quantum yield of fluorescence of the fluorophor and its unquenched lifetime, one thus obtains k_5 .

This yields

$$\phi_E = k_5/(k_4 + k_p) \quad (24)$$

the quantum yield of the exciplex. The above approach can be used at a series of temperatures to obtain temperature coefficients for the rate constants. One does not need to assume $k_5 \neq f(T)$ as is frequently done.

It is generally true that one cannot ignore the finite width and decay of $I_a(t)$. Thus from the convolution theorem⁸ we have

$$I_F^{\text{obsd}}(t) = \int_0^t (c_1 e^{-\lambda_1 t'} + c_2 e^{-\lambda_2 t'}) I_L(t - t') dt' \quad (25)$$

$$I_E^{\text{obsd}}(t) = \int_0^t c_3 (e^{-\lambda_1 t} - e^{-\lambda_2 t}) I_L(t - t') dt' \quad (26)$$

where $I_L(t)$ is $I_a(t)$ distorted by the measuring instrument.^{9,10} The derivation of these equations has been discussed elsewhere.^{9,10} Deconvolution methods for recovering the parameters λ_1 and λ_2 in eq 25 and 26 from the observed fluorescence decay measurements have also been discussed elsewhere.¹⁰ Thus it will be assumed that the δ -pulse response of the luminescence system can be recovered from the experimental decay curve by numerical techniques or the parameters in an assumed decay law determined by iterative methods.

It is not uncommon that two components are absent in the fluorescence decay of the fluorophor even when the emission spectrum clearly indicates emission from both A^* and $(AQ)^*$ with an isoemissive point. Measurements in the region in which the decay is predominantly due to the exciplex are found to give similar decay curves as obtained from measurements of the decay of A^* itself. The decay is close to a single exponential with decay constant λ . Frequently λ is found to be a rather strong function of $[Q]$ and it is not unusual to observe that, for the exciplex, λ follows the empirical equation

$$\lambda = \frac{A + B[Q]}{1 + C[Q]} \quad (27)$$

It can be shown that eq 11 reduces to eq 27 if the following approximation is valid

$$[(k_4 + k_3[Q])^2 + 2(k_4 - k_3[Q])(k_p - k_1 - k_2)]^{1/2} \cong k_4 + k_3[Q] + \frac{2(k_4 - k_3[Q])(k_p - k_1 - k_2)}{k_4 + k_3[Q]} \quad (28)$$

This is related to the condition quoted by Birks,¹¹ *i.e.*

$$k_4, k_3[Q] \gg k_1, k_2, k_p \quad (29)$$

to which must be added

$$k_4 + k_3[Q] > 2(k_4 - k_3[Q])(k_p - k_1 - k_2) \quad (30)$$

The conditions quoted in eq 28 and 29 thus yield for the exciplex

$$\lambda = \frac{\lambda_0 + (k_3 k_p / k_4)[Q]}{1 + (k_3 / k_4)[Q]} \quad (31)$$

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

$$S^{-1} = (k_3/k_4)(k_p - k_1 - k_2) = (k_3/k_4)(k_p - \lambda_0) \quad (32)$$

and intercept I given by

$$I^{-1} = k_p - k_1 - k_2 = k_p - \lambda_0 \quad (33)$$

Thus

$$S/I = k_4/k_3 \text{ and } k_p = I^{-1} + \lambda_0$$

and the $[Q]$ dependence of λ alone for this situation fails to yield the complete set of rate constants, but rather yields only k_p and the ratio k_3/k_4 . It is assumed that one knows k_1 and k_2 . However, from the steady-state quenching measurements, we have

$$\frac{1}{k_3} = \frac{1}{k_q} - \frac{k_4}{k_3 k_p} \quad (34)$$

where

$$k_q = K_{sv} \lambda_0$$

When this equation is used with values of k_3/k_4 and k_p , one obtains values for k_3 . Once k_3 is known, k_4 can be deduced. These results then yield k_5 from eq 6 since now k_p , k_3 , and k_4 are known. The success of this approach in the analysis of this so-called rapid equilibrium limiting case depends critically upon being able to obtain a significant number from the subtraction of $1/k_q$ and $k_4/k_3 k_p$, and this in turn depends upon two factors: (a) the uncertainties in S and I and (b) the actual magnitude of k_q and $k_3 k_p / k_4$.

The relative $[Q]$ dependence of the numerator and denominator in eq 31 can be judged by examining the function

$$\left[\frac{\lambda}{\lambda_0} - 1 \right] \frac{1}{[Q]} = \frac{(k_3 k_p / k_4 \lambda_0) - (k_3 / k_4)}{1 + (k_3 / k_4)[Q]} \quad (35)$$

Absence of $[Q]$ dependence over a given range of $[Q]$ implies that $(k_3/k_4)[Q] \ll 1$ which can be informative in connection with the magnitude of k_3/k_4 .

The parameters in eq 31 can also be recovered by nonlinear least squares using

$$\lambda_i^{\text{calcd}} = \lambda_i^{\text{est}} + \left(\frac{\partial \lambda}{\partial \lambda_0} \right)_{\text{est}} \Delta \lambda_0 + \left(\frac{\partial \lambda}{\partial B} \right)_{\text{est}} \Delta B + \left(\frac{\partial \lambda}{\partial C} \right)_{\text{est}} \Delta C \quad (36)$$

The residual ρ_i is defined as follows

$$\rho_i \equiv \lambda_i^{\text{calcd}} - \lambda_i^{\text{obsd}} \quad (37)$$

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

$$\frac{\partial}{\partial \Delta \lambda_0} (\sum \rho_i^2) = 0$$

$$\frac{\partial}{\partial \Delta B} (\sum \rho_i^2) = 0, \text{ etc.} \quad (38)$$

One then corrects the estimated λ and its derivatives with respect to λ_0 , B , and C and repeats the calculation until a satisfactory fit is obtained.

Another approach to the analysis of the data involves starting with

$$2\lambda_{1,2} = [\lambda_0 + k_3[Q] + k_4 + k_p \pm \{(k_p + k_4 - \lambda_0 - k_3[Q])^2 + 4k_3 k_4 [Q]\}^{1/2}] \quad (39)$$

$$\text{Let } c = \lambda_0 - k_4 - k_p \quad (40)$$

$$d = 2\lambda - \lambda_0 - (k_4 + k_p) \quad (41)$$

Then from eq 39

$$d^2 - 2dk_3[Q] - c^2 = (2ck_3 + 4k_3 k_4)[Q] \quad (42)$$

If one estimates k_p , one can then calculate k_3/k_4 from the slope of $(\lambda - \lambda_0)^{-1}$ vs. $[Q]$. Then from $k_q = (k_3 k_p)/(k_4 + k_p)$ one can obtain k_3 and k_4 . This uses only the slope of the $(\lambda - \lambda_0)^{-1}$ vs. $[Q]^{-1}$ plot and not the more uncertain intercept. One can then calculate the left-hand side of eq 42 and plot the result against $[Q]$. If k_5 has been correctly estimated, one should get a straight line with a slope $2ck_3 + 4k_3 k_4$. Now one varies k_5 until this situation prevails. This

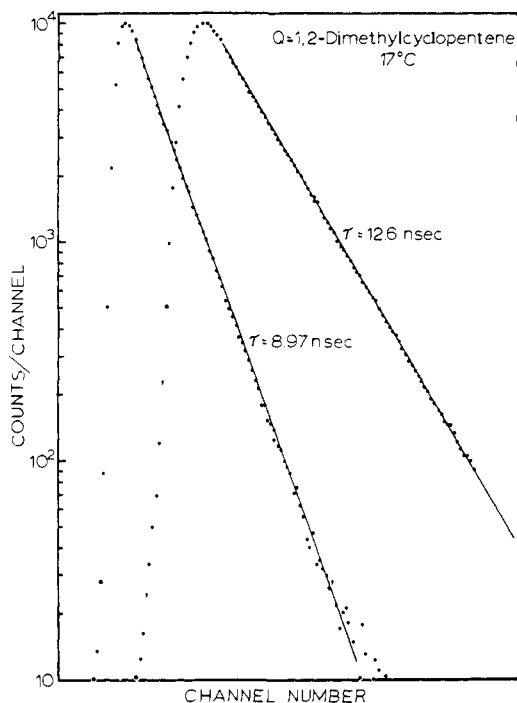


Figure 1. Typical exciplex fluorescence decay curves for α -cyanonaphthalene unquenched and quenched 1,2-dimethylcyclopentene in hexane at 25°.

approach is subject to several variations depending upon which rate constant is selected as the starting point. k_5 is a logical choice because there exists an upper bound given by the asymptote of λ vs. $[Q]$ at high $[Q]$.

Another method uses the "m" equation (eq 9). Since $m = \lambda$ one can write from eq 9

$$\lambda^2 + (\lambda_0 + k_3[Q] + k_4 + k_p)\lambda + (k_4\lambda_0 + k_p\lambda_0 + k_3k_p[Q]) = 0 \quad (43)$$

λ is known as a function of $[Q]$ and one can for each concentration measurement rearrange eq 43 to give

$$C_{i3}k_3 + C_{i4}k_4 + C_{i5}k_p + C_{i6} = 0, \quad i = 1, 2, 3, \dots \quad (44)$$

This set of simultaneous equations can then be solved for k_3 , k_4 , and k_p provided one has sufficient data. This method is sensitive to subtraction of numbers of similar magnitude and frequently may fail to give meaningful results. It does not appear to have been used to analyze this type of kinetics.

II. Experimental Section

Fluorescence lifetimes were measured with the single photon technique described elsewhere.^{9,12} The decay curves were deconvoluted by iterative convolution^{10,12} and in some cases by the exponential series method of Ware and Nemzek.¹⁰ Steady-state measurements of fluorescence quenching were done with an apparatus described by Ware and Lewis.¹³ In all cases the solutions were purged with nitrogen and the temperature was carefully controlled in both the decay-time and steady-state measurements. The solvent in all cases was hexane (spectral grade) which was twice passed through a column of basic alumina with the retention of the middle fraction. α -Cyanonaphthalene was recrystallized and then sublimed three times under vacuum and stored in a freezer. Tetramethylethylene was purified by distillation at 73° with rejection of the tail fraction. This was followed by column chromatography on basic alumina just prior to use. Dimethylcyclopentene-1,2 was purchased from Chemical Sample Co. with the stated purity of 99%.

It was chromatographed on alumina and showed only one peak upon analysis by gas chromatography. Dimethylcyclohexene-1,2 was purified by alumina chromatography and showed no sign of impurity by glc. Methylcyclopentene-1 was purified by distillation and the fraction boiling between 77 and 78° (760 mm) was collected and chromatographed on alumina. There was no sign of any impurities by glc.

III. Results and Discussion

The α -Cyanonaphthalene-Olefin System. From the discussion in section I, it is clear that systems in which both the fluorophor and exciplex are fluorescent provide in theory the opportunity to measure all the pertinent rate constants and test proposed kinetic schemes (in practice the situation can be quite different!). For this reason, Taylor's¹⁴ observation that various olefins yield fluorescence exciplexes upon quenching the first-excited singlet of α -cyanonaphthalene was viewed with considerable interest. The quenching of excited singlets by olefins is rather general^{15,16} and is of interest because of the presumed impossibility of direct energy transfer (no energy acceptor levels nearby) and because of the importance of olefin reactions in photochemistry and in the measurement of intersystem crossing. However, the fact that these olefin-aromatic systems constitute an important class of exciplex which is amenable to photokinetic studies, is perhaps their most interesting aspect.

Taylor¹⁴ investigated a series of olefins as quenchers for α -cyanonaphthalene and reported the following observations. (a) The quenching constant k_q , calculated from the Stern-Volmer constant divided by the unquenched lifetime, was found to be inversely related on a log scale to the olefin ionization potential. (b) The maximum in the exciplex emission was also found to be approximately inversely related to the olefin ionization potential. (c) The exciplex between α -cyanonaphthalene and 1,2-dimethylcyclopentene had an apparent dipole moment of 11 D. (d) The temperature dependence for $I_E/I_F[Q]$ was interpreted in terms of an exciplex binding energy of 6.7 kcal.

Taylor's experiments were confined to steady-state measurements and the rate constants were interpreted with a lifetime of α -cyanonaphthalene obtained from oxygen quenching.

We have examined the steady-state and transient photokinetics of the α -cyanonaphthalene quenching by methylcyclopentene, dimethylcyclopentene, dimethylcyclohexene, and tetramethylethylene. Experiments have been done as a function of temperature in hexane solvent. This section reports the results of these measurements.

Measurements of the fluorophor decay of these systems with the complete exclusion of exciplex emission are somewhat difficult due to the large overlap of spectra. The exciplex emission on the other hand is more easily measured. Both emissions follow a single exponential decay quite accurately and give nearly the same decay constant. Attempts to resolve the decay curves into two components, *i.e.*, either the sum or difference of exponentials, fail to give meaningful results. Typical decay curves are shown in Figure 1. It is found that the single exponential decay constants for the exciplex emission as a function of $[Q]$ follow eq 27 accurately. An example is given in Figure 2 where the observed and calculated (eq 27) curves for α -cyanonaphthalene quenched by 1,2-dimethylcyclopentene are given as a function of temperature. Thus it would appear that we are observing one of the two limiting decay constants for the rapid equilibrium case.

From plots of $(\lambda - \lambda_0)^{-1}$ vs. $1/[Q]$ (see Figure 3) one can get k_p and k_3/k_4 from S/I using eq 32 and 33. From eq 38 one can calculate A , B , and C by nonlinear least-

Table I. Results of Steady-State (k_q) and Transient Fluorescence Quenching Measurements

Quencher	Temp, °C	S/I, M	λ_0 , nsec ⁻¹	$k_q \times 10^{-9}$, M ⁻¹ sec ⁻¹	$k_p \times 10^{-9}$, sec ⁻¹	A, nsec ⁻¹	B $\times 10^{-9}$, M ⁻¹ sec ⁻¹	C $\times 10^{-9}$, M ⁻¹
Tetramethyl- ethylene	17	0.153	0.0479	1.33	0.247	0.0484	1.47	5.58
	25	0.253	0.0505	1.14	0.317	0.0490	1.44	4.99
	30	0.448	0.0517	1.08	0.463	0.0508	1.15	2.97
	35	0.355	0.0525	1.02	0.378	0.0509	0.952	1.70
1,2-Dimethyl- cyclopentene	17	0.033	0.0479	2.99	0.141	0.0490	3.60	24.6
	25	0.0576	0.0505	2.77	0.178	0.0507	3.16	18.1
	35	0.101	0.0525	2.16	0.237	0.0517	2.88	13.7
	45	0.145	0.0531	1.70	0.282	0.0539	2.02	4.69
1,2-Dimethyl- cyclohexene	17	0.226	0.0479	0.492	0.148	0.0482	0.606	3.98
	25	0.286	0.0501	0.441	0.166	0.0489	0.465	2.49
	35	0.487	0.0525	0.384	0.215	0.0537	0.414	1.75
	45	0.528	0.0531	0.324	0.231	0.0556	0.297	0.650

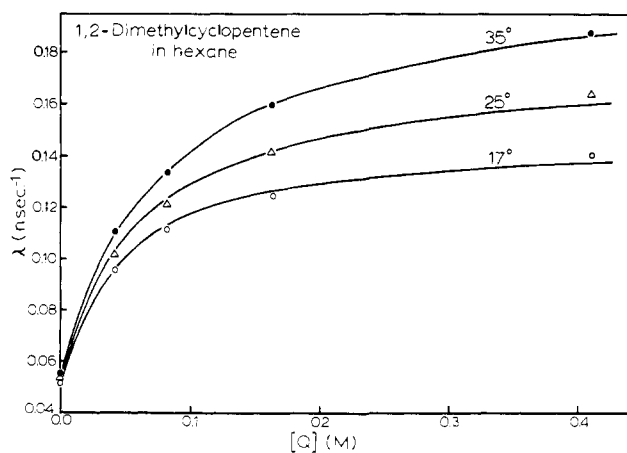


Figure 2. Exciplex fluorescence decay constant in hexane as a function of 1,2-dimethylcyclopentene concentration. Points, experimental. Lines, best fit using eq 27.

Table II. Transient and Steady-State (k_q) Rate Constants for α -Cyanonaphthalene Quenched by 1-Methylcyclopentene in Hexane

Temp, °C	$d\lambda/d[Q] \times 10^{-9}$, M ⁻¹ sec ⁻¹	$k_q \times 10^{-9}$, M ⁻¹ sec ⁻¹
10.5	0.27	0.24
20	0.24	0.22
30	0.20	0.20
40	0.17	0.17

squares fitting in eq 27. The results are given in Table I for tetramethylethylene, 1,2-dimethylcyclohexene, and 1,2-dimethylcyclopentene.

1-Methylcyclopentene is in a class by itself. The exciplex decay curves for 1-methylcyclopentene were strictly exponential and plots of λ vs. $[Q]$ were linear with a slope that agreed within an experimental error with that predicted from steady-state measurements. At 17° there may be slight discrepancy between the steady-state and transient measurements. These results are given in Table II.

All four olefins gave linear Stern-Volmer plots with negative temperature coefficients, *i.e.*, k_q decreased with increasing temperature. An example is shown in Figure 4. The results are given in Table I in terms of k_q . For tetramethylethylene, dimethylcyclohexene, and dimethylcyclopentene, one cannot directly compare k_q and $d\lambda/d[Q]$ because the latter is a function of $[Q]$. It is thus necessary to pursue the analysis in terms of individual rate constants. The temperature coefficients for k_q are of the order of -2 to -5 kcal, with the negative temperature coefficient indicating that $(k_4 + k_p)$ increases faster with temperature than k_3k_p (assuming k_3 increases with temperature). The

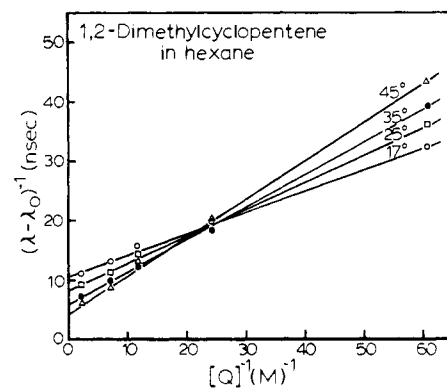


Figure 3. Linearization of the curves shown in Figure 2.

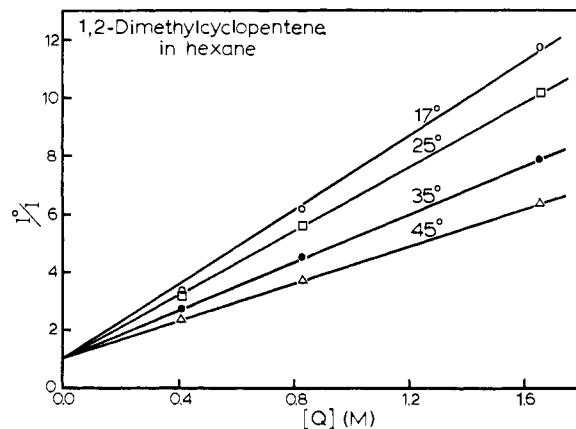


Figure 4. Steady-state Stern-Volmer plots for α -cyanonaphthalene quenched by 1,2-dimethylcyclopentene in hexane.

temperature range was not sufficient to expose any curvature arising from the fact that k_p and $k_4 + k_p$ are in fact sums of rate constants.

Several methods of analysis have been attempted to extract individual rate constants. Method I involves the analysis $(\lambda - \lambda_0)^{-1}$ vs. $1/[Q]$ for slope and intercept to obtain k_3/k_4 and k_p . Method II involves the least-squares analysis to get the coefficients A, B, and C of eq 27. Method III uses eq 41 in connection with eq 27 and involves iteration of k_5 until the left-hand side of eq 42 gave the slope calculated from the right-hand side. In several cases method III failed. These three methods gave values for k_3/k_4 and k_p that agreed to better than 10%. The variations in k_3/k_4 and k_p reflect uncertainties introduced by the numerical methods of analysis coupled with uncertainties inherent in the data. They can, to some extent, be averaged out by calculating the average values of k_3k_p/k_4 and k_p . The results are given in Table III. If one now plots $\log(k_3k_p/k_4)$ and

Table III. Rate Parameters Determined by Various Numerical Methods^a

Quencher	Temp. °C	$k_3/k_4, M^{-1}$				$k_p \times 10^{-9}, \text{sec}^{-1}$				$k_3 k_p/k_4, M^{-1} \text{sec}^{-1}$			
		I	II	III	Av	I	II	III	Av	I	II	III	Av
Tetramethyl- ethylene	17	5.58	6.54	6.14	6.06	0.247	0.265	0.260	0.257	1.62	1.47		1.54
	25	4.99	3.96		4.47	0.317	0.288		0.302	1.24	1.43		1.33
	30	2.79	2.23		2.51	0.463	0.388		0.425	1.03	1.15		1.09
	35	1.70	2.28		1.99	0.378	0.560		0.469	1.06	0.95		1.00
1,2-Dimethyl- cyclopentene	17	30.3	24.6	34.4	29.8	0.141	0.146	0.138	0.141	4.27	3.59	4.74	4.20
	25	17.4	18.1	19.9	18.4	0.178	0.175	0.170	0.174	3.09	3.17	3.28	3.18
	35	9.89	13.7	10.77	11.45	0.237	0.209	0.225	0.223	2.34	2.87	2.42	2.54
	45	6.90	7.69	7.40	7.30	0.282	0.262	0.267	0.270	1.94	2.01	1.88	1.94
1,2-Dimethyl- cyclohexene	17	4.42	3.98		4.21	0.148	0.152		0.150	0.655	0.605		0.630
	25	3.49	2.49		2.99	0.166	0.186		0.176	0.580	0.463		0.502
	35	2.05	1.75		1.90	0.215	0.237		0.226	0.441	0.414		0.428
	45	1.89	0.65		1.27	0.235	0.456		0.343	0.444	0.296		0.370

^a Method I: slope-intercept. Method II: least-square fit to λ vs. $[Q]$. Method III: fit to $d^2 - 2dk_3[Q] - c^2 = (2ck_3 + 4k_3k_4)[Q]$.

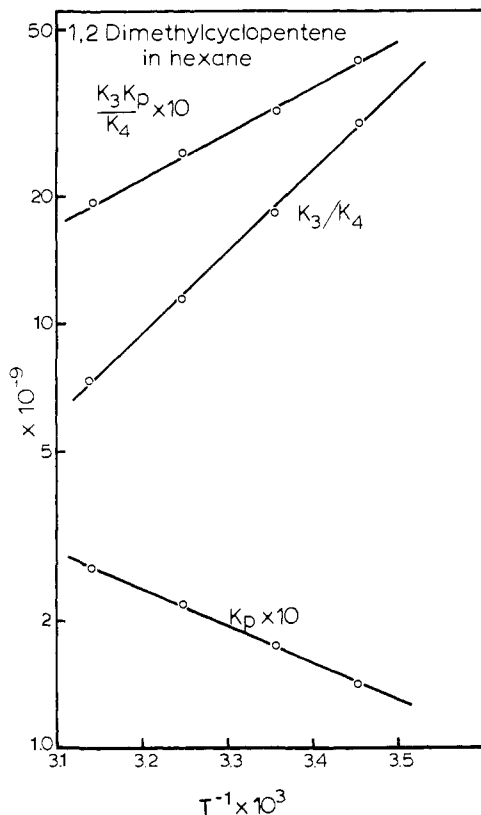


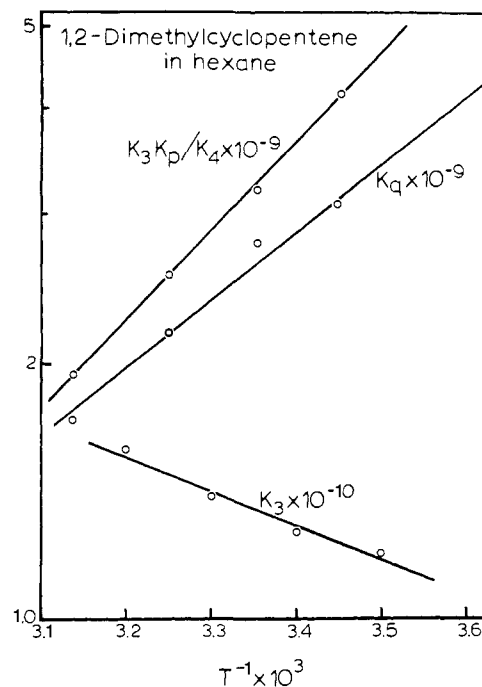
Figure 5. Typical Arrhenius plots for some of the rate parameters given in Table III.

Table IV. Values of k_3 and k_4 Calculated from Equation 34

Quencher	Temp. °C	$k_3 \times 10^{-10},$ $M^{-1} \text{sec}^{-1}$	$k_4 \times 10^{-9},$ sec^{-1}	IP, eV
1,2-Dimethyl- cyclopentene	17	1.2	0.4	7.84
	25	1.3	0.7	
Tetramethyl- ethylene	17	1.1	1.8	8.05
	25	1.4	3.1	
1,2-Dimethyl- cyclohexene	17	0.24	0.58	8.04
	25	0.25	0.75	
1-Methyl- cyclopentene	17	~2 ^a	>100	8.46

^a Assumed.

$\log(k_q)$ vs. $1/T$, good Arrhenius plots are obtained with the two lines diverging as the temperature is lowered (see Figure 5). Further averaging is accomplished by fitting straight lines to these points. Then k_3 can be calculated from k_q and $k_3 k_p/k_4$ obtained from the best lines of the Arrhenius plots, and this can be done at several temperatures. The resulting k_3 values are found to decrease with

Figure 6. Typical Arrhenius plots used to obtain k_3 from eq 34.

decreasing temperatures with temperature coefficients in the range of 1–2.5 kcal. The actual k_3 values that are obtained are of course subject to considerable error due to the subtraction of similar numbers in eq 34. However, this method would appear to give results at 17° reliable to 25–50%, which is sufficient for our purposes. Less confidence is placed in the temperature coefficients of k_3 than in the value for the rate constant themselves obtained at 17° since the error rapidly increases as the two lines converge.

Typical plots are shown in Figures 5 and 6. From k_3 and k_3/k_4 one can then calculate k_4 and the results obtained for both rate constants are given in Table IV.

1-Methylcyclopentene presented special problems. k_q was almost indistinguishable from $d\lambda/d[Q]$. By using eq 35 we established for several sets of data that $(k_3/k_4)[Q]$ is much less than unity and therefore

$$\lambda \cong \lambda_0 + (k_3 k_p/k_4)[Q] \quad (45)$$

$$k_q = k_3 k_p / (k_4 + k_p)$$

one concludes that $k_4 \gg k_3$ such that $C < 0.05$. This then yields a reasonable interpretation of the data, especially when one considers that $k_q \ll k_{diff}$, which suggests that $k_p/(k_4 + k_p) \ll 1$, i.e., $k_4 \gg k_p$. If $k_3 = k_{diff}$, then $k_4 \geq 2 \times 10^{11} \text{sec}^{-1}$.

Table V. Activation Energies and Exciplex Formation Enthalpies for the Quenching of α -Cyanonaphthalene Quenched by Various Olefins

Quencher	$\Delta E^*(k_q)$, kcal	$\Delta E^*(k_3/k_4)$, kcal	$\Delta E^*(k_p k_3/k_4)$, kcal	$\Delta E(k_p)$, kcal	$-\Delta H_C$, kcal			IP, ^c eV
1-Methylcyclopentene	-2.0		-2.0					8.46
Tetramethylethylene	-3.3	-11.9	-3.8	7.2	11.9	11.0	11.5	8.05
1,2-Dimethylcyclohexene	-2.8	-7.9	-4.7	4.3	7.9	9.0	8.5	8.04
1,2-Dimethylcyclopentene	-4.1	-9.1	-5.0	4.0	9.1	9.0	9.0	7.84

^a Note 1. Equivalent to $-\Delta E^*$ for k_3/k_4 ; $\Delta H_C = \Delta E_4^* - \Delta E_3^*$. ^b Note 2. Calculated from ΔE associated with $k_p I/S$ since this yields $\Delta E_p + \Delta E_3 - \Delta E_4$. ^c Note 3. See ref 14.

Table VI. Ground-State Repulsion Energies for Three Exciplexes of Olefins with α -Cyanonaphthalene in Hexane^a

Quencher	ΔE_4^* , ^b kcal	ΔH_R , ^c kcal	$-\Delta H_C$	IP, eV
Tetramethylethylene	13	3.8	11.2	8.05
1,2-Dimethylcyclohexene	10.5	5.3	8.7	8.04
1,2-Dimethylcyclopentene	10.8	3.2	9.0	7.84

^a $\Delta H_R = \Delta E_\infty + \Delta H_E + h\nu_E$. See text. ^b Note 1. Assuming $\Delta E_3^* = 0.078$ eV for all olefins. ^c Note 2. Assuming $\Delta E_\infty = 3.87$ eV.

From Arrhenius plots of k_3/k_4 , $k_3 k_p/k_4$, and k_p one can calculate the temperature coefficient of k_3/k_4 , which is equivalent to the enthalpy of formation of the exciplex. One can also calculate the temperature coefficient of k_p . Reference to Figure 6 indicates that the data are reasonably satisfactory for the calculation of these temperature coefficients. In addition, calculation of the temperature coefficient for k_3/k_4 from either $k_3 k_p/k_4$ and k_p or directly from k_3/k_4 yields consistent results. Again the calculation is based on averaged values of these combined rate constants as well as the average value of k_p , the averaging being done over the methods of data analysis employed.

The temperature coefficients are presented in Table V for dimethylcyclopentene, dimethylcyclohexene, and tetramethylethylene. The only temperature coefficient for 1-methylcyclopentene that can be extracted is $\Delta E_p^* + \Delta E_3^* - \Delta E_4^*$, this from k_q .

The compounds in Table V are arranged according to olefin ionization potential. There may be a general trend with ionization potential in that the compound with the lowest ionization potential has a low value of k_4 and *vice versa*. However, tetramethylethylene and dimethylcyclohexene, which have similar ionization potentials, have rather different k_4 , a difference that is regarded as the outside experimental error although this is difficult to prove beyond all doubt. For 1-methylcyclopentene even if k_3 were low, say $10^9 M^{-1} \text{ sec}^{-1}$, k_4 would still have to be $>10^{10}$ per sec.

Taylor¹⁴ reports a Stern-Volmer constant for 2,5-dimethyl-2,4-hexadiene which when coupled with our lifetime for α -cyanonaphthalene gives $k_3 k_p/(k_4 + k_p) = 1.8 \times 10^{10} M^{-1} \text{ sec}^{-1}$, *i.e.*, nearly diffusion controlled. This can be rationalized by assuming that the low-ionization potential will result in $k_4 < 10^8$. If $k_4 \ll k_p$ then $k_q \cong k_3 \cong k_{diff}$. Both this molecule and 1-methylcyclopentene yield little additional information since none of the photophysical features giving individual rate constants are present.

The values of $-\Delta H_C = k_3/k_4$ are also listed in Table V. There seems to be no correlation with the olefin ionization potential. Since ΔE_3^* is not accurately known, it is conceivable but not likely that when ΔE_4^* is indeed calculated, it will show a trend with ionization potential. How-

Table VII. Test of Equation 31 for High and Low Quencher Concentration

Quencher	[Q], M	$\sqrt{\alpha^2 + \beta}$ or $(\alpha + \beta)/2\alpha$
1,2-Dimethylcyclopentene	0.05	9.81×10^8
	1.0	1.23×10^{10}
Tetramethylethylene	0.05	2.41×10^9
	1.0	1.26×10^{10}
1,2-Dimethylcyclohexene	0.05	7.67×10^8
	1.0	2.92×10^9
1-Methylcyclopentene	0.05	2.04×10^{11b}
	1.0	2.17×10^{11b}

^a $\alpha = k_4 + k_3[Q]$; $\beta = 2(k_4 - k_3[Q])(k_5 - k_1 - k_2)$. Parameters from Tables III and IV. ^b $k_4 = 2 \times 10^{11}$; $k_3 = 2 \times 10^{10}$.

ever, this requires an exceptionally large ΔE_3^* for dimethylcyclohexene and a negligible temperature coefficient for ΔE_3^* for tetramethylethylene. Both situations seem unlikely. The observed ΔH_C values are of the same order of magnitude as found for other exciplexes.¹⁻⁵ From the conservation of energy one has $\Delta E_\infty = \Delta H_C + \Delta H_R + h\nu_E$ where ΔE_∞ is the energy for the transition $A \rightarrow A^*$, ΔH_E is the repulsion energy in the ground state, ΔH_C is the heat of formation of the exciplex, and $h\nu_E$ is the exciplex emission energy at the fluorescence maximum. Table VI lists these energies. The values for ΔH_R are of the same magnitude but somewhat smaller than those observed for amine-aromatic exciplexes.¹⁻⁵ No correlations are apparent among the data in Table VI.

The assumptions leading to eq 31 can be tested using the rate constants obtained from the above analysis. Let us define

$$\alpha = k_4 + k_3[Q]$$

and

$$\beta = 2(k_4 - k_3[Q])(k_5 - k_1 - k_2) \quad (46)$$

Then for internal consistency between eq 11 and eq 31, one must have (*vide supra*)

$$\sqrt{\alpha^2 + \beta} = \alpha + (\beta/2\alpha) \quad (47)$$

In Table VII are listed values for both the right-hand side and the left-hand side of eq 47 calculated at two concentrations for all the quenchers used. To three significant figures, the equality holds and eq 31 is a valid approximation to eq 11 over the rate constant and concentration range in question.

Knowledge of the rate constants k_3 , k_4 , and k_p permit us to calculate k_5 for the exciplex between α -cyanonaphthalene and 1,2-dimethylcyclopentene. From Taylor's data it can be shown that for this olefin $\Phi_E/\Phi_F[Q] = 14$ at 25°. From eq 6 we calculate that $k_5 = 10^7 \text{ sec}^{-1}$, based upon our measurement of the quantum yield of α -cyanonaphthalene (0.21 at 25°) which gives $k_1 = 1 \times 10^7 \text{ sec}^{-1}$.

This may be compared to the pyrene-dimethylaniline exciplex⁷ where $k_5 = 5 \times 10^6$ and $k_1 = 2 \times 10^6 \text{ sec}^{-1}$. The magnitude of k_5 is determined by the various configurations important in the description of the exciplex state. The transition dipole M^E for an exciplex can be expressed as¹⁷

$$M^E \propto \sum_i a_i \langle \Phi_n(\text{AQ}) | r | \Phi_i(\text{A}^*\text{Q}) \rangle + \sum_j b_j \langle \Phi_n(\text{AQ}) | r | \Phi_j(\text{AQ}^*) \rangle + \sum_k c_k \langle \Phi_n(\text{AQ}) | r | \Phi_k(\text{A}^*\text{Q}^-) \rangle + \sum_l d_l \langle \Phi_n(\text{AQ}) | r | \Phi_l(\text{A}^*\text{Q}^-) \rangle \quad (48)$$

where the symbols are self-explanatory. This equation can be used to rationalize practically any k_1/k_5 ratio either greater or less than unity because of the variety of transitions from which the exciplex can derive oscillator strength. From $k_5 = 10^7 \text{ sec}^{-1}$, one can calculate that $\Phi_E = 0.01$.

If one includes 2,5-dimethyl-2,4-hexadiene in this discussion, we can then consider five olefins covering an IP range of about 1 eV. The hexadiene has the lowest IP and Taylor¹⁴ observed it to quench at a diffusion-controlled rate, implying $k_3 \cong k_{\text{diff}}$, and $k_4 \ll k_5$. This represents one extreme with the diffusion control preventing one from measuring individual rate constants. At the other extreme we have 1-methylcyclopentene with the highest IP of the set. Here the quenching as measured by k_q is very inefficient and our kinetic studies indicate that $k_4 \gg k_p$. Again the kinetics are of limited utility because steady-state and transient measurements agree and there is no curvature to analyze. These two compounds have about 1 eV difference in their IP in the gas phase. In between these fall the three compounds which exhibit quenching kinetics such as to yield useful additional information.

Both k_3 and k_4 are observed to vary with quencher and no simple interpretation of k_q is valid. However, the compound with the lowest IP has the lowest value of k_4 observed, and the k_4 values are all two to three orders of magnitude lower than the rate constant for the separation of two noninteracting species in hexane (10^{11} sec^{-1}).¹⁸ These three compounds are regarded as intermediate cases. k_q is much less than k_{diff} principally because $k_p < k_4 \ll k_{\text{diff}}$.

It is probably unwise to conclude anything from the absence of strong correlation between k_4 or k_p and the IP for these three intermediate cases, since they span only about 0.2 eV in the gas phase IP and one does not know how the solution IP's are ordered relative to the gas-phase values over this small energy range. Suffice to say that no correla-

tion with the gas-phase IP is apparent for k_4 , k_p , ΔH_C , or ΔH_R for these three intermediate cases. However, for the 1-eV range represented by the set of five compounds discussed above, there appears to be a strong correlation of k_4 with IP. This is to be expected, for if the IP of the olefin is high enough only a very weak complex would be expected and k_4 should approach k_{diff} yielding very inefficient quenching, whereas for a low IP a strong complex is formed and diffusion-controlled quenching is expected with insignificant feedback (k_4).

The methods described in this paper are quite general and can be applied to any exciplex system exhibiting emission from both species. There are unfortunately remarkably few olefin-aromatic exciplexes with sufficiently large Φ_E to give significant exciplex emission. A search is currently being conducted for additional examples, as well as for experimental conditions which will improve the accuracy with which individual rate constants and temperature coefficients can be determined.

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