Exciplex Photophysics. III. Kinetics of Fluorescence Quenching of α-Cyanonaphthalene by Dimethylcyclopentene-1,2 in Hexane

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Abstract: The photophysics of the interaction of α-cyanonaphthalene in its first excited singlet state with dimethylcyclopentene-1,2 as a quencher is reported over the temperature range of 0 to −40 °C in hexane. In this temperature range the system exhibits the typical photokinetics of a feedback system with two-component monomer decay. From an analysis of the decay kinetics, four rate constants associated with exciplex formation and decay have been determined along with their temperature coefficients. By combining these data with that of an earlier study a rather complete picture of the photophysics of this system is obtained.

I. Introduction

In 1971 Taylor[1] reported the interesting observation of a new red-shifted emission associated with the quenching of α-cyanonaphthalene by olefins such as tetraphenylethylene and various substituted cyclopentenes and cyclohexenes. In paper I of this series,[2] the photokinetics of several α-cyanonaphthalene–olefin systems were investigated with the purpose in mind of establishing the quenching mechanism and obtaining information regarding properties of the exciplex such as binding energy and entropy. The three systems studied in detail and reported in paper I all exhibited behavior characteristic of the so-called rapid-equilibrium limit. Only one-component exponential decay was observed. By combining steady state and lifetime data it was possible to obtain most of the rate constants, albeit with considerable uncertainty.

Computer simulation of the kinetics of the α-cyanonaphthalene–dimethylcyclopentene-1,2 system using the rate constants and temperature coefficients given in paper I indicated that if this system was studied from 0 to −50 °C in hexane, one should see two-component monomer decay and the growth and decay of the exciplex. The analysis of these intrinsically richer decay data was predicted to yield all the rate constants of the standard exciplex mechanism and their temperature coefficients without recourse to steady state data. The latter measurement therefore would provide a check of the decay studies. In addition, the large uncertainties associated with the calculation of k_3, k_4, and k_p (see paper I) are eliminated when one is able to observe two-component decay curves. Thus, it appeared attractive to study this particular system at low temperature in order to check the conclusions in paper I and confirm or discredit the mechanism advanced therein.

In the present paper we present a fairly exhaustive photophysical study of the α-cyanonaphthalene–dimethylcyclopentene-1,2 system in hexane from 0 to −40 °C. To the best of our knowledge, this is the first exciplex system investigated in such detail over a temperature range great enough that one sees the rapid equilibrium behavior at high temperature and the two-component decay of the monomer at low temperature.

II. Experimental Section

Transient decay curves were measured using the time-correlated single-photon counting technique.[3-5] The flash lamp was operated at a high voltage of 6.5 kV and a repetition rate of 25 kcycles. Deuterium at ½ atm pressure was used as the flash gas.

The following combination of filters was used in the path of the exciting light: (i) a Corning 7-54 glass filter; (ii) 5-cm optical path length of $NiSO_4 \cdot 6H_2O$ in water (300 g/l.); (iii) 1-cm path length of 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate (Calbiochem, Cation X) in water (170 mg/l.).[6] This filter combination transmitted ca. 20% of the incident radiation at its wavelength of maximum transmission, 263 nm. It was virtually opaque (<0.05% transmission) from 300 to 340 nm and from 360 to 420 nm.

Sample fluorescence of appropriate wavelength was selected with a Jarrell-Ash monochromator, *f*/3.5 aperture, 0.25-m path length, 300-nm blaze, linear dispersion of 1.65 nm/mm, 2-mm slits. The monochromator was set at 325 nm to isolate monomer emission and at 400 nm for exciplex emission. Thus the slight window in the excitation filter between 340 and 350 nm (maximum transmission, 1%) did not present a problem as regards detection of scattered light. The small contribution of monomer fluorescence to the exciplex decay curve does not affect the lifetimes extracted from this curve.[7]

When the rate constant for exciplex formation is close to the diffusion-controlled value it is desirable to avoid the short-time portions of the decay curves when analyzing the transient data.[7] For this reason the exciplex decay curves were not used in the determination of the decay law parameters. The monomer decay curves were analyzed using the iterative convolution, least-squares technique described elsewhere.[3,7] Some of the curves were also analyzed using the method of moments.[8] The rising edge of the decay curve must be used in this method and therefore we prefer the least-squares method for the analysis of these types of data.

Fluorescence spectra were measured with a standard two-monochromator spectrofluorimeter, with a 90° viewing angle. The instrument was corrected for wavelength response in the region below 400 nm by using a tungsten lamp supplied by Eppley Laboratory and in the region above 400 nm by comparison of a spectrum of quinine bisulfate with the known corrected spectrum. Care was taken to shield the samples from irradiation by the xenon arc lamp during the time in which they were coming to thermal equilibrium.

Spectral grade hexane was passed twice through a column containing equal amounts of 60–120 mesh silica gel and basic alumina. Recrystallized 1-cyanonaphthalene was sublimed three times under vacuum and stored in a freezer. 1,2-Dimethylcyclopentene, purchased from Chemical Samples Co. with a stated purity of 99%, was chromatographed on a column of basic alumina immediately prior to use. The solutions were prepared at room temperature. Olefin concentrations at low temperatures were corrected for solvent contraction using the density of *n*-hexane at these temperatures.[9] The room-temperature concentration of cyanonaphthalene was 5×10^{-5} M in all solutions.

The solutions decomposed upon prolonged exposure to the arc lamp of the spectrofluorimeter. Decomposition occurred under room light when cells were used which had been washed with chromic acid cleaning solution. Thus, chromate ions were purged from all glassware used in handling the solutions[10] and cleaning with chromic acid was avoided.

All samples were degassed using the freeze–pump–thaw technique on a grease-free, mercury-free vacuum line.

Measurements were made on solutions contained in 1-cm square quartz cells. Both instruments used for the measurements were equipped with aluminum cell holders into which the cells fitted snugly. The holders contained coils through which coolant was circulated and were jacketed with an insulating foam. Evacuated window assemblies were contained in the foam in the paths of the exciting and emitted light. Anhydrous ethyl alcohol was used as the coolant. It was cooled by a Neslab Model Eric-44 refrigerating unit and circulated with a Neslab Model TE9 circulating bath. Dry nitrogen was flushed continuously through the cell compartment. Temperatures were measured using a bead thermistor purchased from Fenwall Electronics, Inc. The thermistor was calibrated against accurate thermometers and a copper-constantan thermocouple. Quoted temperatures are accurate to ±0.3 °C.

Samples were allowed to equilibrate for 30 min before measurements were taken.

III. Results and Discussion

The experiments between 0 and −40 °C in hexane yielded the following qualitative results. (a) The steady state fluorescence quenching gave linear Stern-Volmer plots with slope increasing to a maximum and then decreasing with decreasing temperature. (b) The ratio of the exciplex to monomer emission yield, ϕ_E/ϕ_M, was a linear function of [Q] with slope increasing with decreasing temperature. (c) The monomer decay could be characterized exactly by two decay constants, λ_1 and λ_2, obtained by deconvolution with a δ-pulse response function $A_1e^{-\lambda_1 t} + A_2e^{-\lambda_2 t}$. λ_1 and λ_2 were in general nonlinear functions of [Q] but $\lambda_1 + \lambda_2$ was linear with a slope that increased with increasing temperature. At −0.3 and −11 °C $1/(\lambda_2 - \lambda_0)$, where λ_0 is the reciprocal of the unquenched monomer lifetime, was a linear function of 1/[Q]. (d) The exciplex growth and decay fit quite well $A_3e^{-\lambda_1 t} - A_3'e^{-\lambda_2 t}$ but A_3 was not exactly equal to A_3' and the short lifetime did not exactly agree with that obtained from the monomer decay curve. Typical decay curves are illustrated in Figures 1 and 2.

These observations are in qualitative agreement with the well-known excimer or exciplex mechanism.[2,7,11] That is

$$\begin{tikzcd}
& A \arrow[r, "I_a(t)"] & A^* & & \\
& A^* + Q \arrow[dl, "k_1"'] \arrow[dr, "k_2"] \arrow[rr, shift left, "k_3"] & & (AQ)^* \arrow[ll, shift left, "k_4"] \arrow[r, "k_6"'] \arrow[d, "k_5"] & \text{product} \\
A + h\nu_F & & A & A + Q + h\nu_F &
\end{tikzcd}$$

The appropriate equations are[2,7,11]

$$I_M(t) = C_1e^{-\lambda_1 t} + C_2e^{-\lambda_2 t} \quad (1)$$

$$I_E(t) = C_3(e^{-\lambda_1 t} - e^{-\lambda_2 t}) \quad (2)$$

$$\lambda_{1,2} = \tfrac{1}{2}[k_1 + k_2 + k_3[Q] + k_4 + k_p \pm \{(k_1 + k_2 + k_3[Q] - k_4 - k_p)^2 + 4k_3k_4[Q]\}^{1/2}] \quad (3)$$

$$k_p = k_5 + k_6 \quad (4)$$

One also has

$$\lambda_1 + \lambda_2 = k_1 + k_2 + k_3[Q] + k_4 + k_p \quad (5)$$

$$\lambda_1\lambda_2 = (k_1 + k_2)(k_4 + k_p) + k_3k_p[Q] \quad (6)$$

Another useful equation is the indicial equation used to derive eq 1 and 2. This is

$$\lambda^2 - [k_1 + k_2 + k_3[Q] + (k_4 + k_p)]\lambda + (k_1 + k_2)(k_4 + k_p) + k_3k_p[Q] = 0 \quad (7)$$

Finally, the two steady state equations are

$$K_{SV} = \frac{k_3k_p}{(k_1 + k_2)(k_4 + k_p)} = \left[\frac{I_M^0}{I_M} - 1\right]\frac{1}{[Q]} \quad (8)$$

$$\frac{\Phi_E}{\Phi_M} = \left(\frac{k_5}{k_1}\right)\left(\frac{k_3}{k_4 + k_p}\right)[Q] \quad (9)$$

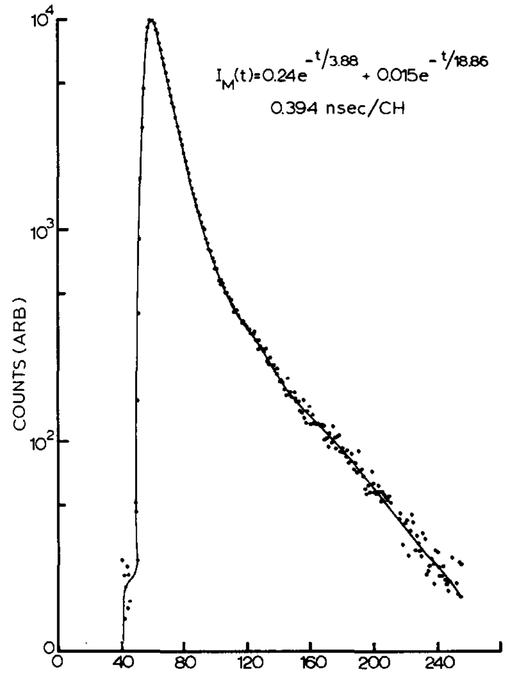

Figure 1. Typical monomer decay curve: α-cyanonaphthalene + dimethylcyclopentene-1,2 (2.85×10^{-2} M) at −31 °C.

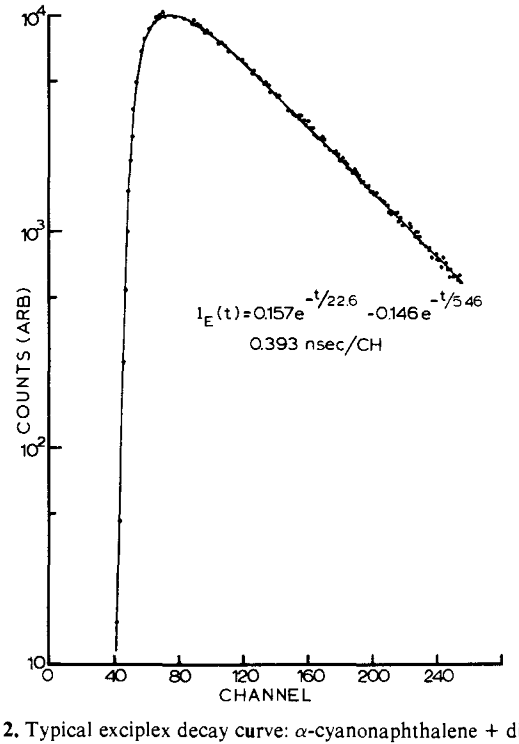

Figure 2. Typical exciplex decay curve: α-cyanonaphthalene + dimethylcyclopentene-1,2 (1.92×10^{-2} M) at −40 °C.

These equations will now be utilized to calculate individual rate constants on the assumption that the mechanism is valid. The observations given above provide only qualitative evidence for this belief, and we now show that the quantitative aspects are consistent with that model.

For the determination of individual rate constants, only λ_1 and λ_2 obtained from the monomer two-component decay were used. These were judged the most reliable because slight distortion on the leading edge of the exciplex curve due to diffusion control transients[7,12] leads to small but consistent errors in λ_1 and λ_2 obtained from $I_E(t)$. This will be discussed in more detail below.

Table I. Rate Constants in Hexane at Various Temperatures

t, °C	$k_1 + k_2 \times 10^{-7}$, s^{-1}	$k_3 \times 10^{-8}$,[a] M^{-1} s^{-1}	$(k_4 + k_p) \times 10^{-8}$, s^{-1} *b*	*c*	*d*	$k_4 \times 10^{-8}$, s^{-1} *e*	*f*	*g*	*h*	$k_p \times 10^{-8}$, s^{-1} *e*	*f*	*g*	*h*
−0.3	5.38 ± 0.01	98.8 ± 5.6	2.13 ± 0.16	2.10 ± 0.24	2.12 ± 0.13	1.11 ± 0.25	1.14 ± 0.06	1.11 ± 0.16	1.14 ± 0.06	0.98 ± 0.08	0.978 ± 0.01	1.01 ± 0.09	0.98 ± 0.007
−11	5.38 ± 0.01	88.5 ± 1.9	1.26 ± 0.05	1.26 ± 0.07	1.26 ± 0,04	0.49 ± 0.07	0.49 ± 0.02	0.46 ± 0.05	0.49 ± 0.02	0.77 ± 0.02	0.767 ± 0.002	0.80 ± 0.04	0.767 ± 0.002
−22	5.34 ± 0.01	78.0 ± 1.0	0.82 ± 0.02	0.84 ± 0.03	0.83 ± 0.02	0.22 ± 0.04	0.20 ± 0.01	0.18 ± 0.03	0.20 ± 0.009	0.62 ± 0.01	0.624 ± 0.002	0.65 ± 0.02	0.624 ± 0.002
−31	5.30 ± 0.01	66.7 ± 0.7	0.62 ± 0.02	0.63 ± 0.03	0.62 ± 0.02	0.11 ± 0.03	0.10 ± 0.007	0.07 ± 0.03	0.10 ± 0.007	0.52 ± 0.01	0.524 ± 0.002	0.55 ± 0.02	0.524 ± 0.002
−40	5.26 ± 0.01	60.6 ± 0.6	0.49 ± 0.02	0.57 ± 0.04	0.50 ± 0.02	0.12 ± 0.04	0.036 ± 0.009	0.040 ± 0.025	0.040 ± 0.008	0.44 ± 0.01	0.463 ± 0.004	0.46 ± 0.02	0.461 ± 0.003

[a] From eq 5 [b] From intercept of eq 5. [c] From intercept of eq 6. [d] Weighted average of *b* and *c*. [e] From slope of eq 6, using k_3. [f] From eq 7. [g] From steady state data. [h] Weighted average of *e* and *f*, omit *g*.

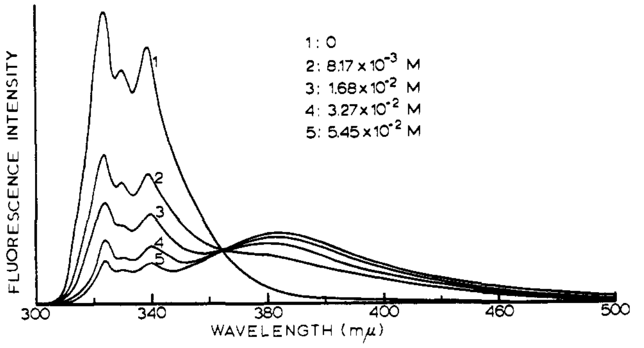

Figure 3. Arrhenius plots of k_3, k_4, k_p. Open circle values were taken from paper I.

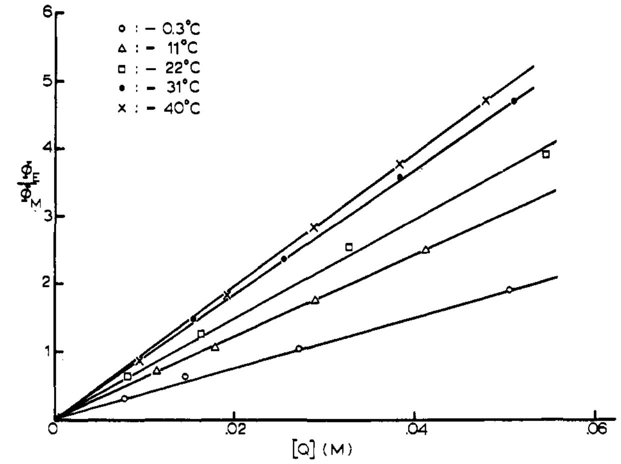

Figure 4. Arrhenius plot of k_3/k_4. The four high-temperature points were taken from paper I.

Deconvolution to obtain λ_1 and λ_2 was employed as indicated above. In all cases, excellent fits to the sum of two exponentials were obtained by the Marguardt least-squares procedure with typical χ^2 of 1.0 ± 0.2. This is illustrated in Figures 1 and 2.

The sum $(k_1 + k_2)$ was not broken down into individual rate contants. In Table I are listed the values for this sum. There is a slight decrease with temperature, probably due to the nonradiative component ($\phi_F \cong 0.21$ at 25 °C), but fluorescence quantum yield measurements as a function of temperature probably could not be made easily with sufficient precision to permit a definite statement on this point.[13]

The rate constant k_3 was always obtained from the least-squares slope of $(\lambda_1 + \lambda_2)$ vs. [Q]. Concentrations in all cases were corrected for solvent contraction with temperature. The resultant values of k_3 obtained are given in Table I. The decrease with temperature is consistent with a concomitant decrease in the diffusion coefficients of A* and Q with temperature. The magnitudes reported are as expected for a diffusion-controlled reaction and correspond quite well to what was predicted from extrapolation on the data in paper I.[2]

The sum $(k_4 + k_p)$ was obtained both from the intercept of $(\lambda_1 + \lambda_2)$ vs. [Q] and from eq 6. The values were averaged. Then eq 7 was used to obtain k_4 and k_p. Equation 6 also yielded k_4 and k_p. These two sources of k_4 and k_p were averaged to finally yield best values. The variation of $(k_4 + k_p)$ and the individual k_4 and k_p values along with the equations used are given in Table I.

From fluorescence decay measurements alone there is no satisfactory route to k_5 and k_6. However, these constants can be obtained by combining steady state and transient data using eq 9. The results are given in Table IV. A typical spectrum from which Φ_E/Φ_M was derived is shown in Figure 3. In Figure 4 are illustrated typical Φ_E/Φ_M vs. [Q] plots as a function of temperature.

As can be seen from Table I, at temperatures above about 0 °C, $k_4 > k_p$, but as the temperature is lowered $k_p > k_4$. At about 0 °C they happen to be equal. k_4 shows a much stronger temperature dependence than k_p and is thus responsible for the negative temperature coefficients observed for $d(\Phi_E/\Phi_M)/d[Q]$. If we went to low enough temperatures k_4 would become insignificant relative to k_p and the decay would no longer exhibit the characteristic two components of the excited state feedback process. Also, the increase in K_{SV} as the temperature is lowered is due to the rapid decrease in k_4, but once $k_4 \ll k_p$, K_{SV} decreases with decreasing temperature because K_{SV} is now proportional to k_3.

Clearly between 0 and −40 °C, the approximation $k_3/(k_4 + k_p) = k_3/k_p$ is a poor one, and thus plots of ln $(\Phi_E/\Phi_M[Q])$ as a function of $1/T$ are useless in this temperature range for determining $\Delta E_3^{\ddagger} - \Delta E_p^{\ddagger}$. Likewise, at temperatures above 0 °C, k_4 is not sufficiently greater than k_p for the approximation $k_3/(k_4 + k_p) = k_3/k_4$ to be valid and yield $\Delta H°$. In paper I it was correctly pointed out that this probably accounts for the higher $\Delta H°$ obtained by Ware, Watt, and Holmes as compared with that of Taylor.[1]

For example, if one takes k_3, k_4, and k_p from Table I and Tables III and IV of paper I and constructs an Arrhenius plot of $k_3/(k_4 + k_p)$ over the temperature range examined by Taylor,[1] one obtains a "ΔH" of −7.7 kcal whereas he reported

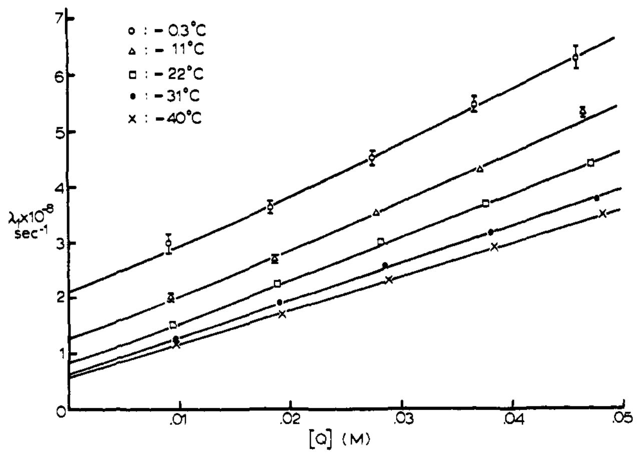

Figure 5. Corrected fluorescence spectra of α-cyanonaphthalene + dimethylcyclopentene-1,2 at −22 °C.

Table II. Comparison of Steady State and Lifetime Data for K_{SV}/τ_0

t, °C	$k_3k_p/(k_4 + k_p) \times 10^{-8}$,[a] $M^{-1}\,s^{-1}$	$(k_1 + k_2)K_{SV} \times 10^{-8}$,[b] $M^{-1}\,s^{-1}$	Discrepancy, %
−0.3	45.6 ± 3.9	46.9 ± 0.6	3
−11	53.9 ± 2.1	56.4 ± 0.7	4.6
−22	58.8 ± 1.6	61.5 ± 0.8	4.6
−31	55.9 ± 1.5	58.7 ± 0.5	5.0
−40	55.9 ± 1.8	55.8 ± 0.6	0.0

[a] From decay measurements. [b] Steady state K_{SV}.

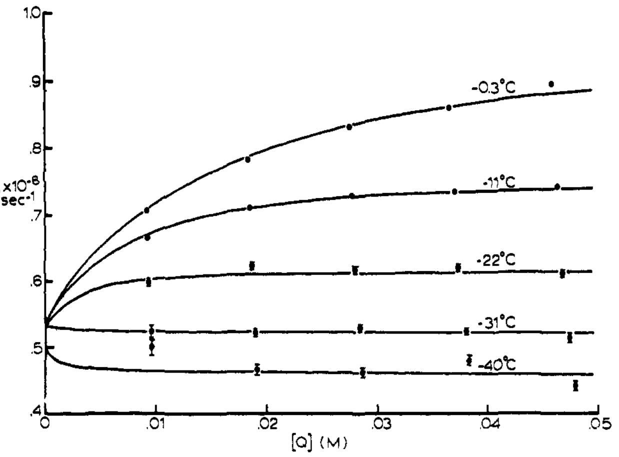

Figure 6. Exciplex-monomer fluorescence ratio vs. [dimethylcyclopentene-1,2].

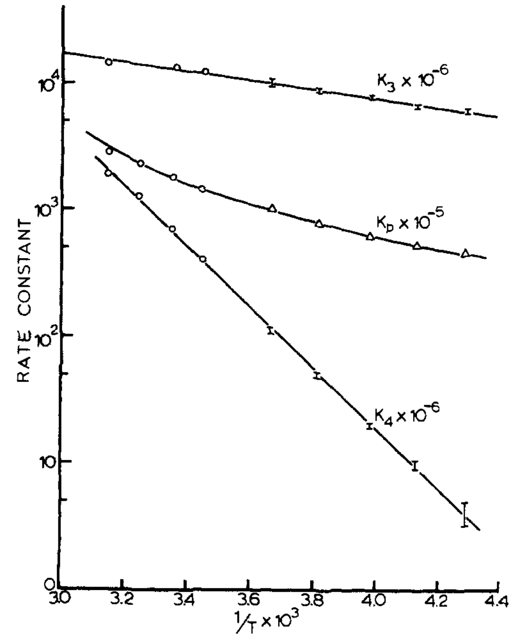

Figure 7. Comparison of experimental and calculated λ_1.

−6.7. The value from k_3/k_4 of approximately −9 kcal may be compared with these lower values. The measurements reported here thus point up the dangers in using ln $(\Phi_E/\Phi_M[Q])$ vs. $1/T$ for $\Delta H°$ and $\Delta E_3^{\ddagger} - \Delta E_p^{\ddagger}$ determinations without independent evidence for the validity of the intended approximation.[7,14,15]

Once k_1, k_2, k_3, k_4, and k_p had been determined at the five temperatures two tests of consistency were performed. (a) The rate constants were substituted into eq 3 and λ_1 and λ_2 calculated as $f[Q]$. The results are plotted in Figures 5 and 6. As can be seen the calculated lines describe quite well the dependence $\lambda_i([Q],T)$. (b) K_{SV} was calculated by substituting the rate constants into eq 8. The observed steady state value was about 4 to 5% greater than that calculated from the rate constants obtained by decay measurements (see Table II).

As has been discussed[7,12] in detail elsewhere, one expects $[(I_M^0/I_M) - 1](1/[Q])$ to exceed $k_3k_p/(k_4 + k_p)$ from transient measurements by about $(1 + R'/\sqrt{\tau_0 D})$ where $\tau_0^{-1} = k_1 + k_2$. R' is related to and nearly identical with the encounter radius, and D is the mutual diffusion coefficient. Reasonable values for R' and D (6 Å and 3×10^{-5} cm^2 s^{-1}) yield a 6 to 7% correction in the temperature range of 0 to −40 °C. This is of the order of the discrepancies shown in Table II, which average about 5%. On the basis of extensive studies[7,12] of the effect of a time-dependent k_3 on exciplex kinetics it is possible to say for a 20 ns $(1/(k_1 + k_2))$ that no serious distortions are expected for the monomer decay except on the very initial portion of the decay and on the rising edge of the exciplex curve. The k_3 obtained from $(\lambda_1 + \lambda_2)$ will be larger than the equilibrium value by only a few percent. However, the distortion of the rising side of the exciplex decay makes the short lifetime established from the analysis of the curve uncertain. A larger effect is anticipated in the steady state data and was observed as reported above.

Arrhenius plots were made (see Figure 7) for k_3, k_4, and k_p over the temperature range 45 to −40 °C. These plots utilize data both from this work and paper I. These plots illustrate the consistant nature of the results based on the rapid equilibrium approximation (paper I) at high temperature and the present measurements which establish the rate constants at low temperature with a much higher level of confidence. As can be seen from Figure 7, the values of k_3 all fit nicely on a straight line with $\Delta E^{\ddagger} = 1.6 \pm 0.1$ kcal. This is within 0.1 kcal of that expected for a diffusion-controlled reaction in hexane. The agreement is not quite as good for k_4 between the two sets, but still quite satisfactory. The low-temperature data give $\Delta E_4^{\ddagger} = 10.5$ kcal whereas in paper I 10.8 kcal was found.

In Figure 8 is plotted ln (k_3/k_4) vs. $1/T$. If all the points are used with equal weight, $\Delta H° = -9.3 \pm 0.1$ whereas just the low-temperature data yields -8.80 ± 0.3 kcal. In paper I, −9.0 kcal was reported. Again the agreement is gratifying.

From k_3/k_4 and $\Delta H°$ (assumed independent of temperature) one can calculate $\Delta G°$ and $\Delta S°$ for the excited state equilibrium. The results are given in Table III for the low-temperature work. The constancy of $\Delta S°$ is expected on the basis of any reasonable estimate of ΔC_p and the large negative value suggests a rather tight and rigid exciplex. Values of this magnitude have been obtained for excimers[11] and also recently for the anthracene-*N*,*N*-dimethylaniline exciplex.[7]

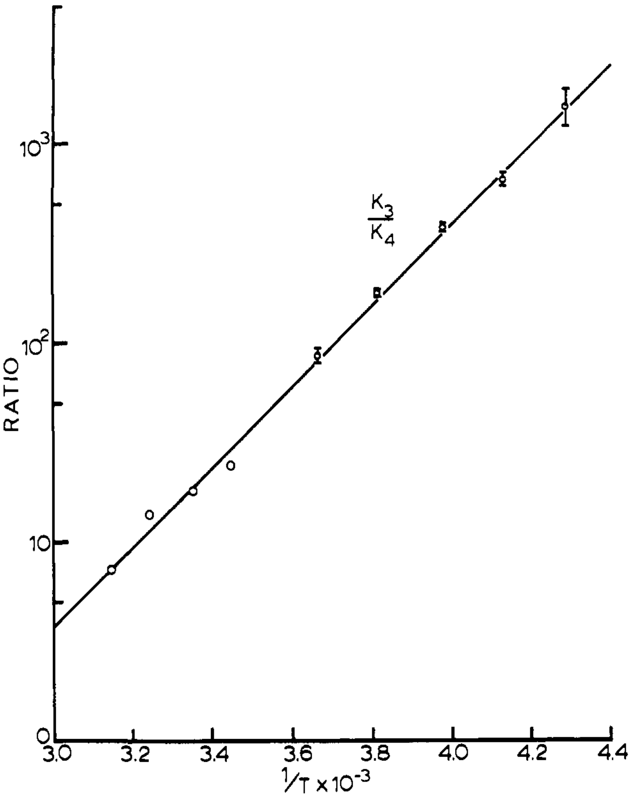

Figure 8. Comparison of experimental and calculated λ_2.

From k_4 and $\Delta E_4^{\ddagger}$, A_4 in $k_4 = A_4 \exp\{-\Delta E_4^{\ddagger}/RT\}$ can be calculated. When log A_4 and $\Delta E_4^{\ddagger}$ are plotted in Figure 9 of ref 7 it can be seen that the point falls near the line for the amine aromatic exciplexes. This may be indicative of similar charge transfer, a hypothesis consistent with the similar $\Delta H°$ value as compared say to anthracene-*N,N*-dimethylaniline or other amine aromatic exciplexes. The thermodynamic data are summarized in Tables III and V.

Over the temperature range of 45 to −40 °C, k_p exhibits a pronounced curvature in its Arrhenius plot. This curvature cannot be due to the simple sum of two functions derived from k_5 and k_6, i.e., $A_5 \exp(-\Delta E_5^{\ddagger}/RT) + A_6 \exp(-\Delta E_6^{\ddagger}/RT)$, because subtraction of k_5 as a function of temperature does not linearize ln k_p vs. $(1/T)$. It follows that k_6 is probably a composite of two or more nonradiative channels out of (AQ*). One of these could be

$$(AQ^*) \rightarrow (A^- \cdots Q^+) \rightarrow A + Q$$

where (A^-Q^+) is the ion pair. In addition, one can have internal conversion and intersystem crossing in (AQ)*, one or both of which might be temperature dependent.

It is of interest to compare the values of $\Delta H°$ and $(h\nu_E)_{\max}$ with those predicted by the correlations with oxidation and reduction potentials reported by Weller and co-workers.[16,17]

The central problem in such a comparison is to establish $\Delta E_{1/2} = E(A^-/A) - E(D^+/D)$, where $E(A^-/A)$ is the reduction potential of the acceptor (α-cyanonaphthalene) and $E(D^+/D)$ is the oxidation potential of the donor. $E(A^-/A)$ has recently been measured by Arnold and Maroulis[18] against Ag|Ag⁺ ($AgNO_3$ in acetonitrile) with the resultant value of −2.3 V (−2.0 vs. SCE) which agrees with −2.0 reported by Beens.[19]

The reduction potential of α-cyanonaphthalene is observable under approximately reversible conditions.[18] Unfortunately, this is not true for olefins in acetonitrile.[20] The best estimate one can make electrochemically for $E(D^+/D)$ for dimethylcyclopentene is approximately 2 V vs. SCE. This gave $\Delta E_{1/2}$ = 4.2 V. Because of the irreversible nature of the oxidation, only an extrathermodynamic value is measurable. It is doubtful that the oxidation potential is much lower than 1 V, and it may well be considerably higher. For example, for diphenyl-substituted ethylenes[18] approximately reversible oxidation potentials are in the range of 1.8 V. Nevertheless, a reversible potential for dimethylcyclopentene is not available and it is exceedingly dangerous to base conclusions on these irreversible potentials.

Table III. Thermodynamic Values for the Exciplex Equilibrium

	T, K				
	273	262	251	242	233
log (k_3/k_4)	1.94	2.25	2.58	2.82	3.18
$-\Delta G°$, kcal/mol	2.42	2.70	2.97	3.13	3.39
$-\Delta S°$, eu	23.3	23.2	23.1	23.3	23.1

Table IV. Values of k_5 and k_6 from Φ_E/Φ_M

t, °C	$\Phi_E/\Phi_M[Q]$	k_5/k_1	$k_5 \times 10^{-6}$,[a] s^{-1}	$k_6 \times 10^{-8}$, s^{-1}
−0.3	37.2 ± 1.1	0.80 ± 0.07	8.0 ± 0.1	0.90 ± 0.07
−11	60.9 ± 1.1	0.87 ± 0.07	8.6 ± 0.4	0.68 ± 0.04
−22	72.2 ± 2.2	0.77 ± 0.03	7.7 ± 0.3	0.55 ± 0.02
−31	92.1 ± 1.0	0.86 ± 0.02	8.6 ± 0.2	0.44 ± 0.01
−40	99.1 ± 1.2	0.82 ± 0.03	8.2 ± 0.3	0.38 ± 0.02

[a] Using $k_1 = 1 \times 10^7$ s^{-1} and assumed constant (see ref 13 and Table I of this paper). Φ_F taken[2] as 0.21 at 25 °C.

Table V. Activation and Thermodynamic Parameters

Property kcal/mol	This work	Reported in paper I	Combined data
$\Delta E_3^{\ddagger}$	1.60 ± 0.1		
$\Delta E_4^{\ddagger}$	10.5 ± 0.3	10.8	10.8 ± 0.1
$-\Delta H°$	8.8 ± 0.3	9.0	9.3 ± 0.1

Two points of view will be advanced. (a) Consider $E(D^+/D) \cong 2$ V (SCE). This is inconsistent with Weller's correlation[16] as can be seen from the following

$$(h\nu_E)_{\max} = E(A^-/A) - E(D^+/D) - 0.15 \text{ eV} \quad (10)$$

which gives $E(A^-/A) - E(D^+/D) = 3.4$ eV and which would require $E(D^+/D) \cong 1.2$ eV. Likewise, the correlation[16]

$$-\Delta H° = \Delta E_{0\text{-}0} - [E(A^-/A) - E(D^+/D)] - 0.15 \quad (11)$$

where $\Delta E_{0\text{-}0}$ is the $A \rightarrow A^*$ energy for α-cyanonaphthalene, fails for $E(A^-/A) - E(D^+/D) = 4.2$ V giving in fact a positive $\Delta H°$ whereas for a stable exciplex $\Delta H°$ is negative. (b) If one attempts to estimate $E(D^+/D)$ for dimethylcyclopentene from the correlation between $E(D^+/D)$ and ionization potential using[21,22] $E(D^+/D) = \text{IP} - 6.5$ eV, one finds that $E(D^+/D) \cong 1.3$. This is in fair agreement with what we expect from eq 10 or eq 11 (in the latter assuming $\Delta H°$ as the measured value and calculating $E(A^-/A) - E(D^+/D)$). Thus it seems dangerous to draw conclusions regarding the nature and structure of the exciplex from the success or failure to obtain correlations typical of strong CT-type exciplexes. One might be tempted to describe the aromatic-olefin exciplex more in terms of a mixed excimer[16] rather than a strong CT-type exciplex. Unfortunately, if such arguments are to be made by analogy, then one needs the true thermodynamic oxidation potential of the olefin in polar solvent which may be impossible to acquire experimentally.

Comparison of the shapes of λ_2 vs. [Q] plots at −0.3 and −11 °C shown in Figure 6 with plots of λ vs. [Q] in paper I suggests that the rapid equilibrium approximation might be valid here also. As noted above, plots of $(\lambda_2 - \lambda_0)^{-1}$ vs. $[Q]^{-1}$ were linear for both −0.3 and −11 °C. Since

$$(\lambda_2 - \lambda_0)^{-1} = (k_p - \lambda_0)^{-1} + [(k_3/k_4)(k_p - \lambda_0)]^{-1}[Q]^{-1} \quad (12)$$

k_p can be calculated from the intercept. Such an analysis yielded values of $k_p = 0.102$ ns^{-1} at −0.3 °C and 0.0779 ns^{-1} at −11 °C, in fair agreement with those obtained from direct analysis of the two-component monomer decay curves (Table I). However, for −0.3 °C, k_3/k_4 from eq 12 differed from that calculated from Table I by 50% and a 40% difference was found at −11 °C. These errors are well in excess of the errors predicted from the observed uncertainties in the slopes and intercept.

The reason for this can be seen from the following analysis. Plots were constructed for −0.3 and −11 °C of the rapid equilibrium equation

$$\lambda = \frac{\lambda_0 + (k_3 k_p/k_4)[Q]}{1 + (k_3/k_4)[Q]} \quad (13)$$

as well as λ_2 calculated from the full equation (eq 3). At 25 °C, values of λ_0, k_3, k_4, and k_p reported in paper I were used. The resultant plots are illustrated in Figure 9. Also included on these plots are actual data points obtained in this work (including a repeat of the 25 °C study). The following aspects are noteworthy. (a) The shapes of the two curves for 25 °C are almost identical over a large concentration range with only about a 2% shift. (b) For −0.3 and −11 °C, the two curves diverge significantly at low [Q]. The divergence is worse at −0.3 °C. Since slope-intercept analysis can be strongly influenced by terminal points, the low concentration divergence shown in Figure 9 is responsible for the failure to obtain agreement with regard to the value of k_3/k_4. At either higher or lower temperature the situation is expected to be much improved. Also, if one ignores the low concentration region for the −11 °C case, then k_p and k_3/k_4 from the rapid equilibrium analysis agree with those obtained from the two-component decay curve analysis to within the observed experimental error of slope and intercept. Thus care must be exercised in selecting the concentration range when using the rapid equilibrium approximation.

If judged by K_{SV}/τ_0, dimethylcyclopentene is an inefficient quencher of α-cyanonaphthalene. This study indicates that over the temperature range of about 85 °C, this inefficiency is due entirely to the feedback process and the rate of feedback relative to the other processes which remove the exciplex. It is not due to a slow forward reaction or increased "reflection" during the initial stages of the encounter. Whether or not this will remain the case when the solvent dielectric constant is increased remains an interesting question currently under study which will be the subject of a forthcoming paper in this series.

The photokinetic scheme used in paper I has been confirmed and the data from the two sets of experiments present a consistent picture, in spite of the large change in k_4 as one goes from 45 to −40 °C, a change which causes the system to behave in quite a different manner in the low- and high-temperature regions. There appears no need to use a more complex scheme to describe this exciplex system.

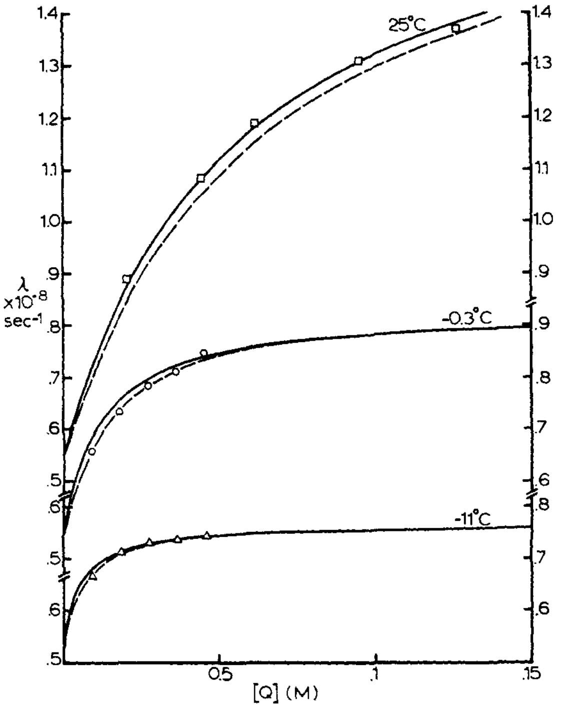

Figure 9. Plots of λ_2 vs. [Q] at three different temperatures: (- - -) calculated using eq 3; (—) calculated using eq 13.

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