

## Exciplex Photophysics. 6. Quenching of $\alpha$ -Cyanonaphthalene by 1,2-Dimethylcyclopentene in Slightly Polar Solvents<sup>†</sup>

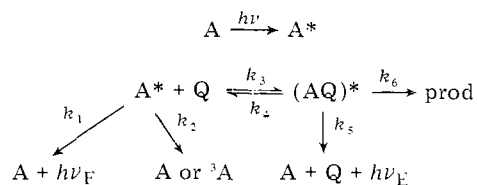
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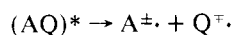
**Abstract:** The kinetic behavior of the exciplex formed between electronically excited  $\alpha$ -cyanonaphthalene and ground-state 1,2-dimethylcyclopentene in nonpolar and slightly polar solvents is reported. Analysis of two-component fluorescence decay curves indicates that in each solvent exciplex formation and decay in general follow the simple "excimer-type" mechanism. Rate constants associated with this type of mechanism were calculated. From their temperature dependence  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  for the exciplex equilibrium reaction in three solvents were determined. As solvent polarity increased  $\Delta S^\circ$  was found to become less negative while the exciplex binding energy remained constant. Trends in the values of the rate constants and thermodynamic properties are compared with other published data. Solvent participation in exciplex formation is invoked in order to account for the observed changes in the thermodynamic properties.

### Introduction

A stoichiometric complex that is associated in the excited state and dissociated in the ground state is referred to as an exciplex.<sup>1,2</sup> Both 1:1 and 1:2 intermolecular exciplexes exist,<sup>3-6</sup> as well as intramolecular exciplexes.<sup>7-13</sup> The photokinetics of intermolecular exciplex formation has now received considerable attention and in nonpolar solvents there is reason to believe that the following model gives an adequate representation of the pertinent reactions.<sup>4,14-17</sup>



Attempts to obtain all the rate constants and their temperature coefficients in nonpolar solvents have been few in number,<sup>15-19</sup> nor have there been many investigations of the effect of solvent polarity on exciplex photokinetics and the associated activation parameters.<sup>20,21</sup> In very polar solvents such as acetonitrile there is direct evidence<sup>22-24</sup> for the formation of radical ions, i.e.



If the solvent polarity is reduced below about  $\epsilon = 12$ , radical ion formation ceases to be an important exciplex degradation pathway.<sup>25</sup> However, in the range  $\epsilon = 2-12$ , there are conflicting reports as to the effect of solvent polarity on the exciplex binding energy<sup>18,20,21,26,27</sup> and there have been no detailed studies which involved the measurement of individual rate constants and their temperature coefficients. It is the purpose of this work to partially fill this gap.

Based on a limited number of observations and exploratory experiments it appeared to us that the critical range of solvent polarity was between 2 and 10; above about  $\epsilon = 10$  one observes only highly efficient quenching, whereas in hexane the regeneration of monomer gives rise to two-component decay and inefficient quenching. This polarity range therefore seemed particularly interesting for solvent effect studies.

The goals of the research as conceived were (a) to establish the quenching mechanism in several slightly polar solvents ( $\epsilon$

= 2-10); (b) to determine the rate parameters associated with this mechanism as a function of temperature for the various solvents; (c) to compare rate constants obtained for steady-state vs. transient measurements in those cases where this was possible. From these observations, we hoped to obtain the appropriate thermodynamic and activation parameters characterizing each step of the quenching mechanism and thus gain insight into how the solvent polarity alters the photophysical behavior.

The system selected for study was one that we had already extensively investigated in hexane:  $\alpha$ -cyanonaphthalene quenched by 1,2-dimethylcyclopentene. In hexane, this system has been studied<sup>16,18</sup> in the rapid equilibrium limit at high temperatures (10-60 °C) and in the low-temperature region (-40 to 0 °C) where two-component monomer decay and the growth and decay of the exciplex can both be seen and subjected to quantitative analysis for rate parameters. This paper reports studies of this system in diethyl ether (DEE), ethyl acetate (EtAc), tetrahydrofuran (THF), and acetonitrile.

### Experimental Section

Fluorescence lifetimes were determined by the single-photon technique.<sup>28-30</sup> A Jarrell-Ash monochromator was used between the sample and the photomultiplier and the exciting light was selected by a filter. For experiments in hexane and diethyl ether, the following combination was used: (1) a Corning 7-54 color glass filter; (2) 5-cm optical path length of NiSO<sub>4</sub>·6H<sub>2</sub>O in water (300 g/L); (3) 1-cm path length of 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate (Calbiochem, Cation X) in water (170 mg/L).<sup>31</sup> For experiments in ethyl acetate a Corning 7-54 filter plus a Corion 2900-Å interference filter (10% transmission, opaque below 270 nm and above 310 nm) were used. Exciplex emission was measured at 400 nm, whereas the monomer was observed at 325 nm, both with a bandwidth of 7 nm.

After a fairly extensive examination of deconvolution methods, it was concluded that for two-component monomer and exciplex decay curves, iterative deconvolution provides the most satisfactory method for recovery of the rate parameters. The statistic  $(\chi^2)_r$ , the reduced  $\chi^2$ ,<sup>32</sup> was used as a measure of success and decay parameters were accepted if  $0.8 \leq \chi_r^2 \leq 1.1$ .

Stern-Volmer constants and quantum yield ratios were calculated from fluorescence spectral data obtained by means of a standard spectrofluorimeter with a 90° viewing angle.

Spectra were corrected for the wavelength response of the detector before being used to calculate quantum yield ratios. Correction factors for the fluorimeter had been obtained<sup>33</sup> in the wavelength region below 400 nm with a tungsten lamp supplied by Eppley Laboratory<sup>34</sup> and in the region above 400 nm by comparison of a spectrum of quinine bisulfate, which has a well-known spectrum.<sup>35</sup>

<sup>†</sup> Publication No. 191 from the Photochemistry Unit, Chemistry Department, University of Western Ontario, London, Ontario, Canada N6A 5B7.

Absorption spectra, which were not used in quantitative calculations, were recorded on a Cary 118C spectrophotometer.

$\alpha$ -Cyanonaphthalene, 1,2-dimethylcyclopentene, and hexane were purified as reported previously.<sup>19</sup> All the solvents were spectral grade except diethyl ether, which was reagent grade. Ethyl acetate and dimethoxyethane were obtained from Fisher Scientific Co., diethyl ether from BDH Chemicals, and tetrahydrofuran from Caledon Laboratories Ltd. These solvents were refluxed over calcium hydride for 12 h in an atmosphere of dry nitrogen and then fractionally distilled; the middle fractions of the distillations were retained. Before ethyl acetate was refluxed it was washed with a 5% aqueous solution of sodium carbonate and with a saturated aqueous solution of sodium chloride. It was then stored for 12 h over anhydrous potassium carbonate, filtered, and then refluxed.<sup>36</sup> Diethyl ether and tetrahydrofuran were used within 48 h of distillation.

Absorption and fluorescence spectra of the solvents showed no indication of impurities. Solutions of the olefin alone in each of the solvents had no absorption peaks at wavelengths longer than the olefin cutoff. The same solutions, when irradiated with 275-nm light, showed no impurity fluorescence.

Samples were degassed by freeze-pump-thaw cycles in a grease-free, mercury-free vacuum line. Care was taken to minimize exposure to light. Cuvettes (1 cm square) were used and low temperatures were achieved in a cell block cooled by circulation of a liquid from a Neslab refrigerating unit. Temperatures were accurate to  $\pm 0.3\%$ .

## Results

The assumed photokinetics require that

$$[A^*](t) = a_1 e^{-\lambda_1 t} + a_2 e^{-\lambda_2 t} \quad (1)$$

$$[(AQ)^*](t) = a_3 (e^{-\lambda_1 t} - e^{-\lambda_2 t}) \quad (2)$$

where

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

and

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

Steady-state analysis yields (where  $\phi_M$  and  $\phi_E$  represent the quantum yields of monomer and exciplex, respectively)

$$\left( \frac{\phi_M^0}{\phi_M} - 1 \right) = \frac{k_3 k_p [Q]}{(k_4 + k_p)(k_1 + k_2)} \quad (5)$$

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

In the above equations, it has been assumed that  $k_3 \neq f(t)$ . Rate constants were determined as follows:  $k_1$  from the unquenched lifetime  $(\tau)_{Q=0} = (k_1 + k_2)^{-1}$  and the quantum yield  $\phi_M^0 = k_1/(k_1 + k_2)$ ;  $k_2$  from  $k_1$  and  $(\tau)_{Q=0}$ ;  $k_3$  from the slope of  $\lambda_1 + \lambda_2$  vs.  $[Q]$ , since  $\lambda_1 + \lambda_2 = k_1 + k_2 + k_3[Q] + k_4 + k_p$ ;  $k_4$  and  $k_p$  from a plot of  $\lambda_1 \lambda_2$  vs.  $[Q]$  since  $\lambda_1 \lambda_2 = (k_1 + k_2)(k_4 + k_p) + k_p k_3 [Q]$ .

One obtains  $k_4 + k_p$  from the intercept and  $k_p$  from the slope. Since  $k_3$  is known,  $k_4$  is calculated from  $k_4 + k_p$ . Problems can arise here if  $k_4 \ll k_p$ .

$k_5$  was obtained from eq 6;  $k_5$  is obtained by plotting  $\phi_E/\phi_M$  vs.  $[Q]$ . The slope gives

$$\frac{k_5}{k_1} \frac{k_3}{k_4 + k_p}$$

from which  $k_5$  is calculated since all other constants are known.

Since  $k_p = k_5 + k_6$ , and  $k_5$  is known, one can calculate  $k_6$ . Again problems arise if  $k_p \approx k_5$ .

In another publication,<sup>17</sup> other methods are discussed for evaluating some of the rate constants in the exciplex photokinetic scheme, but they offer no real advantage over the direct approach outlined above.

Once the constants  $(k_1 + k_2)$ ,  $k_3$ ,  $k_4$ , and  $k_p$  have been determined, one can calculate the Stern-Volmer constant  $K_{SV}$

$$K_{SV} = \left[ \frac{I_m^0}{I_m} - 1 \right] \frac{1}{[Q]} = \frac{k_3 k_p}{(k_1 + k_2)(k_4 + k_p)} \quad (7)$$

and compare with values derived from steady-state measurements. Discrepancies are interpreted in terms of failure of the assumption that  $k_3 \neq f(t)$ <sup>37</sup> as discussed below.

In each solvent the rate constants were determined as a function of temperature. When linear  $\ln k_i$  vs.  $1/T$  plots are obtained, one can calculate the parameters in the equation

$$k_i = A_i e^{-\Delta E^*/RT} \quad (8)$$

From the temperature coefficient of the ratio of  $k_3/k_4$ , we obtain  $\Delta H^\circ$ , the enthalpy of the excited-state equilibrium, and from  $A_3$  and  $A_4$  we obtain the entropies of activation of the forward and reverse reactions in the excited-state equilibrium. Finally, from conservation of energy, we have

$$h\nu(A \rightarrow A^*) = \Delta H^\circ + (h\nu_E)_{\max} + E_R \quad (9)$$

where  $(h\nu_E)_{\max}$  is the maximum in the exciplex emission and  $E_R$  is the repulsive potential energy in the Franck-Condon ground state at the equilibrium separation of A and Q in the exciplex.

It is emphasized that the rate constants  $k_3$ ,  $k_4$ , and  $k_p$  are obtained without recourse to steady-state data. It is only when one calculates  $k_1$ ,  $k_2$ ,  $k_5$ , and  $k_6$  that it is necessary to use  $\phi_M^0$  and  $\phi_E/\phi_M$ , the latter ideally as a function of  $[Q]$ .

Likewise, one obtains  $\Delta H^\circ$  without recourse to the arguments of Stevens and Ban,<sup>38</sup> i.e.

$$\text{if } k_4 \gg k_p$$

$$\frac{\phi_E}{\phi_M} = \frac{k_3}{k_4} [Q]$$

If this is true, then of course we obtain  $\Delta H^\circ$  from  $\ln [\phi_E/(\phi_M[Q])]$  vs.  $1/T$ , but as Selinger and McDonald<sup>39</sup> point out, there are many cases where it is not clear that this is a valid approximation. One obviously needs individual rate parameters to establish  $\Delta H^\circ$  with certainty, unless one can measure over so wide a temperature range that one sees the undistorted limiting behavior for  $k_4 \gg k_p$ . Significant distortions are hard to distinguish from the slight nonlinearity in such plots. Finally, it is emphasized that  $K_{SV}$  is a function of  $k_3$ ,  $k_4$ ,  $k_5$ , and  $k_6$  as well as  $(\tau)_{Q=0}$ . Changes in  $K_{SV}$  are clearly almost impossible to interpret unless one has values for the individual rate constants, since all are potentially functions of both temperature and solvent.

Rate constants and activation parameters for the system  $\alpha$ -cyanonaphthalene-1,2-dimethylcyclopentene in hexane have already been published.<sup>16,19</sup> In Tables I and II are presented the values of  $k_0 (=k_1 + k_2)$ ,  $k_3$ ,  $k_4 + k_p$ ,  $k_4$ , and  $k_p$  for the solvents diethyl ether (DEE) and ethyl acetate (EtAc). At temperatures lower than the lowest temperature quoted, the reverse reaction was too slow and it was not possible to obtain good two-component decays, whereas at temperatures above the highest listed, there was danger of cells breaking because of excessive pressure. In Table III are presented the values of  $k_1$  and  $k_5$  for all three solvents. These were observed to be independent of temperature within experimental error. In Table IV are listed for DEE and EtAc values of  $k_p$  and  $k_6$  as a function of temperature. Table V lists the observed lifetime of  $\alpha$ -cyanonaphthalene in various solvents from hexane to acetonitrile. In Figure 1 are presented Arrhenius plots of  $k_3$  and  $k_p$  for EtAc and DEE. These may be compared with Figure 7 of ref 19, which gives the equivalent plots for hexane. Figure 2 gives the temperature dependence of  $k_4$  for all three solvents. In Tables VI and VII are summarized the thermodynamic parameters derived from such plots for all three sol-

**Table I.** Rate Constants in DEE

$t, ^\circ\text{C}$	$k_0 \times 10^{-8}, \text{s}^{-1}$	$k_3 \times 10^{-8}, \text{M}^{-1} \text{s}^{-1}$	$(k_4 + k_p) \times 10^{-8}, \text{s}^{-1}$	$k_4 \times 10^{-8}, \text{s}^{-1}$	$k_p \times 10^{-8}, \text{s}^{-1}$
30	0.663 $\pm$ 0.001	122.8 $\pm$ 1.6	1.339 $\pm$ 0.031	0.548 $\pm$ 0.011	0.791 $\pm$ 0.002
20	0.673 $\pm$ 0.001	120.7 $\pm$ 1.0	0.876 $\pm$ 0.020	0.248 $\pm$ 0.007	0.648 $\pm$ 0.002
10	0.674 $\pm$ 0.001	108.0 $\pm$ 0.54	0.706 $\pm$ 0.010	0.168 $\pm$ 0.005	0.538 $\pm$ 0.002
0	0.681 $\pm$ 0.001	92.9 $\pm$ 0.51	0.493 $\pm$ 0.021	0.054 $\pm$ 0.005	0.439 $\pm$ 0.003

**Table II.** Rate Constants in EtAc

$t, ^\circ\text{C}$	$k_0 \times 10^{-8}, \text{s}^{-1}$	$k_3 \times 10^{-8}, \text{M}^{-1} \text{s}^{-1}$	$(k_4 + k_p) \times 10^{-8}, \text{s}^{-1}$	$k_4 \times 10^{-8}, \text{s}^{-1}$	$k_p \times 10^{-8}, \text{s}^{-1}$
50.7	0.826 $\pm$ 0.001	127.0 $\pm$ 2.3	0.944 $\pm$ 0.043	0.182 $\pm$ 0.052	0.762 $\pm$ 0.030
59.4	0.822 $\pm$ 0.002	135.4 $\pm$ 4.1	1.325 $\pm$ 0.067	0.432 $\pm$ 0.081	0.893 $\pm$ 0.045
69.7	0.820 $\pm$ 0.002	142.0 $\pm$ 6.3	1.653 $\pm$ 0.107	0.497 $\pm$ 0.120	1.156 $\pm$ 0.073
80.5	0.813 $\pm$ 0.002	157.7 $\pm$ 8.4	2.081 $\pm$ 0.177	0.724 $\pm$ 0.203	1.357 $\pm$ 0.100

**Table III.** Values of  $k_1$ ,  $k_2$ , and  $k_5$ 

solvent	$k_1 \times 10^{-7}, \text{s}^{-1}$	$k_2 \times 10^{-7}, \text{s}^{-1}$	$k_5 \times 10^{-7}, \text{s}^{-1}$
hexane	1.0	4.5	0.8
DEE	1.3	5.4	0.6
EtAc	1.9	6.6	0.5

**Table IV**

solvent	temp, $^\circ$	$k_p \times 10^{-8}, \text{s}^{-1}$	$k_6 \times 10^{-7}, \text{s}^{-1}$
DEE	0	0.44	3.8
	10	0.54	4.8
	20	0.65	5.9
	30	0.79	7.3
EtAc	50.7	0.76	7.1
	59.4	0.89	8.4
	69.7	1.16	11.1
	80.5	1.36	13.1

**Table V.** Lifetime Data for CNN in Various Solvents at 25  $^\circ\text{C}$ 

solvent	$\epsilon$	$\tau_0, \text{ns}$	$k_0 \times 10^{-7}, \text{s}^{-1}$	$k_1 \times 10^{-7}, \text{s}^{-1}$	$k_2 \times 10^{-7}, \text{s}^{-1}$
hexane	1.9	18.3	5.46	1.0	4.5
DEE	4.3	15.0	6.67	1.3	5.4
EtAc	6.0	11.8	8.48	1.9	6.6
DME	6.8	10.3	9.71		
THF	7.6	9.8	10.2		
CH <sub>3</sub> CN	37.5	9.0	11.1		

vents for the excited-state equilibrium as well as the activation parameters  $\Delta S^\ddagger$ ,  $\Delta G^\ddagger$ , and  $\Delta E^\ddagger$ .

Finally in Table VIII are compared the values of  $K_{SV}/(\tau)_{Q=0} = k_q$  and the equivalent quantity calculated entirely from transient data. Two values are listed for  $\Delta E^\ddagger_p$  in hexane representing the temperature dependence of  $k_p$  in (1) the low-temperature region and (2) the high-temperature region (see Figure 7 of ref 19).

## Discussion

From the observations reported above, coupled with the earlier study in hexane, it would appear that the simple exciplex kinetic model is obeyed over the concentration range employed in this study. (DEE,  $[Q]_{\text{max}} = 4.7 \times 10^{-2} \text{ M}$ ; EtAc,  $[Q]_{\text{max}} = 4.0 \times 10^{-2} \text{ M}$ .)

We have observed nothing that would suggest a different view. Back calculations of  $\lambda_1$  and  $\lambda_2$  as a function of  $[Q]$  and  $T$  from the measured rate constants reproduce the original observations. As will be discussed below, steady-state and transient measurements agree to within the error introduced by the time dependence of  $k_3$ . Thus, in what follows, it will be

assumed that the kinetic scheme is correct and the discussion will center on the individual rate constants.

**Fluorescence Lifetime,  $\tau_0$ , of CNN.** From ref 19 and Tables I and II, it can be seen that changes in temperature have little effect on the deactivation rate processes of excited CNN. However, increased solvent polarity produces a marked decrease in the lifetime. Lifetimes measured in six solvents are presented in Table V together with the values of  $k_1$  and  $k_2$  calculated from relative quantum yield determinations in hexane, DEE, and EtAc. It can be seen from Table V that the rates of both the radiative and nonradiative decay processes increase with increasing solvent polarity, a trend previously observed for CNN in cyclohexane, toluene, and methanol.<sup>40</sup>

It is not known with any degree of certainty by which non-radiative channels  $S_1$  of CNN decays. A quantum yield of triplet formation,  $\phi_T$ , for CNN in benzene of 0.17 has been reported,<sup>41,42</sup> which indicates, when combined with the fluorescence quantum yield,  $\phi_F$ , of about 0.25, a high probability for internal conversion. This  $\phi_T$  may be too low.<sup>42,43</sup> In fact, most of the  $\alpha$ -substituted naphthalenes for which data are available have  $\phi_F + \phi_T = 1$ .<sup>43,44</sup>

The first two excited singlet states of CNN,  $^1L_b(B^-_{3u})$  and  $^1L_a(B^+_{2u})$ , have solvent-independent absorption maxima at 31 150 and 34 130  $\text{cm}^{-1}$ , respectively. Owing to the small energy gap between  $S_1$  and  $S_2$ , strong vibronic coupling probably occurs between these two states;<sup>45</sup> the spectral changes that accompany changing solvent polarity indicate that the nature and extent of this coupling are affected by interaction of excited CNN with the surrounding solvent molecules. Suzuki et al.<sup>46</sup> have calculated that the wave function of the  $^1L_a$  state,  $S_2$ , has an 11% contribution from a charge-transfer "ring to cyano group" reference state. It is therefore not surprising that perturbations by polar solvent molecules influence the radiative and nonradiative transition probabilities.

**Exciplex Formation Reaction.** From the observed values of  $k_3$  it is inferred that the rate of the exciplex formation reaction in the three solvents used is diffusion controlled. Further support for this inference is provided by the calculated activation energies,  $\Delta E^\ddagger_3$ , which compare favorably with the temperature coefficients for viscous flow.

Neglect of the transient effects associated with diffusion-controlled reactions can lead to serious misinterpretation of the exciplex equilibrium data. Because  $\tau_0$  of CNN is greater than 10 ns in the three solvents used in this study and because the temperature ranges employed were such that solvent viscosity was always low ( $\eta = 0.213\text{--}0.656 \text{ cP}$ ), complications due to the transient effect were considered to be small. Steady-state measurements, which are more significantly distorted by the transient effect, were used quantitatively only in the calculation of  $k_5$ .

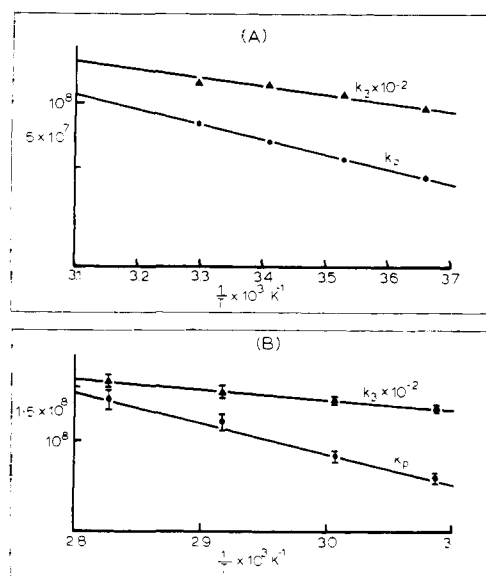


Figure 1. Arrhenius plots of  $k_3$  and  $k_p$ , CNN + DMCP in DEE (A) and EtAc (B).

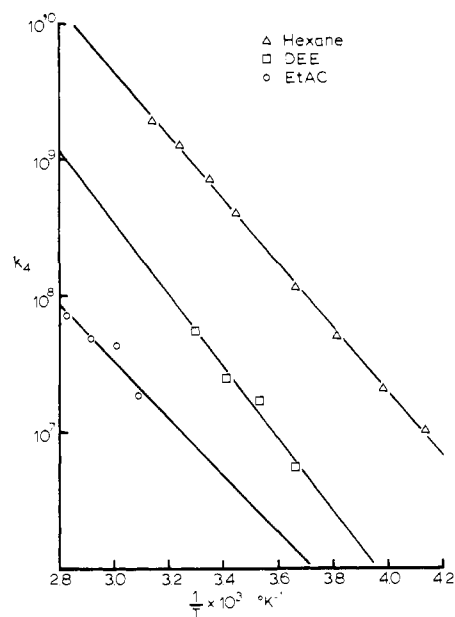


Figure 2. Arrhenius plots of  $k_4$ , CNN + DMCP in three solvents.

Table VI. Activation and Thermodynamic Data in Three Solvents

solvent	$\epsilon$	$\Delta E^\ddagger_3$ , kcal mol <sup>-1</sup>	$\Delta E^\ddagger_4$ , kcal mol <sup>-1</sup>	$\Delta E^\ddagger_p$ , kcal mol <sup>-1</sup>	$-\Delta H^\circ$ , kcal mol <sup>-1</sup>	$-\Delta S^\circ$ , cal deg <sup>-1</sup> mol <sup>-1</sup>
hexane	1.9	1.6 ± 0.06	10.5 ± 0.3	(1) 2.3 ± 0.2 (2) 8.5 ± 0.8	8.9 ± 0.5	23.2
DEE	4.3	1.8 ± 0.06	10.7 ± 0.2	3.3 ± 0.03	8.9 ± 0.5	18.3
EtAc	6.0	1.5 ± 0.3	9.0 ± 2.8	4.6 ± 0.6	7.5 ± 3.0	15.2

Table VII. Activation Entropies and Free Energies in Three Solvents

	hexane					DEE					EtAc			
	-40 <sup>a</sup>	-31	-22	-11	0	0	10	20	30	51	59.5	70	80.5	
$-\Delta S^\ddagger_3$ , cal deg <sup>-1</sup> mol <sup>-1</sup>	8.0	8.1	8.1	8.3	8.4	8.1	8.2	8.2	8.4	9.8	9.9	10.0	10.0	
$-\Delta G^\ddagger_3$ , kcal mol <sup>-1</sup>	3.1	3.2	3.2	3.4	3.5	3.5	3.6	3.6	3.7	4.0	4.1	4.2	4.3	
$\Delta S^\ddagger_4$ , cal deg <sup>-1</sup> mol <sup>-1</sup>	15.2	15.3	15.1	15.0	15.0	9.6	10.5	9.9	10.2	0.3	1.3	0.7	0.6	
$\Delta G^\ddagger_4$ , kcal mol <sup>-1</sup>	6.5	6.3	6.2	6.0	5.9	7.5	7.2	7.2	7.0	8.3	7.9	8.1	8.1	

<sup>a</sup>  $t$ , °C.

Table VIII. Comparison of Steady-State and Lifetime Data in DEE and EtAc

solvent	$t$ , °C	$k_1 \times 10^{-8}$ , <sup>a</sup> M <sup>-1</sup> s <sup>-1</sup>	$k_3 k_p / (k_4 + k_p) \times 10^{-8}$ , <sup>b</sup> M <sup>-1</sup> s <sup>-1</sup>
DEE	0	89.3	82.8
	10	89.2	82.3
	20	89.1	87.3
	30	81.0	72.6
EtAc	51	112.8	102.5
	60	115.9	93.0
	70	110.1	99.3
	80	109.4	102.1

<sup>a</sup> From steady-state measurements. <sup>b</sup> From transient data.

$k_3(t)$  varies rapidly only at times shortly after the excitation; therefore, errors resulting from a disregard of the time-dependent rate constant can be made negligible if the monomer decay curve is fit with the postulated exponential decay function only over some selected long-time region. In the present study this region was chosen to begin at 1.6 ns past the maximum of decay curves for hexane and DEE solutions and at 2.5

ns past the maximum of EtAc solution decay curves; the longer time in EtAc was chosen to compensate for the reduced lifetime of CNN in that solvent. Such a fitting procedure is facilitated by the least-squares deconvolution technique. If the time dependence in  $k_3$  is ignored, deconvolution may yield an erroneously small value of  $\tau_1$ .

Hui and Ware<sup>37</sup> have calculated the time dependence in  $k_3(t)$  for a representative number of exciplex systems. They concluded that, for the CNN-DMCP system, although  $k_3(t)$  is still changing after some hundreds of nanoseconds, the time dependence is extremely small after 1 or 2 ns. The value of  $k_3$  recovered from decay curves analyzed by the foregoing method is only a few percent greater than the steady-state value. They also found that, if  $k_3(t)$  has reached 90% of its limiting value before the time at which analysis of the decay curve begins, calculation of  $k_4$  and  $k_p$  will not be significantly affected; furthermore, errors introduced into the values of thermodynamic properties, which are calculated by means of logarithms of rate constants, are negligible. Their calculations also indicate insignificant errors in  $k_5$  calculated from transient and steady-state data.

**Excited-State Equilibrium.** The kinetics of the CNN-

**Table IX.** Estimates of  $\Delta G^\ddagger_{\text{el}}$ ,  $\Delta S^\ddagger_{\text{el}}$ , and  $\Delta E^\ddagger_{\text{el}}$  for the Reverse Exciplex Equilibrium Reaction

solvent	$(\partial \ln \epsilon / \partial T)_p$ , deg <sup>-1</sup>	$\Delta G^\ddagger_{\text{el}}$ , kcal mol <sup>-1</sup>	$\Delta S^\ddagger_{\text{el}}$ , cal deg <sup>-1</sup> mol <sup>-1</sup>	$\Delta E^\ddagger_{\text{el}}$ , kcal mol <sup>-1</sup>
hexane	0.000 714	3.1	1.9	2.9
DEE	0.0050	3.9	7.0	6.1
EtAc	0.0036	4.3	4.0	5.7

DMCP system in the studied range of solvent polarity are governed by the rate at which the exciplex dissociates into its precursors A\* and Q. The data in ref 19 and Tables I and II illustrate this point; when the solvent is changed from hexane to EtAc,  $k_4$ , the rate constant for the dissociation reaction, changes by about two orders of magnitude, a change that accounts almost entirely for the different experimental observations in the different solvents.

Previously reported variations in  $k_4$  with increasing solvent polarity<sup>26,47</sup> are consistent with the trend illustrated in Figure 2 for the CNN-DMCP system; that is, the rate of the reverse reaction decreases with increasing dielectric constant. A decrease as dramatic as that observed in the present study has been reported for the perylene-*N,N*-diethylaniline (DEA) system.<sup>26</sup> More moderate decreases have been observed in the anthracene-DEA<sup>26</sup> and pyrene-tributylamine<sup>47</sup> systems, whereas only a slight decrease occurs in the pyrene-DEA system.<sup>47</sup>

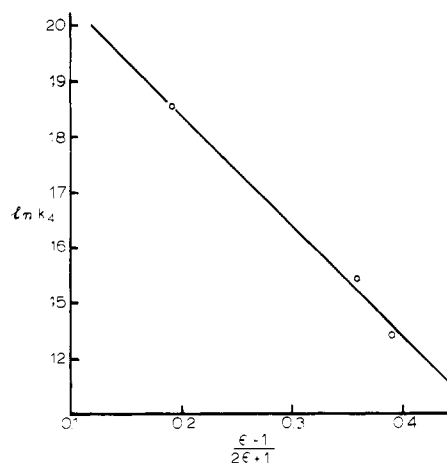
The present results demonstrate that, in the CNN-DMCP system over the studied range of solvent polarity, the decrease in  $k_4$  results not from an increased activation energy, but from a decreased preexponential factor,  $A$ , in the equation

$$k_4 = A_4 \exp\{-\Delta E^\ddagger_4/RT\} \quad (10)$$

It can be seen from Table VII that, whereas the entropy of activation of the forward reaction changes by at most only 2 eu on changing the solvent from hexane to EtAc,  $\Delta S^\ddagger_4$  for the reverse reaction decreases markedly; this decrease gives rise to the increasingly less negative values for the entropy of formation,  $\Delta S^\circ$ .

Contributing to  $\Delta S^\ddagger_4$  are factors that reflect the difference in solvent orientation about the polar complex and the less polar transition state; similarly, the difference in solvent orientation about the complex and the separated partners, A\* and Q, contributes to  $\Delta S^\circ$ . If changes in solvation effects are the major factors in the changes in  $\Delta S^\ddagger_4$  and  $\Delta S^\circ$ , the close correlation between the two, evident in the data in Tables VI and VII, may mean that the transition state is not very polar. It is expected that the molecules of the more polar solvents will be more rigidly ordered about the dipolar complex. But it is also probable that solvent organization in the absence of solutes is greater in media of higher dielectric constant. The CNN fluorescence spectra in DEE and EtAc, when compared with the spectrum in hexane, indicate an increasing amount of solvent perturbation of the CNN\*, and hence, perhaps, a more highly organized solvation shell about the uncomplexed A\* molecules.

In fact the changes observed in  $\Delta S^\ddagger_4$  and  $\Delta S^\circ$  for the CNN-DMCP system are in qualitative agreement with conventional ideas on solvation effects. For example, in ground-state reactions in which neutral molecules react to form ions, the greatest entropy decrease in the formation of the transition state is observed in the least polar solvents.<sup>48</sup> In addition, in acid dissociation reactions, which are in some respects similar to the excited-state exciplex formation reaction,  $\Delta S^\circ$  becomes much less negative in more polar solvents, whereas  $\Delta H^\circ$  decreases only slightly.<sup>49</sup> Conversely, when charge is destroyed in the transition state, as it is in the reverse exciplex equilibrium reaction, a smaller entropy increase is expected to occur in

**Figure 3.** Least-squares plot of  $\ln k_4$  vs.  $(\epsilon - 1)/(2\epsilon + 1)$ .

more polar solvents, i.e.,  $\Delta S^\ddagger$ , which is positive, becomes smaller.<sup>50</sup>

Polar solvents, even in the absence of ionic solutes, tend to be oriented. In nonpolar solvents this tendency is much smaller; therefore, the nonpolar solvents suffer the greatest increase in orientation when influenced by a polar solute.<sup>48</sup>

Although classical electrostatic theories cannot fully explain the observed solvent-dependent behavior of the system, they do provide a basis for a qualitative understanding of the observed enthalpy and entropy changes. Hence, the Born treatment of the solvent as a continuous dielectric medium<sup>51</sup> may be applied in the present instance in support of the arguments stated in the preceding paragraphs. When the polar exciplex, of dipole moment  $\mu_c$ , reverts to a less polar transition state, of dipole moment  $\mu_\ddagger$ , in a medium of dielectric constant  $\epsilon$ , the electrostatically induced free energy change,  $\Delta G^\ddagger_{\text{el}}$ , is given by<sup>52</sup>

$$\Delta G^\ddagger_{\text{el}} = \left( \frac{\mu_c^2}{r_c^3} - \frac{\mu_\ddagger^2}{r_\ddagger^3} \right) \left( \frac{\epsilon - 1}{2\epsilon + 1} \right) = f(\mu) \frac{\epsilon - 1}{2\epsilon + 1} \quad (11)$$

in which  $r$  is the radius of the molecule in which the dipole is embedded. Hence,

$$\Delta S^\ddagger_{\text{el}} = -f(\mu) \frac{3\epsilon}{(2\epsilon + 1)^2} \left( \frac{\partial \ln \epsilon}{\partial T} \right)_p \quad (12)$$

$\Delta E^\ddagger_{\text{el}}$  can then be calculated with the equations

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (13)$$

$$\Delta H^\ddagger = \Delta E^\ddagger - RT \quad (14)$$

Although  $\mu_\ddagger$  and  $r_\ddagger$  are not known,  $f(\mu)$  may be estimated by means of the equation<sup>52</sup>

$$\ln k_4 = \ln k_0 - \frac{1}{RT} f(\mu) \left( \frac{\epsilon - 1}{2\epsilon + 1} \right) \quad (15)$$

$k_0$  is the rate constant in a medium of unit dielectric constant. A plot of  $\ln k_4$  vs.  $(\epsilon - 1)/(2\epsilon + 1)$  has a slope from which  $f(\mu)$  can be calculated.<sup>53</sup> This plot, in which were used  $k_4$  values at 0 °C (that for EtAc was extrapolated from the high-temperature data), is shown in Figure 3. From the slope,  $f(\mu)$  is calculated to be 10.9 kcal mol<sup>-1</sup>, which, when used in eq 11 and 12 together with literature values of  $(\partial \ln \epsilon / \partial T)_p$ ,<sup>52,54,55</sup> yields the values of  $\Delta S^\ddagger_{\text{el}}$  and  $\Delta G^\ddagger_{\text{el}}$  listed in Table IX.  $\Delta E^\ddagger_{\text{el}}$  was calculated with eq 13 and 14. It can be seen that this approach predicts an increase in  $\Delta S^\ddagger_4$  when hexane is replaced by DEE and a decrease when EtAc replaces DEE. The observed results are consistent with the latter change but disagree with the prediction of an increase in going from hexane to DEE. Similarly, the observed changes in  $\Delta E^\ddagger_4$  are consistent with the predictions of the electrostatic theory in the higher solvent

**Table X.** Estimates of  $\Delta G_{el}^\ddagger$ ,  $\Delta S_{el}^\ddagger$ , and  $\Delta E_{el}^\ddagger$ <sup>a</sup>

solvent	$\Delta G_{el}^\ddagger$ , kcal mol <sup>-1</sup>	$\Delta S_{el}^\ddagger$ , cal deg <sup>-1</sup> mol <sup>-1</sup>	$\Delta E_{el}^\ddagger$ , kcal mol <sup>-1</sup>
DEE	6.2	11.0	9.5
EtAc	6.8	6.0	8.8

<sup>a</sup> Data for hexane not included in calculations.

polarity range but not in the lower range. Pearson<sup>52</sup> has observed a similar discrepancy between the results of his calculations and experimental observations in nonpolar solvents; this discrepancy he attributes to a failure of the theory to account for the orientation of the nonpolar solvent molecules in the neighborhood of the dipole. He points out that only the change in density, which is not related to the susceptibility to orientation, influences the temperature coefficient of the dielectric constant in nonpolar media, whereas increased temperature actually reduces the alignment of the polar solvent molecules in the electric field. Therefore, the entropy of activation expression, eq 12, will fail when applied to nonpolar solvents. Bell has shown<sup>56</sup> that eq 11 may also be invalid in media of low dielectric constant.

It appears, therefore, that application of the classical electrostatic model combined with the use of bulk dielectric constants is unsuitable for nonpolar solvents such as hexane; moreover, it gives only a rough indication of solvent effects in polar media.<sup>53</sup> If the treatment using eq 11 and 12 is restricted to the data for DEE and EtAc, the calculated activation values presented in Table X may give a more accurate estimate of the effect of increasing solvent polarity. Although the values in Table X must be regarded as highly approximate, they do indicate that electrostatic effects tend to produce a much larger fractional decrease in  $\Delta S_{el}^\ddagger$  than in  $\Delta E_{el}^\ddagger$  as the solvent polarity increases. Because  $\Delta E_{el}^\ddagger$  appears to depend only on viscosity, it is reasonable to assume that charge separation occurs in the transition state only to a very small extent. The change in  $\Delta S_{el}^\ddagger$  for the equilibrium may therefore be attributed to the "freezing" of the solvent molecules round the complex; the reduction in disorder produced by this process is greater in nonpolar solvents than it is in polar solvents.

Exciplex binding energies have been measured as a function of solvent polarity in only a few systems; the small number of reported trends fit no consistent pattern. Knibbe<sup>26</sup> attributed the increase in  $\Delta H^\circ$  of the 1,2-benzanthracene-DEA exciplex from 8.7 kcal mol<sup>-1</sup> in paraffin ( $\epsilon \sim 2$ ) to 9.7 kcal mol<sup>-1</sup> in toluene ( $\epsilon = 2.4$ ) to a stabilization of the dipolar complex by the more polar solvent. A similar increase in  $\Delta H^\circ$  was reported by Murata et al.;<sup>21</sup> for the naphthyl ethyl ether-dimethyl phthalate exciplex they found a  $\Delta H^\circ$  of 5.3 kcal mol<sup>-1</sup> in benzene ( $\epsilon = 2.3$ ) and 6.9 kcal mol<sup>-1</sup> in EtAc. In contrast, Okada et al.,<sup>20</sup> in their studies of the pyrene-DMA system, calculated that the binding energy decreased from 6.9 kcal mol<sup>-1</sup> in hexane to 2.3 kcal mol<sup>-1</sup> in pyridine ( $\epsilon = 12.3$ ), with  $\Delta H^\circ = -3.9$  kcal mol<sup>-1</sup> in THF ( $\epsilon = 7.4$ ). Moreover, the reported binding energies for the anthracene-DNA exciplex<sup>27</sup> in hexane and toluene are 7.18 and 6.46 kcal mol<sup>-1</sup>, respectively. On the other hand, values of  $\Delta H^\circ$  for the anthracene-DEA exciplex in methylcyclohexane ( $\epsilon = 2.0$ )<sup>26</sup> and in benzene<sup>18</sup> are approximately equal. The present results for the CNN-DMCP system, listed in Table VI, show that, within the experimental errors,  $\Delta H^\circ$  does not change in the dielectric constant range from  $\epsilon = 1.9$  to  $\epsilon = 6.4$ .

There are a number of reasons for doubting whether the values of  $\Delta H^\circ$  reported by Okada et al.<sup>20</sup> and by Murata et al.<sup>21</sup> are valid. First, Stevens-Ban plots<sup>38</sup> were used to calculate  $\Delta H^\circ$ . Such plots frequently yield inaccurate results,<sup>17</sup> particularly when used with the results of measurements in polar solvents, in which  $k_4$  is small. McDonald and Selinger<sup>39</sup> have

argued that, at the temperatures used by Okada et al.<sup>20</sup> for their experiments with the pyrene-DMA system in DEE,  $k_4$  is not sufficiently greater than  $k_p$  to justify the use of a Stevens-Ban plot in the calculation of  $\Delta H^\circ$ . Although it has been denied<sup>57</sup> that Stevens-Ban plots were misinterpreted by Okada et al.,<sup>20</sup> the arguments of McDonald and Selinger probably have some validity. Secondly, if the  $\Delta H^\circ$  value for the pyrene-DMA system in pyridine is combined with free-energy data, a  $\Delta S^\circ$  value of +18 eu is calculated; a positive entropy of formation for the exciplex seems unlikely. Thirdly, because, as is now known, ion formation from the encounter complex occurs to an appreciable extent in the pyrene-DMA system in pyridine,<sup>25</sup> the reported binding energy in this solvent is incorrect. However, when the results in pyridine are rejected, the data in the other solvents, to which such strong objections cannot be made, indicate that  $\Delta H^\circ$  does in fact decrease as polarity increases. It may be mentioned here that, in a recent study of the pyrene-DMA exciplex system,<sup>58</sup>  $\Delta H^\circ$  in DEE was calculated from the temperature coefficients of  $k_3$  and  $k_4$  and was found to be almost equal to the previously reported value in hexane.<sup>20</sup>

In the absence of more extensive or more consistent results for exciplexes the present observations may be compared with  $\Delta H^\circ$  values from studies of analogous systems. Excimers, because the charge-transfer interactions in them are relatively small, do not provide a close analogy. Excimer binding energies are not expected to depend on solvent polarity, and reported  $\Delta H^\circ$  values for excimers show no consistent correlation with solvent dielectric constant.<sup>59-62</sup> Exciplex formation, however, may be reasonably compared to charge-transfer complex formation in the ground state. A search of the literature indicated that, again, no consistent trends in  $\Delta H^\circ$  and  $\Delta S^\circ$  with changing solvent polarity have been observed for strong complexes ( $K_{eq} \geq 1$  in nonpolar solvents). In Table XI the observed trends in the eight complexes for which data were found are listed. Specific interactions of donor or acceptor with the solvent<sup>69</sup> together with difficulties in measuring the equilibrium constant<sup>70</sup> introduce much uncertainty into the reported data for ground-state complexes. Nevertheless, the belief that a more polar solvent leads to a more stable complex is unsupported by the experimental evidence, as the trends listed in Table XI illustrate.

The observed  $\Delta H^\circ$  values cannot be explained without the assumption of a solvent-induced change in the electronic structure of the exciplex. Such an assumption was needed<sup>71</sup> to account for the observed changes with increasing solvent polarity in the singlet-singlet absorption spectrum of the pyrene-DEA exciplex.<sup>71,72</sup> An abbreviated expression for the exciplex wave function, which includes only the two predominant contributions, may be written as

$$\psi_E = a_1\psi_1(A^-D^+) + a_3\psi_3(A^*D) \quad (16)$$

Solvent interactions are included in this configuration. In more polar solvents the exciplex becomes more ionic because of an increase in the weight of the charge-transfer contribution,  $a_1$ , to the total wave function.<sup>73</sup> Thus, the stabilization energy resulting from the interaction between the locally excited and charge-transfer configurations decreases. The consequent decrease in the binding energy offsets, in the CNN-DMCP system, the electrostatic stabilization of the dipolar complex in the polar solvent.<sup>74</sup>

In view of the discovery of direct radical ion formation in more polar media, it seems reasonable to suggest that the solvent molecules participate directly in the exciplex formation, even in solvents of low polarity, and, hence, that the intermolecular separation increases.<sup>20,72,73,75</sup> Such an increase would contribute greatly toward offsetting the effect of electrostatic stabilization on the binding energy.<sup>74</sup> But the greater separa-

**Table XI.** Trends in  $\Delta H^\circ$  and  $\Delta S^\circ$  with Solvent Polarity for Ground-State Charge-Transfer Complexes

donor-acceptor pair	$K_{\text{eq}},^a$ L mol $^{-1}$	change in $-\Delta H^\circ{}^b$	change in $-\Delta S^\circ{}^b$	ref
pyridine-iodine	157	variable	variable	63
tetramethylthiourea-iodine	13 000	constant	decrease	64
<i>N,N</i> -dimethylthioformamide-iodine	1850	constant	decrease	65
triphenylarsine-iodine	1000 $^c$	constant	decrease	66
diethyl ether-iodine	0.97 $^c$	constant		67
thiacyclopentane-iodine	209	increase	increase	67
durene-tetracyanoethylene	3.17 $^d$	decrease	increase	67
trimethylamine-SO $_2$	2500	increase	increase	68

$^a$  In heptane at room temperature.  $^b$  With increasing dielectric constant.  $^c$  In CCl $_4$ .  $^d$  In CH $_2$ Cl $_2$ .

tion of the two partners does not lead to a smaller repulsion energy,  $E_R$ , at the Franck-Condon distance in the ground state. In fact, as the data in Table XII illustrate,  $E_R$  increases as solvent polarity increases. Other exciplexes in nonpolar solvents have similar  $E_R$  values $^{17,20,26}$  to the 4.3 kcal mol $^{-1}$  found for the CNN-DMCP system in hexane. Much larger values, comparable to the 15.4 kcal mol $^{-1}$  for CNN-DMCP in EtAc, have also been found in methylcyclohexane $^{26}$  and also in benzene, $^{18}$  DEE, $^{38}$  THF, $^{20}$  and in the gas phase. $^{76}$  The model we wish to propose involves the polar solvent molecules interacting strongly with the strongly dipolar exciplex. The crowding of the solvent around this dipole influences the donor-acceptor distance. Thus, the increase in repulsive energy in the Franck-Condon ground state at the instant after emission can be viewed as due to the solvent configuration in the exciplex state. The failure of the more polar solvent to stabilize the exciplex (as is manifest in  $\Delta H^\circ$ ) is thus due to the slight increase in separation which results from this solvent crowding effect.

**Deactivation of the Exciplex:  $k_p$ .** Increased solvent polarity has previously been reported to induce a decreased probability of fluorescence in exciplexes $^{77,78}$  and in excited charge-transfer complexes. $^{78,79}$  A similar trend, illustrated by the  $k_5$  values in Table III, was observed in the present study.  $k_5$ , which was calculated with eq 6 on the assumption that  $k_1$ , the CNN fluorescence probability, was temperature independent, showed, itself, no dependence on temperature; average values are listed in Table III. Owing to the difficulty of evaluating the contributions of the various component configurations to the total exciplex wave function, a rigorous calculation of the radiative transition probability is not possible. However, the observed decrease in  $k_5$  supports the opinion, advanced in the preceding section, that the electronic structure of the complex changes as the solvent polarity is changed.  $k_5$  is related to the transition dipole moment,  $M_E$ , for the exciplex through the equation $^{27}$

$$M_E = \left| \frac{3hc^3k_5}{64\pi^4n\nu_\epsilon^3} \right|^{1/2} \quad (17)$$

$M_E$  in turn is given by

$$M_E = \langle \psi_E | \mu_{\text{op}} | \psi_G \rangle \quad (18)$$

in which  $\mu_{\text{op}}$  is the electric dipole moment operator, and  $\psi_E$  and  $\psi_G$  are given by

$$\psi_E = a_1\psi_1(A^-D^+) + a_2\psi_2(A^+D^-) + a_3\psi_3(A^*D) + a_4\psi_4(AD^*) \quad (19)$$

$$\psi_G = \psi_0(AD) \quad (20)$$

Because the ground state is dissociative, it has been assumed for the present argument that charge-transfer contributions to its wave function are negligible. If the second and fourth terms in  $\psi_E$  are neglected,  $M_E$  is given by

$$M_E = a_1 \langle \psi(A^-D^+) | \mu_{\text{op}} | \psi_0(AD) \rangle + a_3 \langle \psi_3(A^*D) | \mu_{\text{op}} | \psi_0(AD) \rangle \quad (21)$$

**Table XII.** Calculated Ground-State Repulsion Energies,  $E_R$  $^a$ 

solvent	$h\nu_E$ , cm $^{-1}$	$\Delta H^\circ$ , kcal mol $^{-1}$	$E_R$ , kcal mol $^{-1}$
hexane	26 110	8.9	4.3
DEE	23 530	8.9	11.7
EtAc	22 730	7.5	15.4

$^a E_{0-0} = 3.81$  eV in all solvents.

The matrix element  $\langle \psi(A^-D^+) | \mu_{\text{op}} | \psi_0(AD) \rangle$  is approximately proportional to the overlap of the donor orbital in D and the acceptor orbital in A; $^{27}$  consequently, it is rather small and decreases with increasing intermolecular distance. As the exciplex becomes more ionic  $a_3$  decreases; thus, the dominating term in  $M_E$ ,  $a_3 \langle \psi_3(A^*D) | \mu_{\text{op}} | \psi_0(AD) \rangle$ , decreases in more polar solvents. According to this view, therefore, both the increasing charge-transfer contribution, which reduces the second term in eq 21, and the probable increase in the intermolecular distance, which reduces the first term, contribute to the decrease in  $k_5$  with increasing solvent polarity. $^{73,77}$

Although  $k_5$  decreases slightly in the more polar solvents, the quantum yield of exciplex emission,  $\phi_E$ , given by

$$\phi_E = \frac{k_5k_3[Q]}{k_0(k_4 + k_p) + k_p k_3[Q]} \quad (22)$$

or, at infinite quencher concentration, by

$$\phi_E^\infty = \frac{k_5}{k_p} \quad (23)$$

increases. In general, in exciplexes,  $\phi_E$  decreases with increasing solvent polarity; $^{22}$  but an increased  $\phi_E$  has also been observed in media of moderate dielectric constant. Obviously, when increased solvent polarity induces an increase in  $k_p$  or a high probability for the photodissociation reaction, with rate constant  $k_3'$ ,  $\phi_E$  will decrease; in the latter circumstance  $\phi_E$  is given by

$$\phi_E^\infty = \frac{k_5k_3}{(k_3 + k_3')k_p + k_3'k_4} \quad (24)$$

However, the present results show that neither of these effects occurs for the CNN-DMCP system in the studied solvents.

It is worthy of note that, in the present range of solvent polarity, both increases $^{26,71,73,78}$  and decreases $^{8,77}$  in  $k_p$  have been observed.

## Summary

Specific interaction of excited species with the surrounding solvent molecules has been advanced in this paper as the explanation of a number of the results measured in the CNN-DMCP system. For instance, the large decrease in the unquenched lifetime of CNN can be accounted for only by assuming that the electronic configuration of the emitting state,  $S_1$ , is modified by interaction with the polar molecules of DEE and EtAc. Similarly, direct solvent participation in exciplex formation gives rise to the large increase in the ground-state

repulsion energy,  $E_R$ , in more polar solvents. On the other hand, conventional theories of solvent effects predict that the exciplex fluorescence maximum shifts to the red and that the entropy of activation of the reverse equilibrium reaction decreases in more polar solvents, both of which occurrences were observed. These theories fail, however, to provide a framework within which the quantitative aspects of either the red shift or the entropy decrease can be evaluated.

It has been maintained that the simple exciplex mechanism is followed in all three solvents with the important exception that the exciplex formation reaction is correctly characterized by a time-dependent rate constant. By the use of the nonlinear least-squares deconvolution technique it was possible to ignore this time dependence without introducing serious errors into the results of decay curve analysis.

Differences in the reported trends<sup>20,21</sup> of the exciplex binding energy,  $\Delta H^\circ$ , with increasing solvent polarity can also be explained by specific solvation effects. Before the role of the solvent in the photophysics of exciplex formation and decay can be understood, many more determinations of  $\Delta H^\circ$  as a function of solvent polarity must be made. Because Stevens-Ban plots do not provide a reliable means of calculating  $\Delta H^\circ$ , the analysis of two-component decay curves measured at a number of temperatures must be performed in order to determine values of the binding energy that can be fruitfully compared.

At the moment a thorough investigation along the lines set out here has not been carried out on any exciplex system. The results of the present study indicate that ordinary theories of solvent effects do not explain the changes that take place in exciplex systems when the solvent is changed. The solvating power of a solvent is frequently not directly related to its dielectric constant,<sup>79-81</sup> a fact that should be recognized when literature data are examined and compared.

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