Communications to the Editor

Chemistry of Exciplexes. III. Exciplex Fluorescence from Anthracene and Substituted Anthracenes in the Presence of 2,5-Dimethyl-2,4-hexadiene

Sir:

A photoexcited molecule may be deactivated by another ground state molecule even when the energy transfer from the excited molecule to the other molecule is energetically unfavorable. Pioneering work from the laboratories of Weller[1] and of Hammond[2] demonstrated that photoexcited arenes may be deactivated by amines and by 1,3-dienes, and exciplexes have been suggested as the intermediates in these deactivations. While arene:amine exciplexes have been characterized by their unique fluorescence, the fluorescence from exciplexes between unsubstituted arenes and 1,3-dienes has not been reported. However, the role of arene: diene exciplexes in these processes has been supported by the detection of exciplex fluroescence from cyanoarenes and dichloroanthracene.[3-6] Recent contributions from many laboratories including ours demonstrated that arenes react photochemically with 1,3-dienes, often in a regiospecific manner, to give a variety of adducts in both high quantum yields and chemical yields.[7-10] These observations imply that product formation may be an important pathway in the decay of arene:diene exciplexes, which may overcome other decay processes including fluorescence, but the role of the exciplex in the photochemistry of arenes has not been conclusively established. This communication deals systematically with the detection and characterization of exciplexes of various arenes with a representative diene, 2,5-dimethyl-2,4-hexadiene (DMHD), and their relationship with photochemistry.

All fluorescence spectra were measured in degassed solutions containing 5×10^{-5} *M* of the anthracene or $1\text{-}5 \times 10^{-4}$ *M* of octafluoronaphthalene, in a Perkin-Elmer MPF-3 spectrofluorimeter with a constant temperature cell compartment, and were uncorrected. The fluorescence lifetimes were determined by time-correlated single photon-counting methods using the deconvolution procedure previously described.[11] Anthracene (A) 9,10-difluoroanthracene (DFA), 9,10-dichloroanthracene (DCA), 9,10-dibromoanthracene (DBA), 9-cyanoanthracene (CNA), 9,10-dicyanoanthracene, (DCNA) and octafluoronaphthalene (OFN) exhibit exciplex fluorescence in the presence of DMHD, which is in each case a broad featureless emission and shifts to red in media of increasing polarity.[6] These results are tabulated in Table I with the known [A*: DEA] system (DEA diethylaniline)[12] in various solvents for comparison. In solvents of polarity higher than hydrocarbons, exciplex fluorescence frequently diminishes and chemical reactions become an important nonradiative process. Preliminary investigations indicate that DCA and DBA undergo photochemical displacements in polar solvents.[13] DMHD has no detectable influence on the absorption spectra of the arenes except DCNA, which exhibits a weak end absorption extending beyond 430 nm. The excitation spectra of exciplex fluorescence coincide with the excitation spectra of the corresponding parent fluorescence except that of [DCNA*:DMHD] which shows a minor change indicating ground state complex formation. The formation of DCNA:diene complex in the ground state will also account for the anomalously high quenching constants ($k_q\tau$, Table I) of DCNA fluorescence by dienes. The [A*: DMHD] and [CNA*:DMHD] systems exhibit appreciably weaker exciplex emissions, which are expected in view of the high chemical reactivities of excited anthracene and cyanoanthracene with DMHD;[7] therefore, these measurements were made at a relatively low temperature and narrow slit width in order to reduce the rate of consumption of the arene.

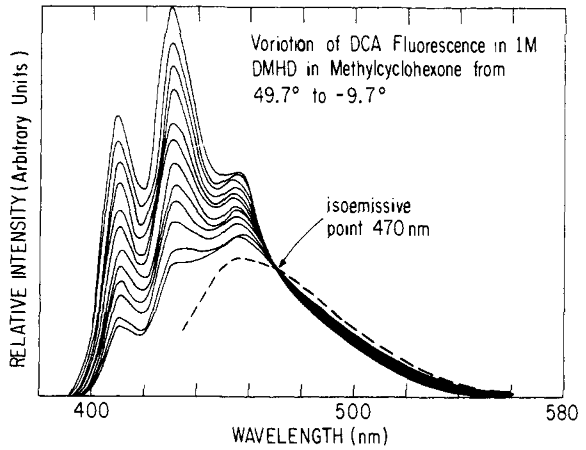

Figure 1.

The red-shift of exciplex fluorescence in polar solvents is a measure of the dipole moment or the polar character of the exciplex.[12] We have found that the extent of solvent shifts of exciplex fluorescence maxima from methylcyclohexane (or cyclohexane) to ethyl acetate among the anthracenes studied increases in the following order: from no detectable shift in anthracene, to DFA, DCA, DBA, CNA, and DCNA. [DCNA*:DMHD] exhibits an exciplex fluorescence in methylcyclohexane but none in ethyl acetate. The situation is analogous to the well-known [A*:DEA] system where the exciplex fluorescence is not detectable in polar solvents, because excited anthracene reacts with DEA to form ion pairs in these media.[12] The ionization potential (IP) of an arene is a measure of its HOMO level or the LUMO level of its excited state. For a given ground state donor, the polarity of arene exciplexes will increase as the IP of the arene component increases.[3] This is found to be the case for cyanoarene exciplexes. However, the IP's of anthracene and dihaloanthracenes do not differ appreciably, while the polarity of their exciplexes with DMHD increases markedly in the series of A, DFA, DCA, and DBA. The increase parallels the size of the substituent, i.e., H < F < Cl < Br, and may be attributed to the polarizability of the substituent. The polarity of exciplexes plays an important role in the orientation of adducts formed in the photocycloaddition of dienes to arenes, which will be discussed in an accompanying communication.[14]

We have also found that the quenching efficiency of DMHD on the fluorescence of most arenes and the profile of total fluorescence emission are dramatically modified by temperature. The results are illustrated by the effect of decreasing temperature from 49.7 to −9.7° over 5° increments on the fluorescence of DCA in methylcyclohexane containing 1 *M* DMHD (Figure 1). The quenching efficiency of DMHD increases by a factor of approximately 4 over this temperature range, and the exciplex fluorescence becomes the major emission at low temperatures. By applying the method of Stevens and Ban[15] to this system, the heat of formation (ΔH), entropy of formation (ΔS), and ground state destabilization energy (E_R) of [DCA*:DMHD] exciplex were found to be −5.74 ± 0.07 kcal/mol, −16.9 ± 0.5 eu, and 4.4 ± 0.2 kcal/mol, respectively.[16] By comparing these values with the well-known [A*:DEA] system,[12] we find that the two exciplex systems have similar ΔS, while the [DCA*:DMHD] system has a considerably smaller ΔH.

We have found that the lifetime of the [DCA*:DMHD] exciplex in methylcyclohexane is 7.5 ± 0.5 nsec, invariable within experimental error from 6.0 to 30.5°, while the lifetime of the [A*:DMHD] exciplex in acetonitrile decreases successively from 7.4 ± 1.4 to 3.5 ± 0.7 nsec as the temperature increases from 2.8 to 50.4°. Since DCA reacts with DMHD with very low quantum efficiency[14] while anthracene reacts with DMHD in acetonitrile to give the $4\pi_s + 4\pi_s$ adduct,[7] the results indicate that the adduct formation contributes to the nonradiative decay of the exciplex or the exciplex is the intermediate in the photocycloaddition. A similar conclusion has been reached by Caldwell and Smith on cyanophenanthrene exciplexes.[5] The result may be expressed in the following equation:

$$\begin{tikzcd}
\mathrm{ArH} \arrow[r, shift left, "h\nu"] & \mathrm{ArH}^{*} \arrow[l, shift left, "-h\nu'\text{, etc}"] \arrow[r, shift left, "+\text{diene}"] & {} \arrow[l, shift left, "-\text{diene}"]
\end{tikzcd}$$

$$\begin{tikzcd}
& & \text{chemical product(s)} \\
\text{encounter exciplex} \arrow[r, shift left] & \text{exciplex} \arrow[l, shift left] \arrow[ur] \arrow[dr, "-h\nu''\text{, etc.}"'] & \\
& & \mathrm{ArH} + \text{diene}
\end{tikzcd}$$

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Table I. Fluorescence of Arenes and Their Exciplexes

Solvents:	cC_6H_{12} (ϵ 2.05), $CH_3cC_6H_{11}$ (2.02)[a]			Ethyl acetate (ϵ 6.0)[a]			1,2-Dichloroethane (ϵ 10.4)[a]			Ethanol (ϵ 24.2)[a]			Acetonitrile (ϵ 36.2)[a]		
System[b]	λ_{max}[c]	$k_q\tau$[d]	ϕ[e]	λ_{max}	$k_q\tau$	ϕ	λ_{max}	$k_q\tau$	ϕ	λ_{max}	$k_q\tau$	ϕ	λ_{max}	$k_q\tau$	ϕ
A (IP 7.43)[f]	378[g]		0.36[g,h]	378			383			378			378		
[Anth*:DEA]	474[i,j]			520[j]			535[j]						None[j]		
[Anth*:DMHD]	430 ± 5[i]	9.1[k]		430 ± 5	6.5[k]		435 ± 5	2.4[k]	0.003[o]	440 ± 5	9.7[k]		455 ± 5	15.2[k]	0.01[l]
DFA (IP 7.49)[f]	395[i]		0.74	398									398		
[DFA*DMHD]	435 ± 3[i]	1.23	0.02[m]	450 ± 3	1.63								460	98	0.01[l]
DCA (IP 7.56)[f]	404[g]		0.56[h]	408						408			409		
[DCA*:DMHD]	450[g,i]	7.0	0.10	475	68.7	0.017				480[o]	113	0.014[o]	500 ± 5[o]	205	
DBA (IP 7.59)[f]	410[g]		0.088[n]	410											
[DBA*:DMHD]	450 ± 5[g]	12	0.003[o]	483 ± 5	28	<0.001[o]									
CNA (IP 7.95)[f]	408[i]		0.66[n]	413											
[CNA*:DMHD]	465[i]	330[k]	0.001[k]	515	390[k]	0.001[k]									
DCNA (IP –)[f]	422[i]			433											
[DCNA*:DMHD]	535[i]	2000	0.001	None	1500										
OFN (IP 8.90)[p]	348[g]		0.16[q]												
[OFN*:DMHD]	400[g]	42.3	0.0023				450	72	0.001[r]	465	26.2	0.0004[r]	None	43.3	

[a] Dielectric constants (ϵ) for solvents at 20° are obtained from "International Critical Table," Vol. VI, pp 83–97, and "Landolt-Börnstein Zahlenwerte und Funktionen," II Band, 6 Teil, pp 618–656. [b] See text for abbreviations. [c] Values given are in nm. Accuracies are ±0.5 nm for parent emissions and ±2.0 nm for exciplex emissions, except as noted. [d] Values given are in M^{-1} at ambient temperature (24 ± 2°), except as noted. [e] ϕ's for exciplexes were determined in 1 *M* diene, except as noted. Accuracies are ±10%. [f] Values for IP's are given in eV, E. S. Pysh and N. C. Yang, *J. Am. Chem. Soc.*, 85, 2124 (1963). Values for substituted anthracenes are obtained by the charge-transfer spectrum method relative to that of anthracene. DCNA does not form any detectable π-complex with common electron acceptors. [g] In cyclohexane. [h] W. R. Ware and B. A. Baldwin, *J. Chem. Phys.*, 43, 1194 (1965). [i] In methylcyclohexane. [j] H. Beens, H. Knibbe, and A. Weller, *J. Chem. Phys.*, 47, 1183 (1967). [k] Measured at 20°. [l] Measured at −10°. [m] Measured at 0°. [n] W. H. Melhuish, *J. Phys. Chem.*, 72, 3531 (1968). [o] Measured in 2 *M* DMHD. [p] IP of OFN is obtained by the charge-transfer spectrum method with TCNE relative to that of naphthalene and agrees well with the literature value of 8.85 eV, C. R. Brundle, M. B. Robin, and N. A. Kuebler, *J. Am. Chem. Soc.*, 94, 1466 (1972). [q] H. M. Rosenberg and S. D. Carson, *J. Phys. Chem.*, 72, 3531 (1968). [r] Measured at 10°.