Exciplex Emission and Photofragmentation Reactions of Contact Ion Pairs Generated via Quenching of Cyanoaromatic Singlets by Amino Alcohols^T

Xiaohong Ci and David G. Whitten*

Department of Chemistry, University of Rochester, Rochester, New York 14627 (Received: June 19, 1990; In Final Form: October 17, 1990)

Intermolecular quenching of singlet cyanoaromatics by 1,2-amino alcohols in nonpolar solvents results in an oxidative fragmentation of the amino alcohol donor concurrent with two-electron reduction of the cyanoaromatic. In several cases the reactive pairs exhibit weak exciplex fluorescence which can be closely correlated with the fragmentation; the attenuation of exciplex fluorescence as well as the photofragmentation as solvent polarity is increased for the intermolecular reaction indicates that a contact ion pair exciplex is the reactive intermediate. Molecules containing both an electron acceptor and an amino alcohol exhibit strong exciplex fluorescence and enhanced photofragmentation efficiencies in nonpolar solvents; both exciplex fluorescence and fragmentation persist in these cases as solvent polarity increases. An increase in fragmentation and decrease in fluorescence yields is observed as solvent polarity or base strength is increased, again indicating that the reactive state is an emissive ion-pair exciplex.

Introduction

The quenching of molecular excited states in solution by potential electron donors or acceptors can lead to a variety of consequences, both chemical and/or physical. The observation of new fluorescence emission accompanying the quenching of perylene singlets by N,N-diethylaniline in nonpolar solvents led to labeling of the emitting species first as a heteroexcimer and subsequently as an exciplex or excited complex.¹⁻⁵ Since their discovery, exciplexes have been the subject of several theoretical treatments. Two main factors, i.e., excitation resonance between the monomer molecules and charge transfer from one molecule to another, are usually considered as the origin of bonding and stabilization in excited complexes.⁶⁻⁸ Although it was suggested quite early by Weller and co-workers that the principal factor in stabilizing such exciplexes was likely charge resonance,⁹ the diverse array of excited-state quenching phenomena that can give rise to some sort of transient complex has led to the recognition that excited-state complexes can be quite diverse. $^{5,7,10-13}$ While nonemitting complexes of various lifetimes and multiplicities have been observed in many different situations,¹⁴ "emissive" exciplexes are usually confined to cases where (a) the emitting state can be considered as a slightly perturbed locally excited state (either singlet or triplet) which shows little charge-transfer character or (b) the emitting state corresponds quite closely to the unperturbed charge-transfer state, $S^+(or -)$, $Q^-(or +)$.^{15,16} The disappearance of exciplex fluorescence as solvent polarity is increased has been noted in several cases. This has led to the suggestion that the emissive exciplex is a contact ion pair (CIP) which can decay or be averted via solvent penetration to give a solvent-separated ion pair (SSIP) (whether or not the SSIP precedes the CIP is dependent upon several factors including solvent polarity, the energetics of the electron-transfer quenching process, the charges on the excited substrate and quencher, etc.).¹⁷⁻¹⁹ The suggestion that exciplexes are, in fact, contact ion pairs is reinforced by chemiluminescence experiments which demonstrate exciplex fluorescence can arise from reaction of ground-state $S^+(-)$ and $Q^{-}(+)$ reactions.²⁰ On the other hand, the frequent appearance of photoproducts via exciplex intermediates in nonpolar solvents-which contrast with products directly attributable to radical ion intermediates-has led to some confusion as to the actual degree of charge separation in fluorescent exciplexes.²¹⁻²⁴

In a number of studies we and others have shown that 1-amino 2-alcohols cleanly fragment when photochemically reacted upon irradiation of various potential electron acceptors.²⁵⁻²⁷ The reaction typically involves two-electron reduction of the electron SCHEME I



TABLE I: Lifetimes^a of Excited Monomer Singlets of Cyanoaromatics and Exciplex Formed with erythro-1 in Benzene

electron acceptor	DCA	TCA	DCN	
lifetime of monomer, ^b ns	13.21	15.22	9.75	
lifetime of exciplex, ^c ns	8.61	7.45	15.1	

^aAll samples were prepared in benzene and vacuum degassed through freeze-pump-thaw cycles. Concentration of acceptor was 1 × 10⁻⁴ M. Lifetimes were measured at room temperature by single photon counting technique. ^b For DCA, $\lambda_{ex} = 378 \text{ nm}$, $\lambda_{em} = 437 \text{ nm}$; for TCA, $\lambda_{ex} = 388 \text{ nm}$, $\lambda_{em} = 464 \text{ nm}$; for DCN, $\lambda_{ex} = 335 \text{ nm}$, $\lambda_{em} = 386 \text{ nm}$. ^cConcentration of *erythro*-1 0.05-0.3 M. Excitation wavelengths were set at 380 nm for both DCA and TCA, and at 305 nm for DCN. Emission wavelengths were set at 450, 500, 550, and 600 nm for DCA; 470, 500, 550, 600, and 630 nm for TCA; 400, 450, and 510 nm for DCN. The lifetimes of exciplex and monomer do not change with emission wavelengths, but the exciplex/monomer ratio increased as emission wavelength shifts to red.

acceptor together with oxidative C-C bond cleavage in the amino alcohol donor according to eq 1. The reaction occurs for a variety

A + ArCH(OH)CH(NR₂)Ar
$$\xrightarrow{h\nu}_{\text{trace H}_2O}$$

AH₂ + ArCHO + Ar'CHO + R₂NH (1)

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[†]This paper is dedicated to Professor Albert Weller.

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Figure 1. Structure of amine donors used in this study.

of amino alcohol substrates and acceptors but with quantum efficiencies which depend strongly upon factors including the

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(14) Emission from exciplexes proceeds by a vertical, Franck-Condon-allowed transition from minimum on an excited-state surface to a low-lying repulsive ground-state surface, which may not be observed because of significant nuclear change for the two states. Such a "nonemitting" exciplex is often of the "moderately polar" type and has properties similar to those of a contact ion pair which frequently does not emit but is chemically reactive. Evidence for the intermediacy of nonemitting exciplexes is often indirect, but convincing cases have been presented for a number of reactions: (a) Chapman, O. L.; Lura, R. D. J. Am. Chem. Soc. 1970, 92, 6352. (b) Yang, N. C.; Yates, R. L.; Masnovi, J.; Shold, D. M.; Chiang, W. E. Pure Appl. Chem. 1979, 51, 173 and references therein. (c) Smothers, W. K.; Meyer, U. S.; Saltiel, J. J. Am. Chem. Soc. 1983, 105, 545. (d) Whitten, D. G.; Roy, J. K.; Carroll, F. A. In The Exciplex; Gordon, M., Ware, W. R., Eds., Academic Press: New York, 1975; p 247. In addition, Weller and Mataga have studied the effect of medium polarity on the fate of exciplexes in solution and found that the exciplex luminescence is quenched in more polar media via electron transfer to form ions which becomes the decay pathway in very polar media. (d) Knibbe, H.; Rollig, K.; Schafer, F. P.; Weller, A. J. Chem. Phys. 1967, 47, 1184. (e) Beebs, H.; Knibbe, H.; Weller, A. J. Chem. Phys. 1967, 47, 1184.

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TABLE II: Quenching Rate Constants^a for Cyanoaromatic Singlets by Diastereomers of 1

electron	k _q , M ⁻¹ s ⁻¹	in benzene	$k_q, M^{-1} s^{-1}$	in CH ₃ CN
acceptor	erythro-1	threo-1	erythro-1	threo-1
DCA	4.1×10^{9}	3.9×10^{9}	1.4×10^{10}	1.2×10^{10}
TCA	9.9 × 10 ⁹	9.1 × 109	3.2×10^{10}	2.8×10^{10}
DCN	7.8 × 10 ⁹	7.2 × 10 ⁹	1.3×10^{10}	1.2×10^{10}

^a All samples were bubble-degassed with dried argon gas for 30 min and sealed with Parafilm prior to each measurement. The quenching experiments were carried out with 5×10^{-5} M acceptor and various concentrations of the diastereomer of 1 in the range 0.005–0.05 M. The quenching constants were obtained from more than five data points in each case from linear Stern-Volmer plots.

TABLE III:	Reduction	Potentials ^a	and	Excited	State	Energies	of
Electron Acc	ceptors and	Calculated	Free	Energy	Chang	zes for	
Excited-Stat	e Quenchin	g				-	

acceptor	$\frac{E_{1/2}^{\text{red}}}{\text{eV}},$	<i>E</i> ¹ *, eV	$\frac{E_{1/2}^{\text{red 1*}}}{\text{eV}},$	donor ^b	ΔG_{exp} , eV
DCA	-0.90	2.90	2.00	erythro-1	-0.58
				threo-1	-0.42
TCA	-0.45	2.89	2.44	erythro-1	-1.02
				threo-1	-0.84
DCN	-1.28	3.75	2.46	erythro-1	~1.06
				threo-1	-0.90

^aVolts vs SCE. ^bOxidation peak potentials are 1.05 and 1.21 eV vs SCE for *erythro*- and *threo*-1, respectively.



Figure 2. (a) Fluorescence spectra of TCA in the absence (full curve) and presence (broken curve) of 0.2 M *erythro*-1. (b) Corrected exciplex fluorescence spectrum.

multiplicity of A*, its structure, the solvent, and the structure and stereochemistry of the amino alcohol donor. For example, when the reaction is carried out using acceptors reacting from their

⁽²⁷⁾ The dynamics of monomer and exciplex in these systems can be represented by Scheme I, where k_a and k_d are the rate constants of the formation and dissociation of exciplex, respectively, k_r and k_r are the rate constants of fluorescence from monomer and exciplex, respectively, k_{nr} and $k_{nr'}$ are the rate constants for nonradiative decay for monomer and exciplex, respectively, k_{nr} and k_{dif} are the rate constants for back electron transfer, radical cation fragmentation, and diffusion of charged radicals, respectively. The lifetime of the excited monomer, $\tau_0 = 1/(k_r + k_q[D] + k_{nr'})$, is dependent on electron donor concentration, decreasing with increasing donor concentration, where the excited monomer is quenched through electron transfer. The exciplex lifetime, $\tau_{0'} = 1/(k_r + k_{nr'} + k_d + k_{dif} + k_{-et} + k_{frag})$, is independent of the donor concentration. Since exciplex formation from excited monomer and ground-state donor is strongly exothermic (see Table I), exciplex dissociation is energetically uphill. In addition, at high donor concentration, the equilibrium is shifted toward exciplex formation, consistent with the observation of exciplex emission at high [D] (>0.1 M). Under these conditions, k_d is negligible and the exciplex lifetime is nearly constant. Because of the overlap between monomer and exciplex, respectively. Both lifetimes were independent of emission wavelength (470-550 nm), although the relative proportions of the decay attributed to each component varied with emission wavelength.

excited singlet states, the overall process shows a pronounced decrease in efficiency with increase in solvent polarity and a strong dependence upon the basicity of the acceptor anion radical (A^{-}). In these cases it appears clearly that the fragmentation can be attributed to reaction of A^- with the donor cation radical (D^{+}) within a contact ion pair formed by single electron transfer quenching of ${}^{1}A^{*}$ (the excited singlet state). The efficiency is limited by competition between back electron transfer and fragmentation; since the latter requires close contact of the A^{+} and D^{+} as well as proper orientation, it can be effectively bypassed by back-electron-transfer processes over greater than collisional distances such as can occur within a SSIP.

Although the oxidative fragmentation can occur with several donor-acceptor combinations in which quenching of ${}^{1}A^{*}$, e.g., ¹thioindigo* (${}^{1}TI^{*}$), leads to no new emission, we have recently observed that exciplex fluorescence does occur for several cyanoaromatics with a variety of amino alcohol donors. In the present paper we report on the characteristics of exciplex emission for these fragmentation/reactive donor-acceptor combinations. The results reported emphasize the identity of the emissive exciplex as the reactive contact ion pair and provide some clear insights into factors controlling its reactivity. We also report studies of intramolecular-acceptor-linked amino alcohols which show both enhanced exciplex emission and fragmentation efficiencies compared to their intermolecular counterparts and reinforce the exciplex-CIP mechanism for oxidative fragmentation.

Results

The fluorescence of several cyanoaromatics [9,10-dicyanoanthracene (DCA), 2,6,9,10-tetracyanoanthracene (TCA), 1,4dicyanonaphthalene (DCN)] is quenched by amino alcohols whose structure is given in Figure 1. In the absence of added electron donor, the fluorescence can be well fit to a single-exponential decay; lifetimes in degassed benzene solution for unquenched monomer fluorescence are given in Table I. Addition of a small amount of amino alcohol (<0.05 M) to benzene or acetonitrile solutions of the cyanoaromatics results in intensity quenching which follows the Stern–Volmer relationship; k_a values determined from intensity quenching of the three cyanoaromatics by erythroand threo-1 are listed in Table II. In acetonitrile, only monomer fluorescence with a reduced lifetime could be detected with increasing concentration of 1. In contrast, double-exponential fluorescence decay for exciplex and monomer is observed at room temperature in benzene solutions at high donor concentration; the monomer lifetime decreases with increasing donor concentration and the exciplex appearing at longer wavelengths has a constant lifetime (Table 1) which is independent of donor concentration.²⁷ Although the strong cyanoaromatic monomer and weak exciplex fluorescence overlap, the exciplex fluorescence can be resolved by subtraction of monomer emission from the total emission in the presence of donor as shown in Figure 2.

Application of the equation derived by Weller indicates that for benzene the exciplex should be more stable than the solvent-separated radical ion pair by about 0.7 eV; in contrast, for acetonitrile the solvent-separated radical ion pair should be more stable than the exciplex by about 0.2 eV. Table III compares the reduction potentials, excited singlet energies, and excited-state reductions for the three acceptors (DCA, TCA, and DCN) used, and free energy changes for the excited singlet quenching by both erythro- and threo-1 through single electron transfer (SET) as estimated from the Weller equation.¹⁸ Exciplex formation, in all of the above cases, is strongly exothermic and energetically favorable.

Exciplex maxima for erythro and threo diastereomers of 1 are listed in Table IV. For each acceptor the exciplex formed with the threo isomer has a higher energy λ_{max} than for the erythro isomer; for either amino alcohol diastereomer, the exciplex energies increase in the series DCN > TCA > DCA. The free enthalpy of exciplex formation in benzene, ΔG_{exp} , is estimated by using a semiempirical equation developed by Weller (eq 2),^{18,28} which takes

$$(A,D) \rightarrow (A^{-}D^{+})$$
 $\Delta G_{exp} = E_{D}^{ox} - E_{A}^{red} + 0.358 \text{ eV}$ (2)

TABLE IV: Exciplex Fluorescence Wavelength Maxima in Benzene

	-					
electron donor ^a	electron acceptor ^b	λ _{max} , nm	E _{obs} , eV	ΔG_{exp} , c	$\frac{E_{\rm D}^{\rm ox} - E_{\rm A}^{\rm red}}{\rm eV},$	-
erythro-1	DCA	567	2.2	2.3	2.0	
threo-1	DCA	529	2.3	2.4	2.1	
erythro-1	TCA	537	2.3	1.9	1.5	
threo-1	TCA	512	2.4	2.0	1.7	
erythro-1	DCN	517	2.4	2.7	2.3	
threo-1	DCN	495	2.5	2.8	2.5	

 ${}^{a}E_{ox}$ (oxidation peak potential) are measured as 1.05 and 1.21 eV vs SCE for *erythro*-1 and *threo*-1, respectively. ${}^{b}E_{red}$ (reduction potential of electron acceptor) are -0.90, -0.45, and -1.28 eV vs SCE, respectively. Calculated from eq 2.

TABLE V: Exciplex Fluorescence Intensity and the Quantum Efficiency of C–C Bond Cleavage of α,β -Amino Alcohol with DCA in Benzene

electron donor	relative exciplex ^a fluoresence intensity	quantum yield ^b of C-C bond cleavage	relative quantum yield
erythro-1	1	6.7×10^{-3}	1
threo-1	6.2	3.5×10^{-4}	0.05
2	4.2	7.6×10^{-5}	0.01
3	6.6	0	0

^aSamples containing DCA as electron acceptor (concentration = 2×10^{-5} M) and electron donor (concentration = 0.2 M for 1 and 2; concentration = 0.05 for 3, which is limited by the solubility of 3 in benzene) were prepared in benzene. Dry argon was bubbled through the sample solutions for 20–30 min prior to each measurement. The maximum intensity of exciplex fluorescence was recorded at the wavelength corresponding to maximum emission changes with electron donor. ^bSamples were prepared in benzene with DCA (2×10^{-5} M) as electron acceptor and vacuum degassed through freeze-pump-thaw cycles. The concentration of various α,β -amino alcohols were adjusted to ensure 50% of excited DCA quenched in each case. The yield of fragmentation product, benzaldehyde, was measured by HPLC.

into account differences in the solvation free energy between hexane ($\epsilon = 1.9$) and benzene ($\epsilon = 2.17$). The actual values calculated from eq 2 (Table IV) show only fair agreement with those obtained by spectral subtraction as described above.²⁸

The intensity of exciplex emission varies with donor structure. For each acceptor investigated, the intensity of emission from the exciplex formed with threo-1 was several times (ca. 6-7) more intense than that formed from the erythro diastereomer. A comparison of exciplex intensity and fragmentation efficiency for amines 1-3 with DCA is listed in Table V. The strongest emission was observed for the amino ether 3 which does not undergo measurable fragmentation under conditions where the amino alcohols are reactive.

Compounds 4 and 6 contain simultaneously an erythro amino alcohol donor and a light-absorbing electron acceptor. Although 4 could have the donor and acceptor formally conjugated, depending upon conformation about the amine nitrogen, in 6 the donor and acceptor are "insulated" by an ethylene group (-C- H_2CH_2-). Although details of the photoreactivity of 6 will be reported subsequently, it is notable that both 4 and 6 undergo efficient fragmentation upon direct irradiation into the acceptor to produce benzaldehyde (and substituted benzaldehyde in the case of 6) and the corresponding reduced acceptor amine. For both intramolecular-acceptor-linked amino alcohols the fragmentation efficiency is relatively high in benzene and, in contrast to the intermolecular examples, shows an increase with increase in solvent polarity in the series: benzene, CH₂Cl₂, CH₃CN, aqueous micellar sodium dodecyl sulfate (SDS), aqueous micellar

⁽²⁸⁾ Equation 2 is derived from eq 8 in ref 18 with the assumption that the average value $\mu^2/q^3 = 0.75^{146}$ and typical charge-transfer exciplexes (U_{dest} $-U_{stab} \sim 0$) are strongly favored in low-polarity solvents. Certain errors may be expected for the simplified solvent correction. Strong positive deviations, as observed with TCA (which is a better electron acceptor in the ground state compared to DCA and DCN), occur at low values of $E_D^{\alpha t} - E_A^{red}$, i.e., with strongly bound electron donor-acceptor complexes, and may reflect the contribution of ground-state binding energy to the exciplex emission.



cetyltrimethylammonium chloride (CTAC). Both of these compounds also exhibit prominent fluorescence in a wide range of solvents. Table VI compares absorption and emission maxima and emission lifetimes for 4 and 6 and 4-cyano-1-aminonaphthalene (5). While all three molecules exhibit fluorescence with a relatively large Stokes shift and characteristics that could be ascribed to an intramolecular exciplex in each case, the behavior of each molecule is guite individual. Thus 4 shows very little solvent sensitivity for either absorption or emission maxima, but the fluorescence lifetime decreases with solvent polarity increase concurrent with an increase in fragmentation efficiency. Compound 5, which undergoes no fragmentation, shows a small red shift in absorption and slightly larger red shift in fluorescence but a strong increase in fluorescence lifetimes as solvent polarity increases. In striking contrast, 6 shows little change in absorption, a modest red shift in fluorescence, and little change in fluorescence lifetime as polarity increases.

Discussion

As pointed out in previous papers, the excited acceptor mediated fragmentation of amino alcohols such as 1 in nonpolar solvents such as benzene can be clearly ascribed to cooperative reaction of the A*- and D*+ in the contact ion pair generated by diffusional quenching.^{26,27} In the critical step determining the quantum efficiency of the process, the A* acts as a base in removing the proton from the D*+ in a step concerted with the C-C bond cleavage (eq 3). This step, analogous to the two-electron "Grob"



fragmentation,²⁹ is followed by subsequent dark-electron-transfer reactions which culminate in two-electron redox of both partners. The observation of a moderate isotope effect on fragmentation efficiencies and a correlation with estimated basicities of the A*support this mechanism. The observation of a solvent-dependent exciplex fluorescence which parallels the fragmentation suggests that the reaction proceeds via the contact ion pair exciplex as indicated as Scheme II, where k_{ex} is the rate constant for exciplex fluorescence and the values k_{-e} and k_{frag} refer to rate constants for the nonradiative back electron transfer and fragmentation process. Since quantum efficiencies for exciplex fluorescence and fragmentation for the reaction with cyanoaromatic singlets are quite low (<0.01 for all of the intermolecular examples investigated thus far), it follows that the decay of the exciplex is governed by the rate of back electron transfer and that k_{-e} values can be estimated from exciplex lifetimes.^{30a} The k_{-e} values thus estimated for erythro-1 and the cyanoaromatics in benzene are 1.2×10^8 , 1.3×10^9 , and 6.6×10^7 s⁻¹ for DCA, TCA, and DCN respectively.^{30b} Since the estimated³¹ free energy changes (-1.95, -1.5, and -2.33 eV, respectively) are large, the back-electron-transfer processes should fall well into the "Marcus-inverted" region and thus the order observed is qualitatively reasonable. Interestingly, the rates of exciplex decay for 1 with all three cyanoaromatics

						$CH_{r}CN + H_{r}O$		
compd	sol	cyclohexane	benzene	CH ₂ Cl ₂	CH ³ CN	(%01)	SDS	CTAC
4	À _{max} , nm	314	316	316		312	316	316
	(absorbance)							
	Amer, nm	357	362	361		358	358	359
	(absorbance)			(2007) 11 V				
	lifetime, ns	$\tau_1 = 0.10 (80\%)$ $\tau_2 = 0.77 (14\%)$	$r_1 = 0.16 (19\%)$ $r_2 = 10 (21\%)$	$\tau_1 = 0.11 (80\%)$ $\tau_2 = 0.87 (20\%)$		$\tau_1 = 0.01 \ (6/\%)$	$\tau_1 = 0.18 (75\%)$	$r_1 = 0.23 (709)$
v	λ nm	334	338	338		340 - 21 - 21 - 21 - 21 - 21 - 21 - 21 - 2	344	348
	(absorbance)							
	Amax, nm	388	402	403		418	418	420
	(absorbance)							
	lifetime, ns	$r_1 = 0.93$	$r_1 = 2.95$	$\tau_1 = 3.26$		$\tau_1 = 6.62$	$\tau_1 = 6.32$	$r_1 = 7.01$
•	λ _{max} , nm	268	280		278	278	274	280
	(absorbance)							
	λ _{max} , nm	382	384		395	416	\sim 420	\sim 420
	(absorbance)							
	lifetime, ns	$\tau_1 = 0.14 \ (74\%)$	$r_1 = 0.45 (12\%)$		$\tau_1 = 0.05 (4\%)$	$\tau_1 = 0.06 \ (6\%)$	$\tau_1 = 0.16 (5\%)$	$\tau_1 = 0.03 \ (7\%)$
		$r_2 = 1.5 (2\%)$	$\tau_2 = 2.4 \ (27\%)$		$\tau_2 = 1.5 (15\%)$	$\tau_2 = 1.5 (49\%)$	$\tau_2 = 1.4 \ (24\%)$	$\tau_2 = 0.9 \ (21\%)$
		$\tau_3 = 25.5 \ (24\%)$	$\tau_3 = 16.2 \ (61\%)$		$\tau_3 = 10.6 \ (81\%)$	$\tau_3 = 4.9 (45\%)$	$\tau_3 = 8.4 \ (70\%)$	$\tau_3 = 5.8 \ (73\%)$

solution for 20 min prior to each measurement. Samples were excited at maximum of absorbance. "Samples were prepared as above. Literation with prosecond single photon counting device with 1 ps (or 10 ps)/channel resolution (mode locked CW Nd:YAG dye laser) with excitation at 305 nm

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^{(30) (}a) $k(1/\tau_0)$. (b) A more precise value of k_{-} can be obtained when uantum yields of both fragmentation and exciplex emission are available.

 $[\]Phi_{\text{frag}} + \Phi_{\text{ax}} + \Phi_{-a} = 1.$ (31) Since the amine potentials are not reversible, the exergonicities must be regarded as estimates

are lower than would be estimated from exergonicities by slightly more than an order of magnitude by using the curves generated by Gould et al.³²⁻³⁴ for back electron transfer between radical ions in the geminate pair (cyanoaromatic acceptors, aromatic hydrocarbon donors) in acetonitrile. However, since the solvent reorganization energies in benzene should be much lower than those for acetonitrile, the parabolic plot of $-\Delta G_{-e}$ vs log k_{-e} should be shifted so as to give values of k_{-e} between 1 and 2 orders of magnitude lower for CIP's in nonpolar solvents, in accord with the measured values.³⁵ That Scheme II is correct and both the fluorescence and fragmentation occur from a common intermediate is implied by the observation that addition of pyridine (0.01 M) enhances the fragmentation efficiency, although exciplex emission is more complex.³⁶

The increase (6-7-fold) in exciplex emission intensity for threo-1 compared to erythro-1 with the different cyanoaromatic acceptors seems most reasonably attributed to the greater exergonicity, and hence slower rate, for the back electron transfer, provided (as seems reasonable) values for k_{ex} are similar for the two donors in each case. The cause for the enhanced emission intensity for cyanoaromatic exciplexes with amines 2 and 3 is less clear; in these cases it seems reasonable that either k_{ex} or k_{-e} changes could account for the large intensity differences.

For the "intramolecular" acceptor amino alcohol molecules 4 and 6 both exciplex emission and fragmentation efficiencies are much higher and the emission and fragmentation reactivity persist as solvent polarity increases. The lack of a polar solvent attenuation of exciplex emission and reactivity is most easily attributed to the linking chain between the redox pair which prevents the separation of the CIP in the intramolecular cases. Since the emissions of both 4 and 5 show only a single broad maxima, with no clear evidence of dual emissions, it seems unlikely that the participation of "TICT" states³⁷ should be involved in either case. Because 5 shows both red-shifted absorption and fluorescence, compared to 4, it seems most reasonable that both processes involve conformations in which the NH₂ group is coplanar with the naphthalene so that formal conjugation with the nitrogen lone pair is maximized. In contrast, for 4 it appears likely that both absorption and emission involve a nonpolar species, but the shifts of the fluorescence are not nearly as pronounced as those observed for similar substituted cyanonaphthalenes in which prominent TICT states exist.³⁷ Emission lifetime studies of 4 using picosecond laser excitation and 1 ps/channel resolution in 2500 effective channels result in good double-exponential decays³⁸ in various solvents; these two lifetimes may correspond to the local excited and charge-transfer states. However, a complete assignment of these emitting states is yet to be obtained.

The be, vior of 6 is even more complex since it involves a formally nonconjugated donor and acceptor and the intermolecular photoreactivity of the reagents is quite different. Nitroaromatics in general are characterized by very weak, short-lived fluorescence and high intersystem crossing efficiencies.^{39,40} The picosecond SPC measurements of p-nitrotoluene in different solvents show very short lifetimes corresponding to very weak fluorescence emission; these short lifetimes, which are very likely due to emission

from singlet excited states of p-nitrotoluene, remain unchanged with the addition of different amounts of 1.41 Direct irradiation of *p*-nitrotoluene in the presence of 1 leads to fragmentation of the amino alcohol in moderate efficiency but to no exciplex fluorescence; presumably the reaction may be initiated by triplet quenching which with other acceptors leads to fragmentation of amino alcohols in very high efficiency.⁴² The observation of exciplex fluorescence in 6 seems to indicate a prominent role of the exciplex-contact radical ion pair in the intramolecular case. The lifetime studies of 6 revealed a triple-exponential decay (see Table VI). The two short-lifetime components are nearly identical with the lifetimes analyzed from *p*-nitrotoluene ($\tau_1 = 0.13$ ns, τ_2 = 1.2 ns in cyclohexane), and these may be attributed to decay of the singlet excited *p*-nitroaromatic, while the long-lifetime component (major component in more polar solvents) is apparently due to the charge-transfer state. The relatively short exciplex lifetimes for both 4 and 6 are consistent with higher values of k_{ex} and k_{frag} in each case. Here again, the back-electron-transfer process which is strongly exergonic should fall into the Marcus-inverted region. Although it is not easy to assess the value for k_{-e} for either compound, it seems reasonable that the exergonicities should be higher than for DCA, TCA, or DCN and hence the back electron transfer could be somewhat slower. The comparison in reactivity of 4 with that of erythro-1-DCA in benzene indicates a reaction efficiency approximately 40 times greater for 4 or ca. 0.4; since the lifetime of the fluorescence is much shorter for 4 than for the 1-DCA intermolecular exciplex, the indicated value of $k_{\rm frag}$ should be in the range $(1-3) \times 10^9$ s^{-1} . For the more polar solvents it seems reasonable that the increase of fragmentation occurs at the expense of fluorescence (especially in comparing benzene with acetonitrile) where the decrease in lifetime closely parallels the increase in fragmentation efficiency to near unity.

Unlike the intermolecular cases, both 4 and 6 are reactive in partially aqueous solutions including anionic and cationic micelles. The rather strong differences in reactivity (in both cases the exciplex lifetime is shorter in cationic CTAC and the fragmentation efficiency is substantially higher) can be attributed to the increased effective basicity in the interface region where 4 and 6 are surely solubilized. Addition of base (increase of pH from 6 to 9) also enhances the reaction of 4 in aqueous solution. This is reasonable in both cases since the acceptor-anion-radical "portion" of the intramolecular radical ion pair cannot easily assist in the deprotonation step as shown in eq 3 for the intermolecular reaction. The enhanced values for k_{frag} for 4 and 6 must reflect other intramolecular interaction modes which assist the fragmentation and which are enhanced by increases in solvent polarity. We are currently extending our studies to a variety of amino alcohol acceptor molecules which have limited or enhanced reactivity and thus can help define the mechanisms for the intramolecular reaction.

Experimental Section

Photochemical and Spectroscopic Studies. All samples were degassed either by bubbling argon through for 30 min or by freeze-pump-that cycles until the vacuum reached 3×10^{-6} Torr or less, and sealed under vacuum. The picosecond laser data were measured by using a mode-locked CW Nd:YAG dye laser single photon counting device with 1-ps resolution. Excitation was set at 380 and 305 nm for the cyanoaromatics (DCA and TCA) and nitroaromatics (4-6), respectively (generated by Rhodamine 6G mixing with the 1064-nm fundamental). The data were analyzed by using a fluorescence decay deconvolution program with iterative convolution and nonlinear least-squares fitting.⁴³ The nanosecond fluorescence lifetimes were measured on a Photochemical Research Associates single photon Counting Fluorescence Lifetime In-

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channel resolution of 0.2 ns/channels gives practically single-exponential decav

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strument with a hydrogen flash lamp. Fluorescence spectra were measured on a SPEX 111CM Fluorolog fluorimeter with a 150-W xenon lamp excitation and a photon counting thermoelectrically cooled detector. UV-visible absorption spectra were measured on a Hewlett-Packard 8451A diode array spectrometer. Visible light irradiations of solutions containing cyanoaromatics were carried out using a 200-W Hg lamp or 100-W tungsten lamp with appropriate filters (for DCA and TCA, a combination of band-pass filter 7-59 and cuttoff filter 0-52 (Corning Glass Works) were used to isolate the 420-nm band; for DCN as acceptor, band-pass filter 7-54 and cutoff filter 0-52 were used to isolate the 350-nm peak). Photolysis of compounds 4 and 6 was conducted using a 200-W Hg lamp with a 0-54 cutoff filter. The detailed photoproduct analyses, kinetic studies, and the synthesis of compounds 1-3 have been reported previously.44

Synthesis of 6. 4-Nitrobenzylamine was obtained from base washing of 4-nitrobenzylamine hydrochloride (Aldrich). Five grams of amine hydrochloride is dissolved into 50 mL of distilled water. The free amine was isolated from hydrochloride salt by gradually addition of 10% NaOH solution until the solution

(44) Ci, X.; Whitten, D. G. J. Am. Chem. Soc., in press.

reaching pH > 12, and then extracted by CH_3Cl . The organic layer was dried under anhydrous MgSO₄, and the solvent was removed in a rotary evaporator, yielding a slightly yellowish powder (>95%). ¹H NMR (300 MHz) in C₆D₆: 2.1 (t, 2 H), 2.4 (t, 2 H), 6.52 (d, 2 H), 7.78 (d, 2 H).

Compound 6 was synthesized through continuous reflux (2 days) of a benzene solution containing 1 g of trans-4-chlorostilbene oxide and 2 equiv of 4-nitrobenzylamine under vigorous stirring. An orange-yellow solid was obtained after removal of the solvent. The crude product was recrystallized 6 times from absolute ethanol and dried in a vacuum oven for 20 h, yielding a slightly yellow powder with a melting point of 126-128 °C (86%). ¹H NMR (300 MHz) in C₆D₆: 2.11 (m, 2 H), 2.24 (m, 2 H), 3.51 (d, 1 H), 4.38 (d, 1 H), 6.40 (d, 2 H), 6.81 (d, 2 H), 6.92 (s, 5 H), 7.08 (d, 2 H), 7.72 (d, 2 H).

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Registry No. erythro-1, 19640-35-8; threo-1, 19640-34-7; 2, 5455-72-1; 3, 107576-76-1; 4, 131545-73-8; 5, 58728-64-6; 6, 131545-74-9; DCA, 1217-45-4; TCA, 80721-78-4; DCN, 3029-30-9.

Resonance Raman Studies on the Intermediate K-590 in the Photocycle of Bacteriorhodopsin

R. Lohrmann, I. Grieger, and M. Stockburger*

Max-Planck-Institut für biophysikalische Chemie, Abteilung Spektroskopie, Am Fassberg, D-3400 Göttingen, FRG (Received: June 25, 1990)

Resonance Raman (RR) spectra of the intermediate K-590 in the photocycle of the retinylidene Schiff base chromophore of bacteriorhodopsin (BR) were recorded at 21 °C, where K has a lifetime of $\sim 2 \mu s$. An aqueous suspension of purple membranes from Halobacteria (16 µM concentration of BR) was flowed across the waist of a laser beam (514 nm) serving for both photolysis and RR excitation. The residence time of the sample in the beam waist was $\sim 2 \mu s$. To subtract the contribution of the parent BR-570, a special experiment was designed in which two spectra, one at a low degree of photolysis (mainly consisting of BR-570) and one at a significantly higher degree of photolysis (mixture of BR-570 and K-590) could be recorded simultaneously. This allowed us to perform the difference procedure with high accuracy. New vibrational features in the spectrum of K-590 were identified in the C=C stretching region. From a comparison with the RR spectra of the parent BR-570 and the subsequent product L-550 the following was concluded: During the photoinduced transition from BR-570 to K-590 a negatively charged counterion is removed from the positively charged Schiff base group. In the subsequent thermal relaxation step to L-550 the β -ionone ring of the retinal moiety approaches a positively charged group in the binding pocket of the chromophore.

1. Introduction

The retinal-binding protein bacteriorhodopsin (BR), which is found in the cell membrane of Halobacteria, acts as a light-driven proton pump. The proton gradient that is established in this way is used by the cell as an energy source to drive metabolic processes under anaerobic conditions. BR's unique function had first been elucidated by Oesterhelt and Stoeckenius.¹ Since then a considerable body of information was collected (for a review see ref 2).

BR is the only integral protein in the so-called purple membrane of Halobacteria where these molecules form a regular two-dimensional array. Purple membranes provide an ideal system to study the biological function of BR molecules in an intact environment by chemical and physical methods. In particular highly diluted aqueous suspensions of purple membrane sheets can be used for spectroscopic studies.

The biological function of BR is controlled by its chromophore (Figure 1) in which a retinal molecule is linked to a lysine residue

of the protein envelope via a C==N bond (Schiff base group, SB). It is mainly the protonation of the SB group that is responsible for the color of the chromophore. But it is thought that the interaction of the positive charge of the chromophore with negatively charged side groups introduces additional shifts of the absorption maxima as a function of the distance.^{3,4} In the parent state the chromophore has its absorption maximum at 570 nm and is therefore denoted by BR-570. In this state its configuration is all-trans⁵ (Figure 1). On light absorption BR-570 undergoes a primary photoreaction and subsequently in the dark runs through various intermediate states, as identified by color changes, until under "normal conditions" (room temperature, neutral pH), it is

^{*} To whom correspondence should be addressed.

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