References and Notes

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Amine Quenching of Aromatic Fluorescence and Fluorescent Exciplexes[1]

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Abstract: Quenching of the fluorescence of naphthalene, a number of naphthalene derivatives, and fluorene by tertiary amines has been studied. In most cases fluorescent exciplexes are produced, although 1,4-diazabicyclo[2.2.2]octane (Dabco) quenches both naphthalene and fluorene very efficiently without producing any exciplex emission. Stern–Volmer constants for quenching, quantum yields and lifetimes for exciplex fluorescence, and shifts of exciplex emission with structural change and solvent properties have been measured. Most of the results can be rationalized qualitatively in terms of structures of the exciplexes involving extensive charge transfer from the amines to the aromatic fluors. Substituent effects on exciplex emission frequencies have been analyzed semiquantitatively as have solvent effects on emission frequencies. Both approaches indicate that the ionic character of the exciplexes is high, but less than 100%. Shifts in emission frequency are well correlated as a function of dielectric constant and polarizability for most solvents, although unexpectedly large red shifts are observed in 1,4-dioxane, benzene, and toluene. In the case of dioxane the anomaly is attributed to submolecular dipole–dipole interaction, and, in the case of the aromatic solvent, to the fact that internal pressures are higher than for aliphatic solvents. The data for mixed solvents consisting of cyclohexane with dioxane or tetrahydrofuran indicate preferential solvation of the exciplexes by the ethers.

There are many reported examples of the quenching of fluorescence of aromatic compounds by species which cannot function by simple transfer of electronic excitation energy because the quenchers do not have sufficiently low lying singlet excited states.[2-22] Two situations are encountered. In some cases, principally exemplified by the quenching of aromatic hydrocarbons by amines,[7-9,14-17] fluorescent exciplexes are formed and readily recognized by the appearance of broad, structureless emission shifted far to the red in comparison with the characteristic emission of the parent aromatic fluor. In other cases very efficient quenching occurs without the appearance of new emission. Familiar examples are quenching of the fluorescence of aromatic hydrocarbons by unsaturated hydrocarbons of rather simple structure.[2,3,5]

The evidence that the fluorescent exciplexes formed from the excited singlet states of aromatic compounds and tertiary amines derive much of their binding energy from charge transfer interaction[7-9,14] is supported by the large medium effects on the wavelengths of the exciplex emission and by the fact that in polar solvents dissociation to separated ion radicals occurs.[9,14,18] A recent example has been reported in which donor and acceptor roles of quencher and quenchee are reversed.[20]

Arguments based upon structure–reactivity relationships have been advanced to associate nearly all quenching without electronic energy transfer to charge-transfer interactions.[10-12]

This view has recently received added support by the observation that fluorescent exciplexes are formed from negatively substituted aromatic compounds and simple olefinic compounds.[12,20] However, we have previously pointed out[5] that there are large discontinuities in correlations of quenching reactivity with ionization potentials and electron affinities when series of compounds in different classes are compared.

In this paper we present the results of a kinetic study of quenching and exciplex emission in the interaction between naphthalenes and fluorene with triethylamine (TEA), *N*-methylpiperidine (NMP), and 1,4-diazabicyclo[2.2.2]octane (Dabco).

Results

In the absence of triethylamine the emission spectrum of naphthalene in cyclohexane shows two maxima at 325 and 344 nm with a shoulder at around 348 nm (Figure 1). In the presence of TEA, the intensity of the naphthalene fluorescence is reduced and simultaneously a new emission band, attributed to an exciplex, is observed. As is usually the case[13] the exciplex emission is structureless and red-shifted from the naphthalene emission with a maximum at 410 nm (Figure 1). Initially, as the quencher concentration increases, the intensity of the 410-nm maximum increases at the expense of the naphthalene fluorescence. Further increase in the quencher concentration results in a reduced intensity of this emission also. At sufficiently high concentration of triethylamine, the naphthalene fluorescence is almost completely quenched and the new
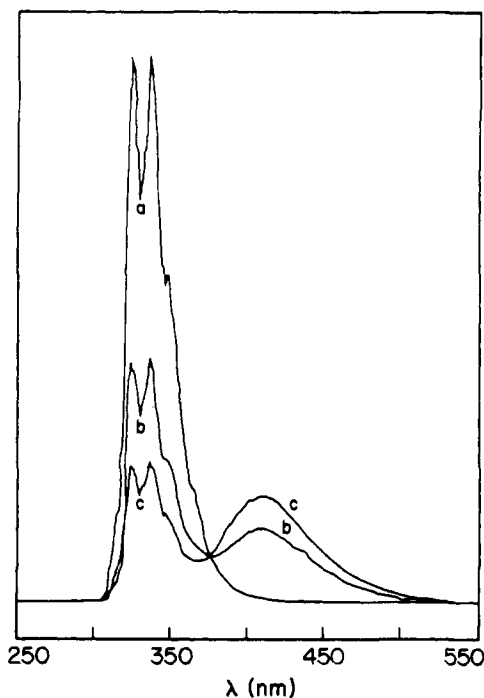
Figure 1. Naphthalene fluorescence quenching by TEA in degassed cyclohexane solution at room temperature. TEA concentration: a, 0.0 M; b, 0.006 M; c, 0.015 M.
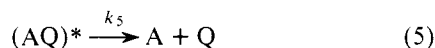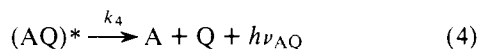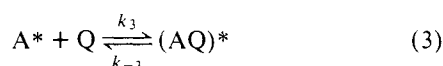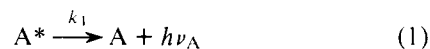
emission is symmetrical about the peak maximum. In all solutions the absorption spectrum of naphthalene is not perturbed in any significant way by triethylamine, excluding the possible formation of bound ground-state molecular complexes. Emission intensity does not change after prolonged irradiation.

The mechanism outlined below is found adequate to account for these experimental observations:

$$A^* \xrightarrow{k_1} A + h\nu_A \tag{1}$$

$$A^* \xrightarrow{k_2} A \tag{2}$$

$$A^* + Q \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} (AQ)^* \tag{3}$$

$$(AQ)^* \xrightarrow{k_4} A + Q + h\nu_{AQ} \tag{4}$$

$$(AQ)^* \xrightarrow{k_5} A + Q \tag{5}$$

$$(AQ)^* + Q \xrightarrow{k_6} A + 2Q \tag{6}$$
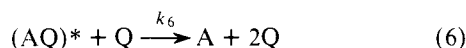
Exciplex Lifetimes. Solution of the rate equations for decay of A^* and $(AQ)^*$ is presented in Appendix A. The solutions given by eq 7 and 8 are appropriate for analysis of data from experiments with high quencher concentrations.

$$[A^*] = \frac{[A^*]_0}{k_1 + k_2 + k_3[Q] + k_{-3} - k_4 - k_5 - k_6 - k_6[Q]}$$
$$\times \{k_1 + k_2 + k_3[Q] - k_4 - k_5 - k_6[Q]\}$$
$$\times e^{-(k_1+k_2+k_3[Q]+k_{-3})t\} + k_{-3}e^{-(k_4+k_5+k_6[Q]t)} \tag{7}$$

$$[AQ^*] = \frac{k_3[A^*]_0[Q]}{k_1 + k_2 + k_3[Q] + k_{-3} - k_4 - k_5 - k_6[Q]}$$
$$\times \{e^{-(k_4+k_5+k_6[Q]t)} - e^{-(k_1+k_2+k_3[Q]+k_{-3})t}\} \tag{8}$$

At high concentrations of the quencher, emission from A^*

Table I. Exciplex Emission Lifetimes at High Concentrations of Quenchers

Quenchee	Quencher	$k_6 \times 10^8$, $M^{-1} s^{-1}$	$(k_4 + k_5) \times 10^7$, s^{-1}
Naphthalene	TEA	1.2	2.9
β-Fluoronaphthalene	TEA	1.5	5.2
β-Chloronaphthalene	TEA	1.4	13.7
β-Methylnaphthalene	TEA	0.5	4.1
Fluorene	TEA	0.5	12.7
Naphthalene	NMP	0.9	3.7
Fluorene	NMP	1.1	9.7

becomes immeasurably small while that of AQ^* is still substantial. Under these conditions eq 8 reduces to

$$[AQ^*] \simeq [A^*]_0 e^{-(k_4+k_5+k_6[Q]t)} \tag{9}$$

The lifetimes of the exciplex emissions (τ_{AQ}) were measured under these limiting conditions and the values of τ_{AQ}^{-1} were plotted against [Q]. The slopes of the Stern-Volmer plots give k_6 values and the intercepts give $(k_4 + k_5)$. The results are summarized in Table I.

Quantum Yields for Fluorescence. Relative quantum yields for emission from A^* were measured at low quencher concentrations where both emissions are important. The values of $k_6[Q]$ (see above) are low enough to permit neglect of reaction 6 in these experiments. A convenient parameter for use in analysis of the date is $C_{1/2}$, the concentration of quencher sufficient to reduce the quantum yield of fluorescence from $A^*(\Phi_{fA})$ to half its value in the absence of any quencher (Φ_{fA}^0). These are conditions such that the rates of decay of singlet excited states through A^* and AQ^* must be equal.

$$(k_1 + k_2)[A^*] = (k_4 + k_5)[AQ^*] \tag{10}$$

For purposes of interpreting steady-state phenomena such as quantum yields of emission, it is permissible to use the steady-state approximation to obtain a relationship between $[A^*]$ and $[AQ^*]$, although this would be entirely inappropriate for analysis of lifetimes. Consequently we write

$$[AQ^*] = \frac{k_3[A^*][Q]}{k_{-3} + k_4 k_5} \tag{11}$$

Combining eq 10 and 11 gives

$$C_{1/2} = \frac{(k_1 + k_2)(k_{-3} + k_4 + k_5)}{k_3(k_4 + k_5)} \tag{12}$$

The relative quantum yields for fluorescence of A^* and AQ^* (Φ_{fAQ}) were measured by comparison of the areas under the emission traces with no correction for variation in reflectance losses with wavelength. According to the mechanism the following relationships should hold.

$$\frac{\Phi_{fA}^0}{\Phi_{fA}} = 1 + \frac{[Q]}{C_{1/2}} \tag{13}$$

$$\frac{\Phi_{fAQ}}{\Phi_{fA}} = \frac{\Phi_{fAQ}^\infty[Q]}{\Phi_{fA}^0 C_{1/2}} \tag{14}$$

Equation 13 is the familiar Stern-Volmer equation. The usual Stern-Volmer constant, K_{SV}, is just $C_{1/2}^{-1}(k_1 + k_2)$. The limiting quantum yield for exciplex emission, Φ_{fAQ}^∞, is the extrapolated quantum yield which would be observed if reaction 6 did not occur. Values for quantum yields for fluorescence are available from the literature[23] for naphthalene (0.23), β-methylnaphthalene (0.32), and fluorene (0.80). Using the comparison method[24] we measured values for β-fluoronaphthalene (0.74) and β-chloronaphthalene (0.06). Figures 2

**Table II.** Data Derived from Fluorescence Yields in Cyclohexane Solution

Quenchee	Quencher	K_{SV}, M^{-1} s^{-1} $\times 10^9$	$C_{1/2}$, M	$\Phi^\infty_{fAQ}/\Phi^0_{fA}C_{1/2}$	Φ^∞_{fAQ}	$k_4 \times 10^7$, s^{-1}	$k_5 \times 10^7$, s^{-1}
Naphthalene	TEA	2.03	4.9×10^{-3}	120.0	0.13	0.4	2.5
β-Fluoronaphthalene	TEA	6.80	1.2×10^{-2}	40.4	0.35	1.9	3.3
β-Chloronaphthalene	TEA	3.78	7.2×10^{-2}	48.6	0.21	2.9	10.8
β-Methylnaphthalene	TEA	0.33	1.2×10^{-1}	4.1	0.15	0.6	3.5
Fluorene	TEA	1.67	9.6×10^{-2}	12.5	0.96	12.2	0.5
Naphthalene	NMP	0.32	3.1×10^{-2}	21.7	0.15	0.6	3.1
Fluorene	NMP	0.25	6.2×10^{-1}	1.9	0.92	8.9	0.8
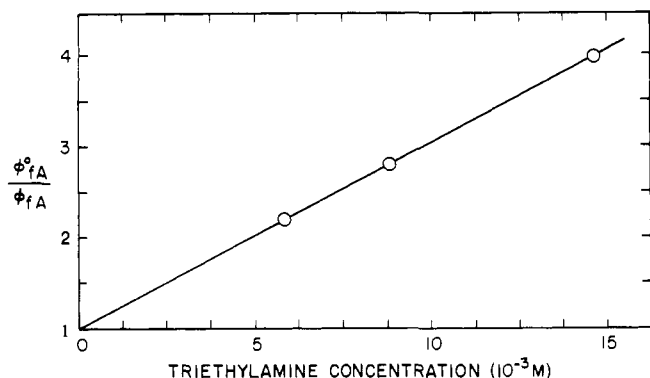
Figure 2. Stern–Volmer plot of naphthalene fluorescence quenching by TEA in degassed cyclohexane solution.

Figure 3. Ratio of fluorescence quantum yield from the exciplex to that from naphthalene as a function of TEA concentration.

and 3 show typical plots of data according to eq 13 and 14. Since $k_4 = \Phi^\infty_{fAQ}(k_4 + k_5)$ and $k_5 = (1 - \Phi^\infty_{fAQ})(k_4 + k_5)$ the two unimolecular rate constants can be extracted by combination of the quenching data with the information in Table I. Table II summarizes all of the derived quantities of interest.

We have treated all of the data by assuming steady-state kinetic conditions. As has been noted by many workers and discussed in depth by Hui and Ware[15,16] the observed results can be considerably distorted by transient effects arising from fast interactions between newly created excited states and closely neighboring quencher molecules. The "slow" phenomena discussed in this paper—fluorescence lifetimes and quantum yields for fluorescence—occur in a time frame such that they are likely to be very little perturbed by transient effects. Interpretation of the higher values of K_{SV} might be modestly altered by their inclusion.

Quenching by Dabco. Dabco (**1**) quenches fluorescence of

1
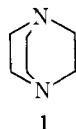
both naphthalene and fluorene very efficiently. However, no exciplex emission is observed under any conditions. Consequently analyses such as have been described for TEA and NMP cannot be carried out. Stern–Volmer treatment of quenching data gives quenching constants in the range usually considered to be diffusion controlled—8.6×10^9 M^{-1} s^{-1} for naphthalene and 11.7×10^9 M^{-1} s^{-1} for fluorene.

Exciplex Emission Energies. TEA exciplexes derived from naphthalene and its derivatives show systematic shifts in energy. Electron-donating substituents shift the emission to higher energy, and electron-accepting substituents produce red shifts. The influence of α substituents is quantitatively greater than that of β substituents, although the direction of shift is always the same for a given substituent irrespective of its point of attachment to the naphthalene nucleus. Table III
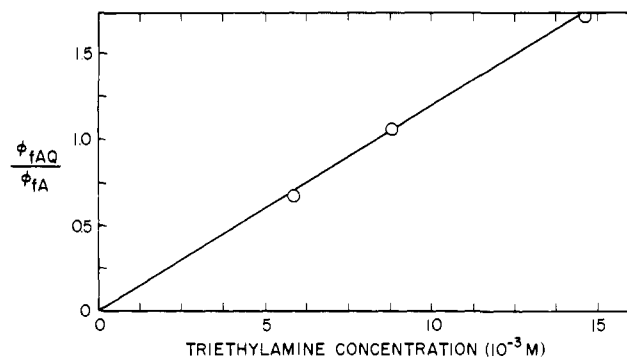
shows the positions of the maxima of the exciplex emissions for the compounds included in our study.

Solvent Effects. The exciplex emission frequencies are highly solvent dependent as has been reported by other authors.[8,10,17] Table IV displays illustrative data for the naphthalene and fluorene complexes with TEA.

As will be shown later the red shifts of the exciplex emissions in the same solvents are much larger than would be expected on the basis of bulk polarizability alone. Because the effects are surely due to micro solvent structure in the vicinity of an exciplex, we studied the shifts for the naphthalene–TEA exciplex in mixed solvent systems consisting of cyclohexane with tetrahydrofuran (THF) and 1,4-dioxane (dioxane). As is shown by Figures 4 and 5 the solvent shifts are not linear functions of the mole fractions of the mixtures.

Discussion

Quenching Constants. With TEA as the quencher the values of K_{SV} for naphthalene and its derivatives vary as might be intuitively expected. The electron-attracting halogen substituents increase quenching rates whereas a methyl group decreases the rate. In fact, a plot of log K_{SV} against Hammett's σ_m constants (not shown) shows a very respectable linear relationship. The positive ρ value indicates that the quenchees

Table III. Emission Maxima of Substituted Naphthalene–TEA Exciplexes in Cyclohexane Solution at Room Temperature

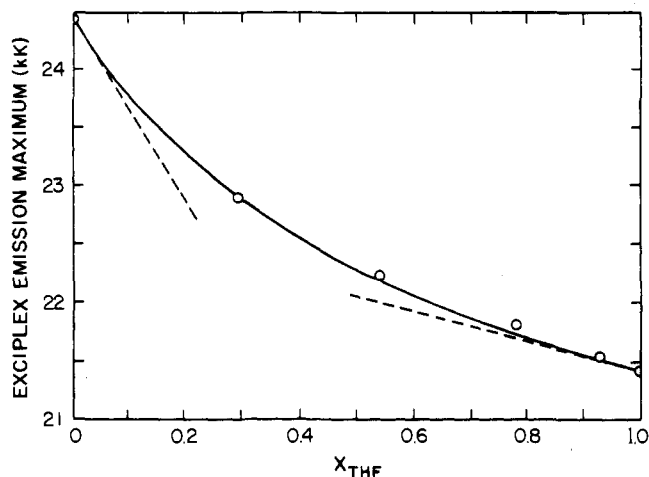|	Quenchee	Exciplex emission maximum, μm^{-1}
1	Naphthalene	2.440
2	α-Methylnaphthalene	2.462
3	β-Methylnaphthalene	2.453
4	α-Fluoronaphthalene	2.395
5	β-Fluoronaphthalene	2.398
6	α-Chloronaphthalene	2.312
7	β-Chloronaphthalene	2.352
8	α-Naphthonitrile	2.095
9	β-Naphthonitrile	2.198

Figure 4. Plot of naphthalene-TEA exciplex emission maxima vs. the mole fraction of tetrahydrofuran in tetrahydrofuran-cyclohexane mixed solvent.
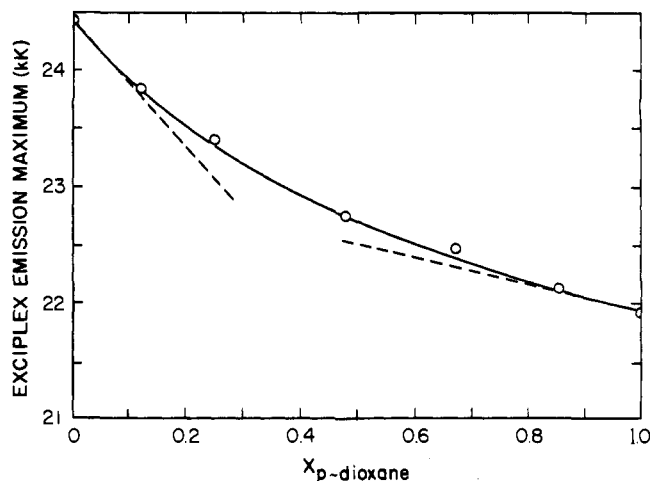

Figure 5. Plot of naphthalene-TEA exciplex emission maxima vs. the mole fraction of dioxane in dioxane-cyclohexane mixed solvent.

Table IV. Naphthalene-TEA and Fluorene-TEA Exciplex Emission Maxima in Different Solvents

| | | Exciplex emission maximum, μm^{-1} | |
	Solvent	Naphthalene-TEA	Fluorene-TEA
1	n-Hexane	2.464	2.643
2	n-Heptane	2.457	2.629
3	Cyclopentane		2.610
4	Cyclohexane	2.440	2.595
5	Cyclohexene	2.430	2.583
6	1,4-Cyclohexadiene	2.357	2.499
7	Di-n-butyl ether	2.338	2.478
8	Diisopropyl ether	2.295	2.458
9	Toluene	2.278	2.453
10	Benzene	2.272	2.442
11	Diethyl ether	2.263	2.441
12	1,4-Dioxane	2.195	2.372
13	1,1-Dichloroethane	2.180	2.363
14	Tetrahydrofuran	2.144	2.284
15	Dichloromethane	2.132	2.294
16	1,2-Dimethoxyethane	2.126	2.269
17	Acetonitrile	a	a
18	Ethanol	a	a

[a] No exciplex emission observed.

serve as electron acceptors. The same kind of Hammett correlation has been observed in the quenching of 1,4-dimethoxybenzene fluorescence by para-substituted benzyl chlorides, a process in which the quenchers are believed to serve as the electron acceptors.[19]

Precise interpretation of the result is not possible since K_{SV} is a complex function, $k_3(k_4 + k_5)/(k_{-3} + k_4 + k_5)$. If k_{-3} is small in comparison with $k_4 + k_5$, the Stern-Volmer constants would be simple rate constants for formation of the exciplexes. All of the quenching constants involving TEA and NMP in cyclohexane are lower than those involving Dabco in the same solvent. Consequently the TEA and NMP rates must be less than diffusion controlled, which allows, but does not demand, the hypothesis that k_{-3} makes some contribution to the observed rate variations. We note that there is no regular correlation between K_{SV} and the quantity $(k_4 + k_5)$, a result which would be easily understood if exciplex formation were irreversible in all cases, making the quenching rates independent of the dynamics of exciplex decay.

Since charge transfer is obviously important in the exciplexes, structural change in the quenchees that make their

electron affinities more favorable would be expected to increase rates irrespective of whether rate variation reflects small barriers to exciplex production ($K_{SV} \simeq k_{-3}$) or binding energies in the exciplexes ($k_{-3} > (k_4 + k_5)$).

The lack of any detectable exciplex emission from Dabco with either naphthalene or fluorene indicates that complexes formed from the diamine must have values of k_5 much larger than those of k_4. The phenomenon may be related to quenching of exciplex emission by high concentrations of TEA. We believe that these rapid nonradiative decay processes are related to the formation of radical ion pairs in polar solvents.[9] Complete electron transfer can be followed not only by separation of the ions but also by production of triplets.[14,17] We would formulate the quenching reaction in nonpolar solvent as follows:

$$AQ^* + Q \rightarrow A^- \cdots Q_2^+ \rightarrow {}^3A^* + 2Q \qquad (15)$$
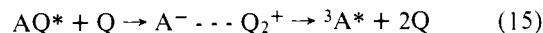
In Dabco, delocalization of the positive charge between the two nitrogen atoms might similarly facilitate very rapid decay to triplets.

We are frankly puzzled by the low quenching reactivity of NMP compared with TEA with both naphthalene and fluorene—a factor of about 6.5 in K_{SV} in both cases. If steric accessibility of the nitrogen in the amine were an important factor, we would expect NMP to be the more reactive. We offer no rationalization since none of merit has occurred to us.

Polarity of the Exciplexes. As has been discussed by many other authors,[9,14,18] the fluorescent exciplexes must be very polar species. We can, in principle, formulate wave functions for the exciplexes with at least the four terms of the equation

$$\psi_{exciplex} = c_1\psi(A^*Q) + c_2\psi(AQ^*)$$
$$+ c_3\psi(A^-Q^+) + c_4\psi(A^+Q^-) \quad (16)$$

The second term in the expansion represents excitation resonance and the last two represent charge transfer interaction. Because of the unfavorable electron affinities of saturated amines there is little question about considering c_4 to be negligibly small. Neglect of $c_2\psi(AQ^*)$ is less justified, because amines have relatively low-lying excited states.[25] However, we will tentatively assume that excitation resonance can be ignored and write in terms of a two-term wave function.

$$\psi_{exciplex} = c_1\psi(A^*Q) + c_3\psi(A^-Q^+) \qquad (17)$$

We have two ways of estimating the polarities of the exciplexes. The first involves comparison of the transition moments of the exciplexes derived from naphthalene and its derivatives
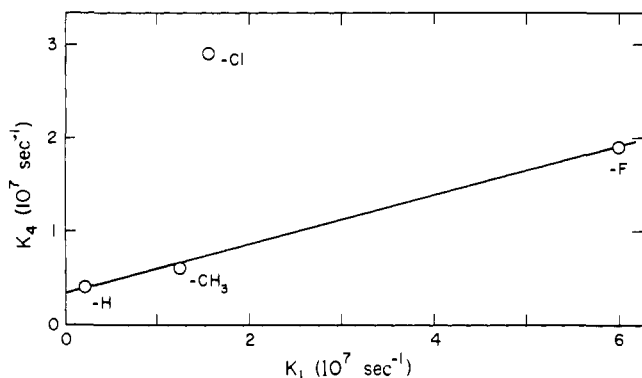
Figure 6. Linear relationship between exciplex and quenchee emission probabilities for β-substituted naphthalene–triethylamine exciplexes in degassed cyclohexane solution.

with those of the parent aromatic compounds. The second depends upon the variation in the emission frequencies of naphthalene–TEA and fluorene–TEA complexes as a function of solvent polarizability.

The transition moment for an exciplex is

$$M = \langle \psi_{exciplex} | er | \psi_0(AQ) \rangle \qquad (18)$$

where $\psi_0(AQ)$ is the ground-state wave function. Using the two-term wave function we can approximate the square of the transition moment

$$|M|^2 = c_1{}^2 \langle \psi(A*Q) | er | \psi_0(AQ) \rangle^2$$
$$+ c_3{}^2 \langle \psi(A^-Q^+) | er | \psi_0(AQ) \rangle^2 \qquad (19)$$

Since the transition moment for the quenchee emission is approximately equal to $\langle \psi(A*Q) | er | \psi(AQ) \rangle$, we expect a linear relationship between the rate constants for emission from the exciplexes and the quenchees:

$$k_4 = c_1{}^2 k_1 + c_3{}^2 k_{CT} \qquad (20)$$

where k_{CT} is the contribution of the exciplex emission probability arising from the charge transfer configuration of the exciplex state to the ground state. Figure 6 shows a plot of k_1 vs. k_4 for the naphthalenic compounds. The expected linear relationship seems to be observed with three compounds, although β-chloronaphthalene deviates badly, having an exceptionally large value of k_4. The slope of the line drawn through the other three data points is 0.26. From eq 20 we see that the slope should equal $c_1{}^2$. This indicates that c_1 is 0.51 and c_2 is 0.86, which is tantamount to assigning 74% ionic character to the exciplexes.

The polar exciplexes should have large dipole moments whereas the ground-state molecules have relatively small dipoles. As has been discussed by others,[6,9,12] changes in solvent–solute interaction should affect the energies of excited states more than those of the ground states. Methods for quantitative treatment of polar solvent effects have been reviewed recently.[26,27] We have followed the approach of McRae[28] and Ooshika.[29] We use their formulation to write down the energies associated with a solute dipole, interacting with solvent dipoles and induced dipoles. If we ignore interaction of the ground states with solvents, the expression for solvent effects on the excited states can be translated into frequency shifts for emissions in solvents as compared to gas phase:

$$\tilde{\nu}_s = \tilde{\nu}_g - \frac{\mu^2}{hca^3}\left[2\left(\frac{\epsilon - 1}{2\epsilon + 1}\right) - \frac{n^2 - 1}{2n^2 + 1}\right] \qquad (21)$$

where $\tilde{\nu}_s$ and $\tilde{\nu}_g$ are emission frequencies in solution and in the gas phase, μ is the dipole moment of the exciplex, a is the radius of a spherical cavity occupied by the molecule, h is Planck's
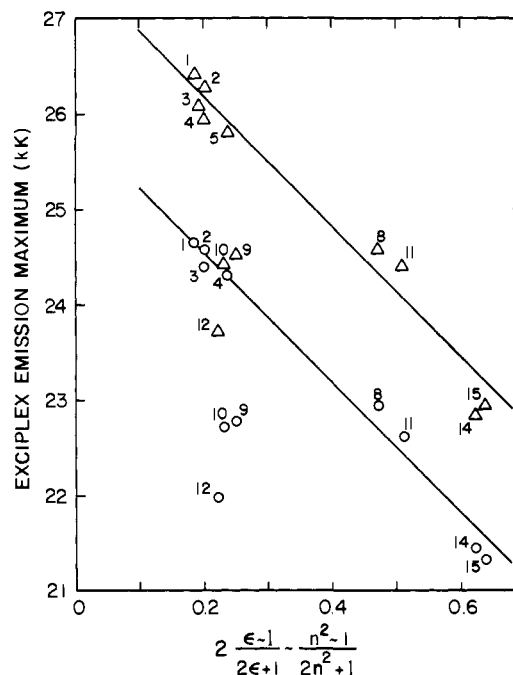

Figure 7. Plot of exciplex emission maxima vs. the function $2(\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 1)$, where ϵ and n are the dielectric constant and refractive index of the solvent at room temperature. O = NT exciplex. $\triangle$ = FT exciplex. The numbers correspond to the entries in Table IV. A few solvents of Table II are omitted from this plot for lack of dielectric constant data.

constant, c is the velocity of light, and ϵ and n are the dielectric constant and refractive index of the solvent. The onset of emission is not readily determined because of the broadness of the emission and because of the overlap with the emission of the parent species. Consequently we used the frequencies of emission maxima as a measure of $\tilde{\nu}_s$. Figure 7 shows a plot of the data from naphthalene–TEA and fluorene–TEA in solvents for which ϵ and n are known. The correlations are reasonably good with the exception of dioxane, benzene, and toluene. The slopes of the lines drawn in Figure 7 are the same, indicating that the naphthalene and fluorene exciplexes have similar dipole moments. The similarity is also indicated by Figure 8, in which $\tilde{\nu}_s$ values for the two series of exciplexes in all solvents are plotted against each other. If we assume that a is 4.5 Å we estimate dipole moments of 11.1 D for the exciplexes, the same as obtained by Kuzmin and Guseva[6] for naphthalene–TEA using a similar analysis. If the value assumed by Kuzmin for the dipole moment with complete electron transfer (17 D) is correct the value derived from experiment again indicates about 65% electron transfer in the exciplex. The result is of limited significance because of the arbitrary assumptions concerning geometry used for the calculation. However, the agreement is probably fortuitous in view of the crude assumptions and approximations put into both treatments. We can only state that both analyses are compatible with the view that the exciplexes are highly, but not completely, ionic.

The unexpectedly large red shifts in 1,4-dioxane, benzene, and toluene are worthy of note since they indicate that bulk polarizability is not a unique predictor of solvent effects. This is not at all surprising since it has long been known that short-range intermolecular interactions may become of great importance in solvation phenomena. We suggest two different approaches to rationalizing the results depending on whether or not the solvent molecules contain polarized bonds.

Dioxane as a solvent does not accommodate to the predictions whereas diethyl ether (DEA) and THF do. However, we
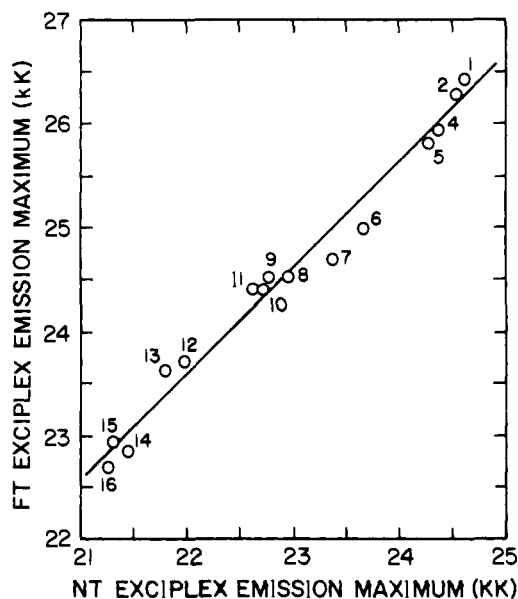
Figure 8. Linear relationship between fluorene-TEA(FT) exciplex emission maximum and naphthalene-TEA(NT) exciplex emission maximum in different solvents.

note that the emission frequencies in all three ether solvents are rather closely grouped. The noncorrelation occurs because THF and DEA have higher dielectric constants than dioxane, which has no permanent electric dipole. This suggests that in the microenvironment of the polar exciplexes dioxane behaves like the other ethers by presenting the negative end of the COC dipoles toward the positively charged partner in the exciplex. There may also be some local interaction between the positive ends of the group moments and the negatively charged moiety. The postulate also casts doubt on the precision of the analysis of dipole–dipole interactions based in terms of bulk dielectric constants.

As a limited test of the validity of associating dioxane with THF and DEA, we carried out a series of measurements in solvent mixtures of THF and dioxane with cyclohexane. Comparison of Figures 4 and 5 shows that there is qualitatively similar nonlinear behavior in the two cases. Apparently the composition of the medium in the vicinity of the exciplexes is not representative of that in the bulk liquid in both cases. The strong initial effects of adding ethers to the hydrocarbon indicate that the exciplex tends to selectively concentrate ether molecules as near neighbors.

The ratio of the mole fractions of ethers in the vicinity of exciplexes to mole fractions in solution can be approximated by the equation[30]

$$(X_1/X_2) = (X_1^0/X_1^0)10^\alpha \qquad (22)$$

where X_1 and X_1^0 are mole fractions of D or THF near the exciplex and in bulk, X_2 and X_2^0 are similar quantities for cyclohexane, and α is the *index of preferential solvation* for the exciplex.

If the solvation energy of an exciplex in the mixed solvent is attributed to contributions from both solvent components, each proportional to the mole fraction around the exciplex, we can write eq 23 and 24 relating emission frequencies in mixed solvents to those in pure liquids:

$$(\tilde{\nu}_g - \tilde{\nu}_{MS}) = X_1(\tilde{\nu}_g - \tilde{\nu}_1) + X_2(\tilde{\nu}_g - \tilde{\nu}_2) \qquad (23)$$

$$\tilde{\nu}_{MS} = X_1\tilde{\nu}_1 + X_2\tilde{\nu}_2 \qquad (24)$$

where $\tilde{\nu}_{MS}$ is the emission frequency in mixed solvent and $\tilde{\nu}_1$ and $\tilde{\nu}_2$ are frequencies in the two pure solvents. Substitution of eq 22 into eq 24 gives

Table V. Naphthalene-TEA Exciplex Emission Maximum in THF-Cyclohexane Mixed Solvent

Mole fraction of THF (X_1^0)	Exciplex emission maximum, μm^{-1}	
	Exptl	Calcd[a]
0.00	2.440	2.440
0.29	2.290	2.290
0.54	2.226	2.218
0.78	2.182	2.173
0.93	2.154	2.152
1.00	2.144	2.144

[a] Calculated by eq 25.

Table VI. Naphthalene-TEA Exciplex Emission Maximum in Dioxane-Cyclohexane Mixed Solvent

Mole fraction of dioxane (X_1^0)	Exciplex emission maximum, μm^{-1}	
	Exptl	Calcd[a]
0.00	2.440	2.440
0.12	2.383	2.383
0.25	2.339	2.338
0.48	2.275	2.277
0.67	2.247	2.240
0.85	2.211	2.212
1.00	2.195	2.195

[a] Calculated by eq 25.

$$\tilde{\nu}_{MS} = \frac{X_1^0\tilde{\nu}_1 10^\alpha + (1 - X_1^0)\tilde{\nu}_2}{1 + (10^\alpha - 1)X_1^0} \qquad (25)$$

From eq 25 we obtain two tangents at $X_1^0 = 0$ and 1.

$$\left\{\frac{\partial\tilde{\nu}_{MS}}{\partial X_1^0}\right\}_{X_1^0 \to 0} = (\tilde{\nu}_1 - \tilde{\nu}_2)10^\alpha \qquad (26)$$

$$\left\{\frac{\partial\tilde{\nu}_{MS}}{\partial X_1^0}\right\}_{X_1^0 \to 1} = (\tilde{\nu}_1 - \tilde{\nu}_2)10^{-\alpha} \qquad (27)$$

The index of preferential solvation, α, is calculated from the ratio of the experimental slopes. For the naphthalene-TEA complex in THF-cyclohexane α is equal to 0.40 and in dioxane-cyclohexane α is 0.33. From the emission maxima in the pure solvents and α one can calculate values of maxima in mixed solvents. Tables V and VI show the comparison of experimental and calculated values which indicate that a single preferential solvation parameter is adequate to fit data of the entire composition ranges.

In an excellent treatment of the solute-solvent interaction in mixed solvents, Yoshino showed that the index of preferential solvation is $\Delta E/2.3nRT$, where ΔE is the difference of solvation energies of the solute in two pure components of the mixed solvent and n is the number of solvent molecules surrounding each solute molecule.[30] The difference of the exciplex emission maxima in two component solvents is taken as the difference of solvation energies. For $n = 15.5$, we have calculated an α value of 0.40 for the THF-cyclohexane mixed solvent and 0.33 for the dioxane-cyclohexane mixed solvent, identical with the experimentally determined α values. This suggests that there are about 16 solvent molecules surrounding each exciplex, a quite reasonable solvation number. A similar solvent sorting explanation has recently been advanced for nonlinear effects on rates of ionic dissociation of exciplexes in mixed solvents.[22]

Some alternative explanation must be sought for the deviant behavior of benzene and toluene. A factor which we have neglected is the change in molar volume of solutes which must occur when exciplexes are formed. Johnson and Offen[31] reported a volume change of -11 cm^3/mol at 296 K on forma-

tion of the pyrene excimer. Even larger volume changes would be expected to accompany formation of highly polar exciplexes because of electrostriction effects. Two typical solvents which obey eq 21, DEA and *n*-heptane, have very similar internal pressures, 2370 and 2510 atm, respectively.[32] The internal pressure of benzene is much larger, 3640 atm.[30] Radiative decay of the exciplexes is a Franck-Condon process so ground-state AQ will be produced under compression. These solvent compression energies will increase as the internal pressures of the solvents increase. Increasing the compression energies should give red shifts in the emission. Unfortunately good data for internal pressures are not available for many of our solvents, but it is likely that they are rather similar for saturated hydrocarbons, ethers, and perhaps chlorinated hydrocarbon, with benzene and toluene falling in a class by themselves.

Conclusions

Comparison of quenching rates, exciplex fluorescence lifetimes, and variation of exciplex emission maxima with structure and solvent all lead to the conclusion that the exciplexes formed from fluorescent aromatic compounds and tertiary amines are highly polar species. The amount of ionic character in the complexes is, however, probably less than 100%.

The naphthalene-TEA exciplex is itself quenched by very high concentrations of TEA. It is proposed that the second mole of amine facilitates complete electron transfer to the naphthalene by formation of an $(Et_3N)_2^+ \cdot$ aggregate, thus providing a fast path for nonradiative decay. Very fast quenching with no detectable exciplex formation by Dabco, a diamine, is probably a related phenomenon.

We find a reasonable correlation of solvent shifts of exciplex emission frequencies with solvent dielectric constant and polarizability. However, there are deviant cases which require special rationalization.

Experimental Section

Materials. Cyclohexane was stirred over concentrated sulfuric acid until the acid layer was not discolored, washed with distilled water, dried over magnesium sulfate, and distilled over metallic sodium through a column packed with glass beads. A middle fraction was collected. Naphthalene, β-fluoronaphthalene, β-chloronaphthalene, and β-methylnaphthalene were recrystallized twice from methanol and sublimed. α-Naphthonitrile was recrystallized from *n*-hexane and sublimed. α-Methylnaphthalene, α-fluoronaphthalene, and α-chloronaphthalene were purified by several vacuum distillations over lithium aluminum hydride with middle fractions being collected each time. Fluorene was recrystallized six times from ethanol and sublimed. Triethylamine (TEA) was refluxed with acetic anhydride and distilled. The distillate was further purified by distillation over barium oxide and metallic sodium, and stored over fresh sodium. TEA was redistilled over sodium just before the sample preparation. *N*-Methylpiperidine (NMP) was prepared according to the procedure of Clark et al.[33] and purified as triethylamine. 1,4-Diazabicyclo[2.2.2]octane (Dabco) was purified by sublimation. Cyclohexane, *n*-hexane, and *n*-heptane were purified as before. Benzene and toluene were purified as described elsewhere.[34] Cyclohexene was distilled over sodium through a column packed with glass beads. 1,4-Cyclohexadiene (Aldrich) was used as received. All ethereal solvents were purified by distillation over either sodium or lithium aluminum hydride. Dichloromethane and 1,1-dichloroethane were stirred with concentrated sulfuric acid until the acid layer was not discolored, washed with distilled water, dried over calcium chloride, and distilled over phosphorus pentoxide. Spectroquality acetonitrile and absolute ethanol were used without further purification.

Measurements. Fluorescence spectra were taken on an Aminco-Bowman spectrophotofluorometer at room temperature. Fluorescence lifetimes were measured with a TRW Model 31A nanosecond spectral source coupled with a TRW Model 32A decay time computer to simulate the fluorescence decay on a Tektronix Type 556 dual beam oscilloscope. Fluorescence spectra were taken on an Aminco-Bowman

spectrophotofluorometer at room temperature. The exciplex emission maxima were determined with reference to mercury lines.

Samples were prepared in 13×100 nm Pyrex test tubes using 3-mL solutions with varying concentrations of the quencher, and were degassed by three freeze-pump-thaw cycles at less than 5×10^4 Torr.

Appendix A

Using the mechanism of eq 1-6 we can formulate the rates of change of [A*] and [AQ*] as follows:

$$d[A^*]/dt = -(k_1 + k_2 + k_3 C)[A^*] + k_{-3}[AQ^*]$$
$$= -X[A^*] + k_{-3}[AQ^*] \quad (A1)$$

$$d[AQ^*]/dt = k_3 C[A^*] - (k_{-3} + k_4 + k_5 + k_6 C)[AQ^*]$$
$$= k_3 C[A^*] - Y[AQ^*] \quad (A2)$$

where C is the concentration of quencher. To solve these two linear equations, we assume

$$[A^*] = A e^{-\lambda t} \text{ and } [AQ^*] = B e^{-\lambda t} \quad (A3)$$

Substituting eq A3 into eq A1 and A2 we obtain

$$(\lambda - X)A + k_{-3}B = 0$$
$$k_3 C A + (\lambda - Y)B = 0 \quad (A4)$$

For a nontrivial solution of A and B, the determinant of coefficients must be zero. We obtain the characteristic equation

$$(\lambda - X)(\lambda - Y) - k_{-3}k_3 C = 0$$

or $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad (A5)$

$$\lambda^2 - (X + Y)\lambda + XY - k_{-3}k_3 C = 0$$

Two roots for the algebraic equation A5 are

$$\lambda_{1,2} = \frac{1}{2}\{(X + Y) \pm \sqrt{(X + Y)^2 - 4XY + 4k_{-3}k_3 C}\}$$
$$= \frac{1}{2}\{(X + Y) \pm \sqrt{(X - Y)^2 + 4k_{-3}k_3 C}\} \quad (A6)$$

From eq A4 we have

$$B_1 = (X - \lambda_1)A_1/k_{-3} \quad (A7)$$

when $\lambda = \lambda_1$. Similarly we have

$$B_2 = (X - \lambda_2)A_2/k_{-3} \text{ for } \lambda = \lambda_2 \quad (A8)$$

We have the general solution for [A*] and [AQ*]

$$[A^*] = A_1 e^{-\lambda_1 t} + A_2 e^{-\lambda_2 t}$$
$$[AQ^*] = B_1 e^{-\lambda_1 t} + B_2 e^{-\lambda_2 t} \quad (A9)$$

$$= (1/k_{-3})\{(X - \lambda_1)A_1 e^{-\lambda_1 t} + (X - \lambda_2)A_2 e^{-\lambda_2 t}\}$$
$$(A10)$$

Applying the initial conditions that at time $t = 0$ [A*] = [A*]$_0$ and [AQ*] = 0 we obtain[*]

$$(1/k_{-3})\{(X - \lambda_1)A_1 + (X - \lambda_2)A_2\} = 0$$

$$A_2 = -\frac{X - \lambda_1}{X - \lambda_2}A_1 \quad (A11a)$$

$$A_1 + A_2 = [A^*]_0 \quad (A11b)$$

Combining eq A11a and A11b we have

$$A_1 = \frac{X - \lambda_2}{\lambda_1 - \lambda_2}[A^*]_0 \text{ and } A_2 = \frac{\lambda_1 - X}{\lambda_1 - \lambda_2}[A^*]_0 \quad (A12)$$

Substituting eq A12 into eq A9 we have the decay equation for aromatic hydrocarbon emission.

$$[A^*] = \frac{[A^*]_0}{\lambda_1 - \lambda_2}\{(X - \lambda_2)e^{-\lambda_1 t} + (\lambda_1 - X)e^{-\lambda_2 t}\} \quad (A13)$$

Substituting eq A12 into eq A10 we have the decay equation for the exciplex emission.

$$[AQ^*] = \frac{[A^*]_0}{\lambda_1 - \lambda_2} \frac{(X - \lambda_2)(X - \lambda_1)}{k_{-3}} \{e^{-\lambda_1 t} - e^{-\lambda_2 t}\} \quad (A14)$$

Equation A14 can be simplified by using relationships from eq A5 and A6 such that

$$\lambda_1 + \lambda_2 = X + Y \text{ or } \lambda_1 - Y = X - \lambda_2$$

$$(\lambda_1 - X)(\lambda_1 - Y) - k_3 k_{-3} C = 0$$

We have

$$\frac{(X - \lambda_1)(X - \lambda_2)}{k_{-3}} = -k_3 C$$

Consequently, eq A14 becomes

$$[AQ^*] = \frac{[A^*]_0}{\lambda_1 - \lambda_2} k_3 C \{e^{-\lambda_2 t} - e^{-\lambda_1 t}\} \quad (A15)$$

To test the validity of eq A13 and A15 assume $C = 0$, no quencher present.

$$X = k_1 + k_2, \quad Y = k_{-3} + k_4 + k_5$$

$$\lambda_{1,2} = \frac{1}{2}\{(X + Y) \pm \sqrt{(X - Y)^2}\}$$

$$\lambda_1 = X, \quad \lambda_2 = Y$$

We obtain

$$[A^*] = [A^*]_0 e^{-(k_1 + k_2)t}$$

$$[AQ^*] = 0 \qquad \text{Q.E.D.}$$

For very high concentration of quencher, $c \to \infty$, we approximate $\lambda_{1,2}$ as follows:

$$\sqrt{(X - Y)^2 + 4k_{-3}k_3 C} = \{(k_1 + k_2 + k_3 C - k_{-3} - k_4 - k_5 - k_6 C)^2 + 4k_{-3}k_3 C\}^{1/2}$$

$$= k_3 C \left\{ \left((1 - \frac{k_6}{k_3} + \frac{k_1 + k_2 + k_{-3} - k_4 - k_5}{k_3 C} \right)^2 + 4 \frac{k_{-3}}{k_3 C} \right\}^{1/2}$$

$$\simeq k_3 C \left\{ 1 - 2\frac{k_6}{k_3} + 2\frac{k_1 + k_2 + k_{-3} - k_4 - k_5}{k_3 C} + 4\frac{k_{-3}}{k_3 C} \right\}^{1/2}$$

$$= k_3 C \left\{ 1 - 2\frac{k_6}{k_3} + 2\frac{k_1 + k_2 + k_{-3} - k_4 - k_5}{k_3 C} \right\}^{1/2}$$

$$\simeq k_3 C \left\{ 1 - \frac{k_6}{k_3} + \frac{k_1 + k_2 + k_{-3} - k_4 - k_5}{k_3 C} \right\}$$

$$= k_1 + k_2 + k_{-3} + k_3 C - k_4 - k_5 - k_6 C$$

where we also use the assumption $k_3 \gg k_6$. Therefore, we have

$$\lambda_1 = k_1 + k_2 + k_3 C + k_{-3}$$

$$\lambda_2 = k_4 + k_5 + k_6 C$$

Substituting into eq A13 we have

$$[A^*] = \frac{[A^*]_0}{k_1 + k_2 + k_3 C + k_{-3} - k_4 - k_5 - k_6 C}$$

$$\times \{(k_1 + k_2 + k_3 C - k_4 - k_5 - k_6 C)e^{-(k_1 + k_2 + k_3 C + k_{-3})t} + k_{-3}e^{-(k_4 + k_5 + k_6 C)t}\} \quad (A16)$$

Substituting into A15 we have

$$[AQ^*] = \frac{[A^*]_0 k_3 C}{k_1 + k_2 + k_3 C + k_{-3} - k_4 - k_5 - k_6 C}$$

$$\times \{e^{-(k_4 + k_5 + k_6 C)t} - e^{-(k_1 + k_2 + k_3 C + k_{-3})t}\} \quad (A17)$$

Again for very large quencher concentration, $C \to \infty$, in eq A16 the first term approximates zero because of the exponential factor and the second term is also approximately zero. Therefore, we have

$$[A^*] \simeq 0 \qquad (A18)$$

In eq A17, the second exponential factor approaches zero much faster than the first exponential factor. Therefore, we have as a limit

$$[AQ^*] \simeq [A^*]_0 e^{-(k_4 + k_5 + k_6 C)t} \qquad (A19)$$

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