Charge-Transfer Quenching of Singlet Excited Complexes

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Abstract: Rate constants in benzene for quenching of several singlet exciplexes, the pyrene excimer, and the corresponding excited monomeric arenes by organic one-electron donors and acceptors are reported. The results can be explained by a frontier orbital treatment, leading to a semiquantitative picture from which order-of-magnitude quenching rates for any exciplex or excimer by any donor can be predicted in principle. In some cases, exciplex substitution occurs, and new emissions are seen as a result of the quenching. The implications of these results for possible termolecular photochemistry are discussed.

Introduction

Exciplexes, MQ_1^*, and excimers, MM^*, have long been known to result from numerous bimolecular photochemical quenching events.[3]

$$M^* + Q_1 \rightleftharpoons MQ^* \qquad (1)$$

$$M^* + M \rightleftharpoons MM^* \qquad (2)$$

The photophysics of exciplexes and excimers is thoroughly worked out.[3-5] For several years, we have been interested in determining their chemistry, i.e., the role of these species as reaction intermediates. Our previous demonstrations[6-10] of exciplexes as obligatory intermediates in certain bimolecular photoreactions utilized *exciplex quenching* as the critical tool. When certain compounds were added to reaction mixtures, exciplex fluorescence and photoproduct were attenuated to the same extent, demonstrating the intermediacy of the exciplex in the reaction. Our first few exciplex quenchers were not selected systematically, yet patterns of quenching efficiency clearly emerged.[11]

$$MQ_1^* \rightarrow \text{products P} \qquad (3)$$

$$MQ_1^* + Q_2 \rightarrow \text{quenching of P} \qquad (4)$$

Exciplex quenching is potentially a powerful tool for examining the intermediacy of exciplexes in the arbitrary bimolecular photoreaction. Others have utilized the technique,[12] especially[12a,b,d,e] after our preliminary communications[7,8,11,13] had appeared. We thought it important to understand the factors which affect the rate constants for exciplex quenching, since this would greatly enhance its utility as a mechanistic tool and since a number of termolecular photochemical and photophysical processes are known in the literature.[14-30] We here present a thorough kinetic study of the process, with examples of widely differing types. Exciplexes, excimers, and the corresponding excited monomers (all as singlets) have been quenched by various electron donors and acceptors. The results can be rationalized with a simple FMO model,[13] and semiquantitative predictions from the model are successfully made. During the course of our study, a new photoprocess, exciplex substitution,[14] was observed and is described.

Methods and Results

The exciplexes studied form upon quenching of arene fluorescence by alkenes or amines. Pyrene excimer was the only excimer studied. All excited complexes were emissive. The arenes were polycyclic and included several with polar substituents. Alkenes were electron poor (esters and nitriles) or electron rich (styrene derivatives). Exciplex quenchers were also amines or alkenes, with the one exception of dimethyl acetylenedicarboxylate. A list of all compounds and the abbreviations we use is given separately.

Compounds Used and Their Abbreviations

Arenes

Phenanthrene (P)
Pyrene
Anthracene
9-Cyanophenanthrene (9CNP)
3,10-Dicyanophenanthrene (3,10-CN_2P)
3,9-Dicyanophenanthrene (3,9-CN_2P)
3-Methoxy-10-cyanophenanthrene (3-MeO-10CNP)
3-Methoxy-9-cyanophenanthrene (3-MeO-9-CNP)
3,6-Dimethoxyphenanthrene (3,6-MeO_2P)

Alkene Components of Exciplexes

Fumaronitrile (FN)
Dimethyl fumarate (F)
trans-β-Methylstyrene (β-MS)
p-Methyl-*trans*-β-methylstyrene (*p*-MeβMS)
trans-Anethole (*t*-An)
p-Methoxy-β,β-dimethylstyrene (*p*-BA)

Amines

Triethylamine (Et_3N)
Diphenylamine (Ph_2NH)
Triphenylamine (Ph_3N)
N,N-Diethylaniline ($PhNEt_2$)
N,N,N′,N′-Tetramethyl-1,4-diaminobenzene (TMPD)
Diethylamine

Alkene Quenchers

2-Methyl-2-butene
2,3-Dimethyl-2-butene (TME)
Styrene
α-Methylstyrene
β-Methylstyrene
trans-Anethole
Dihydropyran
Ethyl vinyl ether (EVE)
Acrylonitrile
Cinnamonitrile
Fumaronitrile
Dimethyl maleate (M)
Dimethyl (2,3-dimethyl) maleate
Dimethyl fumarate
Diethyl fumarate
Dimethyl acetylenedicarboxylate (DMAD)
Anisole

Rate constants k_Q^{Cl} for quenching of a variety of exciplexes (Table I) and the pyrene excimer were for the most part obtained from the Stern-Volmer slopes for steady-state fluorescence quenching combined with both direct and indirect

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Table I. Exciplex Photophysical Parameters[a]

exciplex, M-Q_1	λ_{max}, nm[b]	τ, ns direct[e]	I(argon)[f]/I(air)	τ, ns O_2 quenching[g]	IP(M), eV[h]	IP(Q_1), eV[h]	ΔE_{HOMO}, eV[i]
P-FN	475	19.6	1.80	19.1	7.86[j]	11.15[l]	3.29
P-F	480		1.05	1.2	7.86	11.23[m]	3.37
pyrene-FN	515[c]		1.69	16.4	7.41[j]	11.15	3.74
anthracene-FN	570[d]		1.46	10.9	7.47[j]	11.15	3.68
9CNP-*t*-An	450	10.6	1.42	9.9	8.56[k]	7.83[n]	0.73
3,10CN_2P-*t*-An	484	33.2	2.22	27		7.83	
3,9CN_2P-*t*-An	496	26.6	2.12	26.7	8.75[k]	7.83	0.92
9CNP-*p*-BA	463	33.3	2.41	33.6	8.56	7.93[n]	0.63
3,9CN_2P-β-MS	448		1.45	10.7	8.75	8.37	0.38
3,9CN_2P-*p*-Me-βMS	461		1.56	13.3	8.75	8.00[o]	0.75
P-$PhNEt_2$	408		3.05	48.8	7.86	6.94[p]	0.92
pyrene-$PhNEt_2$	473		4.80	90.5	7.41	6.94	0.47
anthracene-$PhNEt_2$	500	110.0	5.60	109.5	7.47	6.94	0.53
9CNP-$PhNEt_2$	508		3.42	57.6	8.56[k]	6.94	1.62
3,10CN_2P-$PhNEt_2$	566	100.0	4.74	88.5		6.94	
3,9CN_2P-$PhNEt_2$	590	27.4	2.23	30.5	8.75[k]	6.94	1.81
3MeO,9CNP-$PhNEt_2$	489		3.13	50.7	8.14[k]	6.94	1.20
3MeO,10CNP-$PhNEt_2$	495		2.83	43.6	7.94[k]	6.94	1.00
3,6MeO_2P-9CNP	444		1.51	12.1	7.52	8.56[k]	1.04
3,9CN_2P-P			1.96	22.8	8.75[k]	7.86[j]	0.89
9CNP-Ph_3N	470		4.72	88.6	8.56	6.87	1.69

[a] In benzene. [b] Corrected; ±3 nm unless otherwise stated. [c] ±5 nm; asymmetric peak. [d] ±10 nm; very weak asymmetric peak. [e] By nanosecond flash spectroscopy. [f] I_{argon}/I_{air}(exciplex) ÷ I_{argon}/I_{air}(monomer). [g] Calculated assuming $k_Q^{C1}(O_2) = 4.2 \times 10^7\ s^{-1}$ for any exciplex in benzene. [h] Vertical ionization potentials. [i] ΔE_{HOMO} = IP of acceptor component of exciplex − IP of donor component. [j] R. Boschi, E. Clar, and W. Schmidt, *J. Chem. Phys.*, **60**, 4406 (1974). [k] K. N. Houk and E. J. McAlduff, unpublished results. [l] H. Bock and H. Stafast, *Chem. Ber.*, **105**, 1158 (1972). [m] R. Sustmann and H. Trill, *Tetrahedron Lett.*, 4271 (1972). [n] R. A. Caldwell and L. Smith, *J. Am. Chem. Soc.*, **96**, 2994 (1974). [o] Estimated from the IP of *trans*-β-methylstyrene (8.37) and the expected effect of a 4-methyl substituent. [p] Estimated from the IP of *N*,*N*-dimethylaniline (7.14 eV) taking into account the expected effect of ethyl substituents.

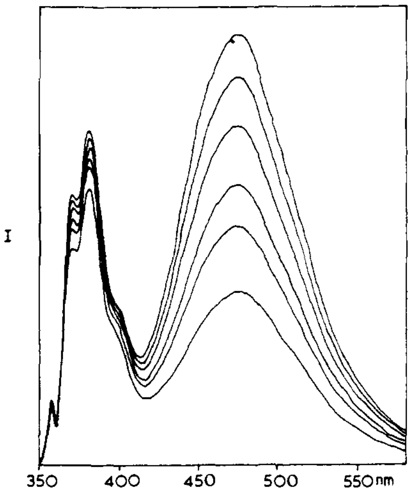


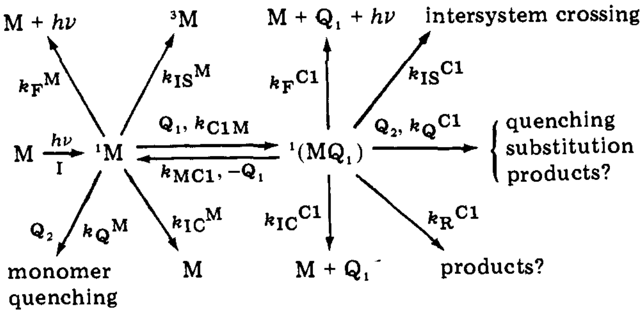
Figure 1. Quenching of the 3,9-dicyanophenanthrene-*trans*-anethole exciplex by diethyl fumarate.

measurements of exciplex fluorescence lifetimes. In two cases, the more direct method of nitrogen laser flash spectroscopy was also used, with excellent agreement between the methods.

In the next few paragraphs, we discuss several examples which illustrate the techniques we use, the pitfalls which arise, and the cross-checks we have made between steady-state and transient studies.

Steady-State Exciplex Fluorescence Quenching. Figure 1 shows one of several typical results of our experiments. Generally, but not always, we have observed quenching of both monomer and exciplex fluorescence simultaneously. Scheme 1, following the notation of Stevens,[3] is applicable. Subscripts to rate constants in Scheme I refer to the photoprocess and superscripts refer to the species (M or the first-formed complex, C1).

Scheme I



The steady-state analysis is essentially that of Medinger and Wilkinson.[15] Let

$$\tau_{C1}{}^{-1} = k_F{}^{C1} + k_{IS}{}^{C1} + k_{IC}{}^{C1} + k_R{}^{C1} + k_{MC1} \qquad (5)$$

Then, in the absence of Q_2, at steady state

$$d^1(MQ_1)/dt = k_{C1M}{}^1(M)^0(Q_1) - \tau_{C1}{}^{-1}{}^1(MQ_1)^0 = 0 \qquad (6)$$

and

$$^1(MQ)^0 = k_{C1M}\tau_{C1}{}^1(M)^0(Q_1) \qquad (7)$$

The analogous equations (8) and (9) follow obviously when Q_2 is added. Note that ^{1}(M) in (8) and (9) is *not* the same as $^1(M)^0$ in (6) and (7), since Q_2 can in principle (and often does) quench ^{1}M and since exciplex quenching by Q_2 will affect the amount of reversion (k_{MC1}).

$$d^1(MQ_1)/dt = k_{C1M}{}^1(M)(Q_1) - (\tau_{C1}{}^{-1} + k_Q{}^{C1}(Q_2))^1(MQ_1) = 0 \qquad (8)$$

$$^1(MQ_1) = \frac{k_{C1M}(M)(Q_1)}{\tau_{C1}{}^{-1} + k_Q{}^{C1}(Q_2)} \qquad (9)$$

Dividing (7) by (9) affords (10):

$$\frac{^1(MQ_1)^0}{^1(MQ_1)} = \frac{^1(M)^0}{^1(M)}(1 + k_Q{}^{C1}\tau_{C1}(Q_2)) \qquad (10)$$

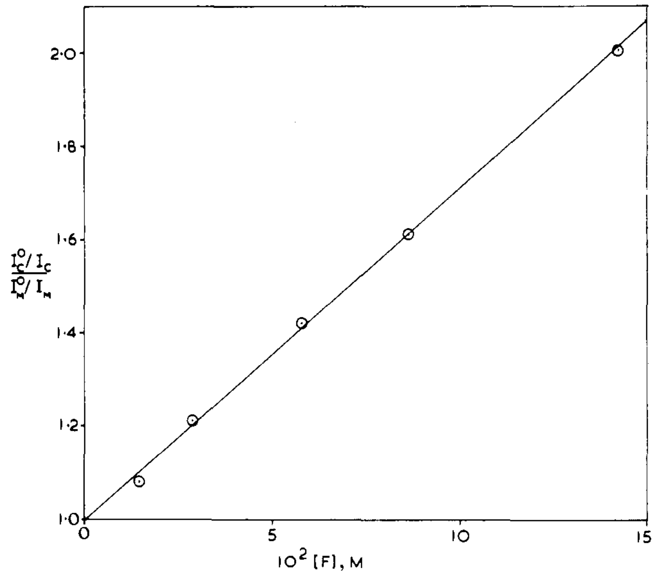


Figure 2. Stern-Volmer plot for quenching of the 3,9-dicyanophenanthrene-*trans*-anethole exciplex by diethyl fumarate.

$$\frac{I_{MQ_1}^0}{I_{MQ_1}} \div \frac{I_M^0}{I_M} = 1 + k_Q^{C_1}\tau_{C_1}(Q_2) \qquad (11)$$

Since the fluorescence intensity due to a species is directly proportional to its (steady-state) concentration, it is clear that normalizing exciplex fluorescence intensities to constant monomer intensity via eq 11 provides essentially a simple Stern-Volmer equation for exciplex fluorescence quenching. The equation is valid within the scope of Scheme I, and additionally automatically corrects for any light absorption by Q_2 or any possible ground-state complexes it forms. It does not apply if MQ_2 produces MQ_1, and it is difficult to obtain good precision on plots of (11) when monomer quenching by Q_2 dominates. Other practical difficulties will be discussed subsequently, but in general we find eq 11 quite successful in quantitating exciplex quenching.

Exciplex Lifetimes. The lifetime of the exciplex τ_{C_1} is of course required in order to calculate $k_Q^{C_1}$ by eq 11. In some cases, τ_{C_1} was measured directly by laser flash spectroscopy, generally analyzing the time profile by deconvolution, under conditions such that reversion to ^1M could be ignored. In other cases, we have utilized eq 11 with oxygen as the Q_2 quencher, i.e., comparing the fluorescence spectra in argon-saturated and aerated benzene. Taking $k_Q^M(O_2) = 3.7 \times 10^7$ s^{-1} and $k_Q^{C_1}(0) = 4.2 \times 10^7$ s^{-1} in benzene at room temperature, as previously discussed,[10,12c] affords τ_{C_1} by an indirect method. Table I includes all cases where both methods have been applied, and excellent agreement results. The average deviation of the two values from one another is 7%. Where the values differ, the direct values are used for subsequent calculations.

Two Examples. The example of Figure 1, the case of quenching of ^{1}(3,9-CN$_2$P···*t*-An) by diethyl fumarate, is illustrative. Analysis by eq 11 required that the spectra of ^1M and $^1(MQ_1)$ be resolvable. In this case, the exciplex and monomer spectra are clearly spectrally well resolved. The data of Table II are plotted according to eq 11 in Figure 2, affording a Stern-Volmer slope $k_Q^{C_1}\tau_{C_1} = 6.70$ M^{-1}. The exciplex lifetime of 26.6 ns (Table I) thus affords $k_Q^{C_1} = 2.5_2 \times 10^8$ M^{-1} s^{-1}.

Not all cases were so well resolved spectrally. Since all arenes showed strong 0,0 and 0,1 bands in their spectra, and since exciplexes were red shifted, wavelengths for each species could be selected where overlap was not substantial. However, in some cases of less than ideal spectral resolution, downward curvature in the plots of eq 11 resulted, and in those cases we took initial slopes.

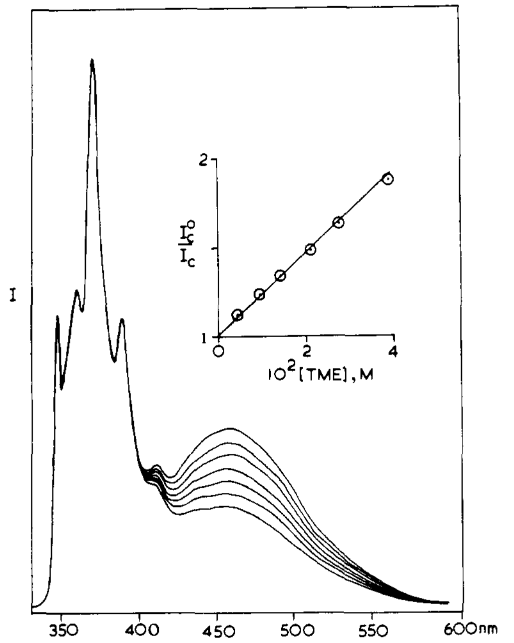


Figure 3. Quenching of the phenanthrene-fumaronitrile exciplex by 2,3-dimethyl-2-butene. Inset: Stern-Volmer plot for exciplex quenching.

Table II. Quenching[a] of the 3,9-Dicyanophenanthrene-*trans*-Anethole Exciplex by Diethyl Fumarate

[F], M	I_M[b]	I_M^0/I_M	I_C[b]	I_C^0/I_C
0	9.47	1.0	12.22	1.0
0.0145	9.22	1.027	11.00	1.08
0.029	9.00	1.052	9.61	1.21
0.058	8.70	1.088	7.91	1.42
0.086	8.50	1.114	6.80	1.61
0.142	7.83	1.209	4.93	2.05

[a] In aerated benzene. [b] Arbitrary units.

Quenching of the P···FN exciplex by TME (Figure 3) provides a somewhat different example. In this case, P quenching is negligible ($k_Q\tau < 0.2$ M^{-1} for TME quenching of P) and the normal Stern-Volmer relationship can be used. The plot is shown in the insert of Figure 3.

"Self-Quenching" of $^1(MQ_1)$. Stern-Volmer slopes for quenching of ^{1}(P···FN) by TME were dependent on P and, to a lesser extent, on FN, decreasing as either is increased. We have previously[10] reported and analyzed similar behavior for ^{1}(P···F) quenched by TME. A general equation is given below as (12). In (12) the subscripts SQ-M and SQ-Q_1 refer to exciplex quenching by M and Q_1, respectively. In the specific case of ^{1}(P···FN) quenching by TME, substantial P quenching is observed, $k_{SQ-M}^{C_1} = 0.90k_Q^{C_1}$, but FN quenching affords $k_{SQ-Q_1}^{C_1} \leq 0.08k_Q^{C_1}$. We accordingly made most measurements of quenching of ^{1}(P···FN) at low P.

$$\frac{1}{\text{S-V slope}} = \frac{1}{k_Q^{C_1}\tau_{C_1}} + \frac{k_{SQ-M}^{C_1}(M) + k_{SQ-Q_1}^{C_1}(Q_2)}{k_Q^{C_1}} \qquad (12)$$

We recognize that the term "self-quenching" is somewhat improperly used, but find it convenient and do not believe that any confusion arises.

Rate Constants by Flash Spectroscopy. In two cases, ^{1}(P···FN) quenched by TME and ^{1}(9CP···*p*-BA) quenched by dimethyl fumarate (F), we determined $k_Q^{C_1}$ directly by the

Table III. Systems in Which Exciplex Substitution ($S_{ex}2$) Is Observed[a]

MQ_1	Q_2	MQ_2	ΔE,[c] kcal mol^{-1}	$k_Q{}^{C1}$, M^{-1} s^{-1}
3,10CN_2P-*t*-An	$PhNEt_2$	3,10CN_2P-$PhNEt_2$	8.6	7.2×10^9
3,9CN_2P-*t*-An	$PhNEt_2$	3,9CN_2P-$PhNEt_2$	9.1	1.0×10^{10}
9CNP-*t*-An	Ph_3N	9CNP-Ph_3N	2.7	1.4×10^{10}
9CNP-*t*-An	$PhNEt_2$	9CNP-$PhNEt_2$	6.8	3.1×10^9
9CNP-*t*-An	Et_3N	9CNP-Et_3N[b]	9.6	9.8×10^7
9CNP-*p*-BA	$PhNEt_2$	9CNP-$PhNEt_2$	5.4	3.2×10^9

[a] In benzene. [b] λ_{max} 530 ± 5 nm; very weak emission. [c] $\Delta E = h\nu_{max}(MQ_1{}^*) - h\nu_{max}(MQ_2{}^*)$ is an approximation to the exothermicity of the reaction.

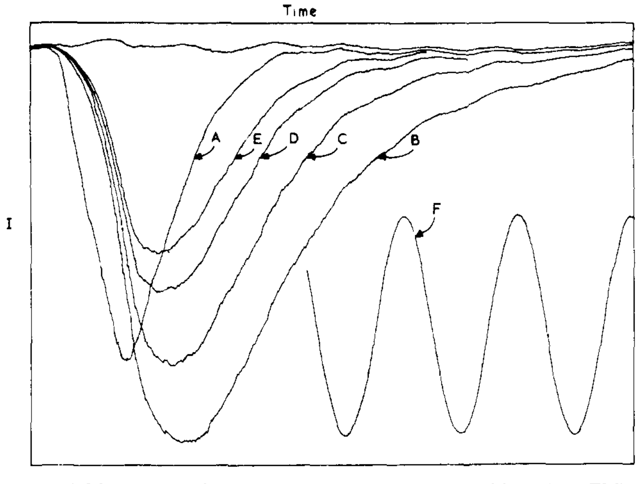


Figure 4. Nanosecond flash spectroscopy data for quenching of (P-FN)* by 2,3-dimethylbutene: A, laser scattered light from sample tube containing only benzene (λ 333.4 nm); B → E, decay of exciplex fluorescence (λ 461 nm) in absence (B) and presence of 2,3-dimethyl-2-butene (TME). For C, [TME] = 0.013 M; for D, [TME] = 0.028 M; for E, [TME] = 0.043 M. F is output signal from 50-MHz quartz oscillator.

dependence of exciplex lifetime on (Q_2). Figure 4 shows the time profiles obtained for the former. For (P) = 1.0×10^{-3} M and (FN) = 0.10 M, τ_{C1} = 19.6 ns. Addition of TME affords the following ((TME), τ_{C1}) pairs: (0.013 M, 13.7); (0.028 M, 10.1); (0.043 M, 7.6). A plot of $\tau_{C1}{}^0/\tau_{C1}$ vs. (TME) (Figure 5) affords $k_Q{}^{C1}\tau_{C1^0}$ = 34.6 ± 1.6 M and $k_Q{}^{C1}$ = 1.7 ± 0.2 × 10^9 M^{-1} s^{-1}. Agreement with the steady-state value of 1.6 ± 0.2 × 10^9 M^{-1} s^{-1} is excellent. Both sets of data are plotted in Figure 5. Similarly, quenching of ^{1}(9CP···p-BA) by F affords $k_Q{}^{C1}$ values of 8.0 ± 0.8 × 10^9 M^{-1} s^{-1} by the lifetime study and 8.7 ± 0.8 × 10^9 M^{-1} s^{-1} by the steady-state technique. We believe that the concordances observed when both transient and steady-state data were obtained, and the accord between lifetime values determined by laser flash photolysis and the oxygen quenching technique, amply validate the assumptions made in oxygen quenching which underlie much of the data we present.

Quenching by Small Polar Molecules. Very high concentrations of weak quenchers are required. If the quencher contains polar functional groups (acrylonitrile being an example), the exciplex is both quenched and its fluorescence red shifted (Figure 6). High concentrations of polar molecules will result in significant changes in the solvent. The red shift has been previously observed[16,17] and attributed to exciplex solvation or to formation of excited termolecular complexes (*exterplexes*). The shift obviously complicates determination of $k_Q{}^{C1}$.

Exciplex Substitution. In most cases, we have only observed exciplex quenching. However, we have in a few cases observed new emissions which we have demonstrated to arise via exciplex substitution (S_{ex}), eq 13. We have described this process previously[14] but did not at that time rule out the possibility that (13) was not an elementary reaction, i.e., that (13a) and (13b) instead occur.

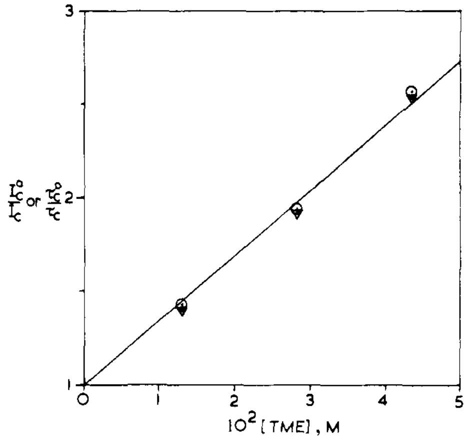


Figure 5. Stern–Volmer plot for quenching of ^{1}(P–FN) by TME in outgassed benzene. Data from both direct lifetime, τ_C/τ_C (▽), and steady-state intensity, $I_C{}^0/I_C$ (⊙), measurements.

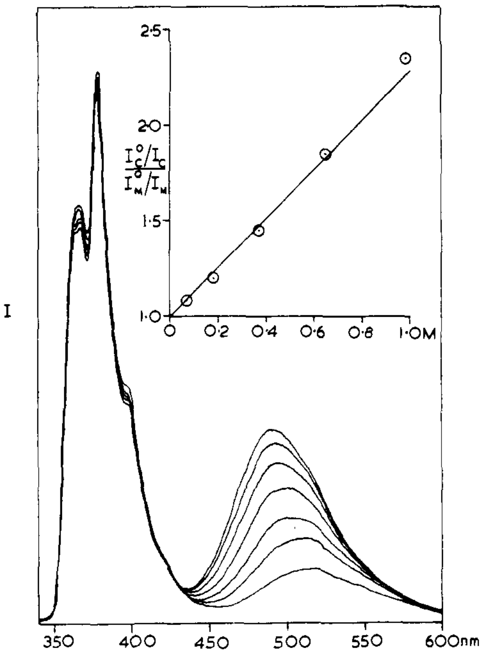


Figure 6. Quenching of the 9-cyanophenanthrene···diethylaniline exciplex by the weak acceptor acrylonitrile. Inset: Stern–Volmer plot for exciplex quenching.

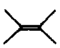
$$^1(MQ_1) + Q_2 \rightarrow {}^1(MQ_2) + Q_1 \qquad (13)$$

$$^1(MQ_1) \rightarrow {}^1M + Q_1 \qquad (13a)$$

$$^1M + Q_2 \rightarrow {}^1(MQ_2) \qquad (13b)$$

The former possibility, $S_{ex}2$, is formally analogous to the familiar second-order ground-state S_N2 and S_E2 substitution processes, and the latter, $S_{ex}1$, is analogous to S_N1 or S_E1

Table IV. Rate Constants[a] (k_Q^{Cl}, $M^{-1}\ s^{-1}$) and ΔE_Q (eV) Values[b] for Donor Quenching of Exciplexes with ΔE_{HOMO}[c] Large (≥1.46 eV)

quencher (IP, eV)[d]	 (8.49)[e]	 (8.34)	 (8.30)	P (7.86)[f]	*t*-An (7.83)[f]	Et_3N (7.50)	Ph_2NH (7.25)	exciplex ΔE_{HOMO}, eV
anthracene–FN			<10^7	5.7×10^8	8.0×10^8	1.2×10^9		3.74
ΔE_Q[b]			−0.89	−0.45	−0.42	−0.09		
pyrene–FN[g]			4.1×10^7		4.35×10^9	2.8×10^9	1.3×10^{10}	3.74
ΔE_Q			−0.89		−0.42	−0.09	0.16	
P–FN[h]	1.5×10^8	2.2×10^9	1.6×10^9	1.5×10^9	1.1×10^{10}	7.0×10^9		3.27
ΔE_Q	−0.63	−0.48	−0.44	0	0.03	0.36		
P–F[i]	5.3×10^8	2.95×10^9	1.8×10^9	3.8×10^9		7.1×10^9		3.37
ΔE_Q	−0.63	−0.48	−0.44	0		0.36		
9CNP–$PhNEt_2$						2.1×10^8	1.2×10^9	1.46
ΔE_Q						−0.56	−0.31	

[a] In benzene; ±10% unless otherwise stated. [b] ΔE_Q = IP of donor component of exciplex − IP of quencher. [c] For exciplexes ΔE_{HOMO} = IP(acceptor) − IP(donor). [d] Vertical ionization potentials. Unless otherwise stated from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Fraxl, and F. H. Field, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 26** (1969). [e] M. P. Niemczyk, N. E. Schore, and N. J. Turro, *Mol. Photochem.*, **5**, 69 (1973). [f] See Table I. [g] Also quenched by Et_2NH (IP = 8.01 eV). $k_Q^{Cl} = 2.0 \times 10^9\ M^{-1}\ s^{-1}$. [h] Also quenched by 2-methyl-2-butene (IP = 8.89 eV), $k_Q^{Cl} = 1.6 \times 10^7$; styrene (IP = 8.47 eV), $k_Q^{Cl} = 2.9 \times 10^7$; α-methylstyrene (IP = 8.50 eV), $k_Q^{Cl} = 3.7 \times 10^7$; β-methylstyrene (IP = 8.37 eV), $k_Q^{Cl} = 2.3 \times 10^8\ M^{-1}\ s^{-1}$; anisole (IP = 8.42 eV), $k_Q^{Cl} = 8.5 \times 10^7\ M^{-1}\ s^{-1}$. [i] Also quenched by 2-methyl-2-butene (IP = 8.89 eV), $k_Q^{Cl} \lesssim 7.0 \times 10^7\ M^{-1}\ s^{-1}$.

Table V. Rate Constants[a] (k_Q^{Cl}, $M^{-1}\ s^{-1}$) and E_Q (eV) Values[b] for Donor Quenching of the Pyrene Excimer and of Exciplexes with ΔE_{HOMO}[c] Small (≤ 1.04)

quencher (IP, eV)[d]	*t*-An (7.83)[e]	Et_3N (7.50)	Ph_2NH (7.25)	$PhNEt_2$ (6.94)[f]	Ph_3N (6.86)	exciplex ΔE_{HOMO}, eV
3,6MeO_2P–9CNP	1.6×10^7	8.7×10^7	4.8×10^9	3.4×10^9		1.04
ΔE_Q[b]	−0.31	−0.02	0.27	0.58		
9CNP–*t*-An		9.8×10^7	3.3×10^8	3.1×10^9	1.4×10^{10}	0.73
ΔE_q		0.33	0.58	0.89	0.97	
9CNP–*p*-BA		5.0×10^7		3.2×10^9	1.3×10^{10}	0.63
ΔE_Q		0.43		0.99	1.07	
pyrene–pyrene[g]			<2.0×10^7	5.9×10^7 [h]	5.4×10^8	0
ΔE_Q			0.16	0.47	0.55	

[a] In benzene; ±10% unless otherwise stated. [b] ΔE_Q = IP of donor component of exciplex − IP of quencher. [c] For exciplexes ΔE_{HOMO} = IP(acceptor) − IP(donor). [d] Vertical ionization potentials. Unless otherwise stated from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Fraxl, and F. H. Field, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 26** (1969). [e] IP data from Table I. [f] Estimated from IP of $PhNMe_2$ (7.14 eV) taking into account the expected effect of ethyl substituents. [g] Also quenched by *N,N,N′,N′*-tetramethyl-1,4-diaminobenzene. IP = 6.75 eV: Y. Nakato et al., *Chem. Phys. Lett.*, **9**, 615 (1971), $k_Q^{Cl} = 7.2 \pm 3.0 \times 10^9\ M^{-1}\ s^{-1}$. [h] In absolute ethanol; ±40%.

(dissociative) processes. The present kinetic analysis distinguishes the two in a simple fashion and shows that the mechanism is in fact $S_{ex}2$.

Table III presents the results of an analysis according to eq 11 of systems in which S_{ex} is observed. The k_Q^{Cl} values are nearly all essentially diffusion controlled and $(Q_1) \gg (Q_2)$ in these experiments. Any ^1M liberated by eq 13a will undergo combination competitively with Q_1 and Q_2, and in all cases k_{C1M} (Scheme I) is diffusion controlled. These considerations make it clear that recapture of ^1M by Q_1 will dominate. The apparent value of k_Q^{Cl} cannot exceed the fraction of ^1M captured by Q_2 (a small number) times the diffusion rate. Clearly, with the possible exception of ^{1}(9CNP···*t*-An) quenched by Et_3N, the high rate constants in the cases studied generally exemplify $S_{ex}2$, and the rates thus may be compared with the other elementary processes k_Q^{Cl} we present.

Discussion

Magnitudes and Structural Variations of k_Q^{Cl}. Early in our investigation, it became clear that some exciplexes are quenched relatively easily by electron donors and some are better quenched by acceptors. Tables IV–VII summarize quenching by donors Q_D (Tables IV and V) and acceptors Q_A (Tables VI and VII). These data can be relatively easily understood by a careful consideration of the energies of the frontier orbitals of the exciplex and the quencher.

An FMO Picture. Consider an exciplex to be composed of two species, each containing a HOMO and a LUMO. Interaction leads to four new exciplex orbitals χ_1–χ_4 (Figure 7). Transfer of an electron from the LUMO of ^1M to χ_3 (primarily on Q_1) produces most of the exciplex stabilization, and the customary formulation of the exciplex as $^1(M\cdot^+\cdots Q_1\cdot^-)$ follows obviously. A donor quencher Q_D should approach and interact preferentially with the electron-poor component of the exciplex, i.e., the M side via χ_2, while acceptor quenchers Q_A should prefer to interact with the Q_1 side via χ_3. The two structures below would then be expected for the two exterplexes, as we have previously discussed and as in fact apparently occurs for the few known stable exterplexes.[18-20]

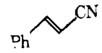
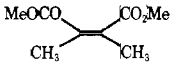
$$^1(Q_D{}^{\delta+}\cdots M^{\delta+}\cdots Q_1{}^{\delta-})$$

$$^1(M^{\delta+}\cdots Q_1{}^{\delta-}\cdots Q_A{}^{\delta-})$$

When electron transfer from Q_D to χ_2 (or from χ_3 to the LUMO of Q_A) is exothermic, it is expected to be very rapid. The rate should fall off as the ionization potential of Q_D increases (i.e., its HOMO becomes lower than χ_2) or as the electron affinity of Q_A decreases, making its LUMO higher than χ_3. A plot of log k_Q^{Cl} vs. ionization potential (IP) of Q_D should show a break at the energy of χ_2 (i.e., the IP of the exciplex), and a fully analogous situation should obtain for acceptor quenchers Q_A. Ionization potentials are more readily accessible than electron affinities, and our best tests of this expectation are therefore for donor quenchers.

Figure 8 shows the plot for the quenching of ^{1}(P···FN) by D_Q. The results are in good agreement with the analysis above.

Table VI. Rate Constants k_Q^{Cl} (M^{-1} s^{-1})[a] for Quenching of Exciplexes by Electron Acceptors and Reduction Potentials for Acceptor Components of Exciplexes and Acceptor Quenchers

	quencher (E_{red})						
exciplex (acceptor E_{red})	DMAD	FN (−1.36)[b,e]	F (−1.51)[c,d]	M (−1.87)[c,d]	 (−1.99)[b,e]		acrylonitrile (−1.67)[b,e]
phenanthrene···PhNEt$_2$ (−2.68)[b,f]		2.5 × 10^9	2.1 × 10^9			8.2 × 10^8	3.8 × 10^8
pyrene-pyrene (−2.32)[b,f]	6.6 × 10^9	1.1 × 10^{10}	1.0 × 10^{10}	1.2 × 10^9	5.6 × 10^7		
pyrene-PhNEt$_2$ (−2.32)[b,f]		6.3 × 10^9		6.0 × 10^9	3.0 × 10^9	2.9 × 10^8	3.7 × 10^7
anthracene···PhNEt$_2$ (−2.07)[b,d]		3.4 × 10^9	3.3 × 10^9		1.6 × 10^8	5.6 × 10^7	3.8 × 10^7
9CNP···PhNEt$_2$ (−1.92)[d,g]		5.1 × 10^9	1.6 × 10^9	2.8 × 10^9		<5 × 10^7	1.35 × 10^8
9CNP···p-BA (−1.92)[d,g]	7.6 × 10^9	7.9 × 10^9			1 × 10^8		
9CNP···*t*-An (−1.92)[d,g]	8.4 × 10^9	7.8 × 10^9	8.7 × 10^9		8.1 × 10^7		
3,9-CN$_2$P···PhNEt$_2$ (−1.51)[d,g]				2.2 × 10^8			2.5 × 10^8

[a] In benzene, ±10%. [b] N. L. Weinberg, Ed., "Techniques of Electroorganic Synthesis", Part II, Wiley, New York, 1975. [c] A. F. Diaz, unpublished results for ethyl esters. [d] In CH_3CN, V vs. SCE. [e] In DMF, V vs. SCE. [f] Values in 75% aqueous dioxane corrected by assuming that a solvent effect identical with that on reduction of anthracene between CH_3CN and 75% dioxane results. [g] S. M. Park and R. A. Caldwell, *J. Electrochem. Soc.*, **124**, 1859 (1977).

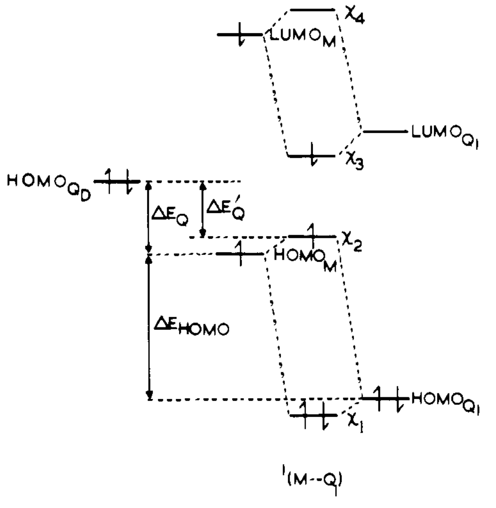


Figure 7. Schematic orbital energy diagram for formation of an exciplex ^{1}(M···Q$_1$) by quenching of ^{1}M by an acceptor Q$_1$. The HOMO of a good donor Q$_D$, a potential exciplex quencher, is also shown.

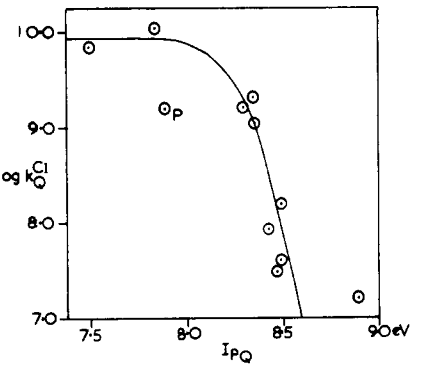
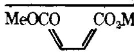
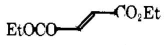


Figure 8. Quenching of ^{1}(P···FN) by electron donors. Plot of log k_Q^{Cl} vs. IP of the quenchers.

In this case, apparently χ_2 is quite close to the unperturbed P HOMO, since it is about at that energy where the break occurs. This is not an unreasonable energy for χ_2. Naively, since the P and FN HOMOs are very different in energy, one might be tempted to say that χ_2 *is* the P HOMO, i.e., that CT is 100% complete. This, however, is not an adequate explanation for the entire set of results we have obtained.

Another factor necessarily considered is the electron-electron repulsion ignored by Figure 7. The effect of removing an electron from M to make the M·$^+$ moiety of ^{1}(M·$^+$···Q·$^-$) relative to their position in Figure 7 is to *lower* χ_2 and χ_4 since there are thereby fewer electron-electron repulsions. Analogously, χ_1 and χ_3 will be raised in energy in a Q$_1$·$^-$ moiety relative to their position in neutral Q$_1$. The simple orbital picture of Figure 7 is modified accordingly in Figure 9. A better rationalization of the apparent equivalency of χ_2 and the P HOMO in ^{1}(P···FN) is the counterbalancing of the destabili-

Table VII. Rate Constants k_Q^{Cl} (M^{-1} s^{-1})[a] for Quenching of Exciplexes by Electron Acceptors and Relevant Reduction Potentials

	quencher	
exciplex	 (−1.87)[b]	 (−1.51)[b]
3MeO9CNP···PhNEt$_2$ (−2.05)[c]	4.4 × 10^9	
3MeO10CNP···PhNEt$_2$ (−2.00)[c]	3.8 × 10^9	
9CNP···PhNEt$_2$ (−1.92)[c]	2.8 × 10^9	
3,10CN$_2$P···PhNEt$_2$ (−1.57)[c]	4.2 × 10^8	
3,9CN$_2$P···PhNEt$_2$ (−1.51)[c]	2.2 × 10^8	
3,9CN$_2$P···βMS (−1.51)[c]		1.3 × 10^8
3,9CN$_2$P···4-Me-βMS (−1.51)[c]		1.6 × 10^8
3,9CN$_2$P···*t*-An (−1.51)[c]		5.3 × 10^8

[a] In benzene, ±10%. [b] A. F. Diaz, unpublished results (in CH_3CN, V vs. SCE). [c] S. M. Park and R. A. Caldwell, *J. Electrochem. Soc.*, **124**, 1859 (1977). In CH_3CN, V vs. SCE for the phenanthrene (acceptor) component of the exciplex.

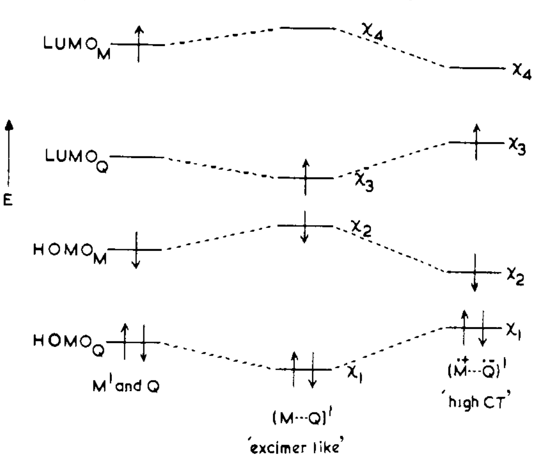


Figure 9. Schematic orbital energy diagram for ^{1}M and Q prior to orbital overlap, ^{1}(M···Q$_1$) with orbital splitting but no electron repulsion ("excimer-like"), and ^{1}(M$^{\delta+}$···Q$^{\delta-}$), including significant changes in electron repulsion ("high CT").

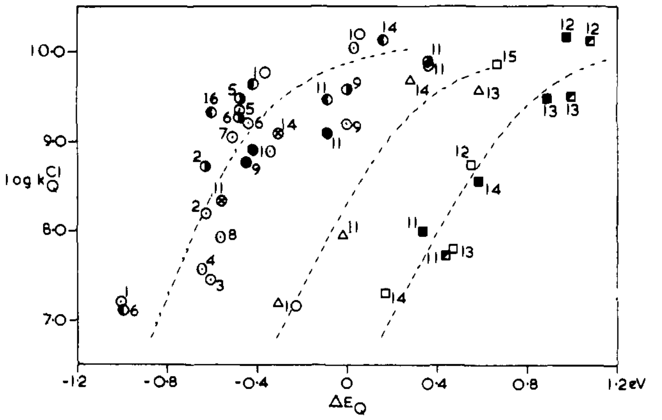


Figure 10. The "master plot" of all exciplex, heteroexcimer, and excimer quenching rates measured for donor quenchers vs. ΔE_Q. Exciplexes: anthracene···FN (●); pyrene···FN (◐); P···F (◑); P···FN (⊙); 9CNP···PhNEt$_2$(⊗); 3,6-MeO$_2$P···9CNP (△); 9CNP···*t*-An (■); 9CNP···pBA (◨); the pyrene excimer (□). Quenchers: (1) 2-methyl-2-butene; (2) EVE; (3) styrene; (4) α-methylstyrene; (5) dihydropyran; (6) TME; (7) β-MS; (8) anisole; (9) P; (10) *t*-An; (11) Et$_3$N; (12) Ph$_3$N; (13) PhNEt$_2$; (14) Ph$_2$NH; (15) TMPD; (16) diethylamine.

zation of χ_2 by orbital interaction relative to the P HOMO and the stabilization resulting from decreased electron repulsion in the P$\cdot^+$ moiety.

The Master Plot and Its Rationale. The analysis above suggested that all quenching of excited complexes could be fit by a single plot of the form of Figure 8. The proper abscissa for this for Q_D is the $\Delta E_Q'$ of Figure 7, rather than IP, since that is a measure of exothermicity or endothermicity applicable to each case. Unfortunately, $\Delta E_Q'$ requires that one know the energy of χ_2, an experimentally inaccessible quantity at present, while ΔE_Q values, being solely determined by properties of the monomer and quencher, are readily available. Assuming that the cancellation of effects exemplified above for χ_2 of ^{1}(P···FN) will either generally occur or, if not, that the balance between orbital interaction destabilization and decreased electron repulsion will vary in some systematic fashion with exciplex structure led us to the plot of Figure 10, the "master plot", of log k_Q^{Cl} vs. ΔE_Q.

In fact, Figure 10 shows clearly that quenching of the exciplexes and the one excimer studied by donors fits for the most part into two families. On the left of Figure 10, one finds the exciplexes with substantial charge transfer (Table IV). We have measured charge transfer qualitatively by ΔE_{HOMO}, the energy difference between the HOMOs of M and Q_1. Exciplexes with high ΔE_{HOMO} are quenched much more efficiently by donors of a given ΔE_Q than would be true for exciplexes with low ΔE_{HOMO}. In fact, the exciplexes with low ΔE_{HOMO} and the pyrene excimer ($\Delta E_{HOMO} \equiv 0$) of Table V form the family on the right of Figure 10. The displacement of the two lines with respect to one another is about 1.0–1.1 eV; i.e., to obtain the same quenching rate for an exciplex of low ΔE_{HOMO} that one finds for an exciplex of high ΔE_{HOMO} requires a donor about 1 eV better in the former case. Interestingly, the middle line of Figure 10 represents the heteroexcimer ^{1}(3,6-MeO$_2$-P···9CNP), with intermediate ΔE_{HOMO}. This system was studied *after* observation of the two extremes of behavior as a test of the predictive nature of the master plot. Doubtless many other heteroexcimers will also fall in this region.

The source of the effect of ΔE_{HOMO} on quenching rates is suggested by Figures 7 and 9. When ΔE_{HOMO} is large, χ_2 must be close to the HOMO of M, i.e., $\Delta E_Q' \cong E_Q$. Note that, for the leftmost line, the approach to a diffusion-controlled rate is around $\Delta E_Q = -0.4$, i.e., IP(Q_D) $\sim$ IP(M) + 0.4. Such an occurrence suggests that the HOMO of such exciplexes is actually somewhat below that of the corresponding (donor) monomer since $\Delta E_Q' \sim 0$ is the point at which the curve is expected to break. For the exciplexes with low ΔE_{HOMO} and the pyrene excimer, the more scanty data suggest $\Delta E_Q \sim$ 0.6–0.8 eV for the approach to diffusion control, consistent with the fact that, as ΔE_{HOMO} decreases in the exciplex, the orbital splitting increases and polarity decreases. The decrease in polarity in this case will make the effect of electron repulsion in Figure 9 less significant.

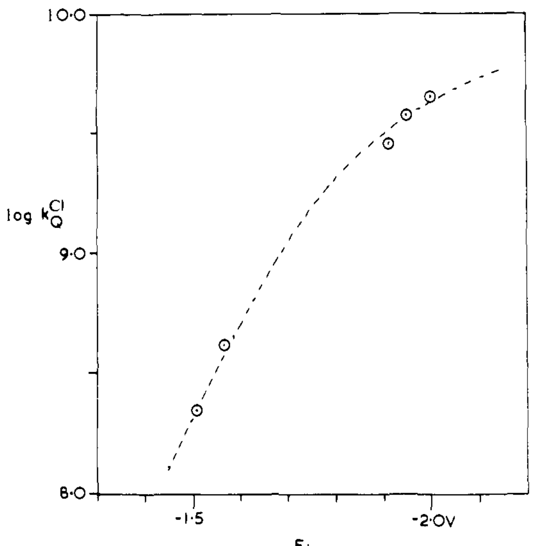


Figure 11. Plot of log k_Q^{Cl} for quenching of substituted cyanophenanthrene···PhNEt$_2$ exciplexes by dimethyl maleate. Abscissa: $E_{1/2}$ for the cyanophenanthrene, from S. M. Park and R. A. Caldwell, *J. Electrochem. Soc.*, **124**, 1859 (1977).

Quenching of Exciplexes by Electron Acceptors. Tables VI and VII present somewhat less complete data for the quenching of exciplexes by electron acceptors. We have not yet attempted a detailed treatment of these data analogous to Figure 10, since electron affinities are in general unavailable. We have, therefore, taken reduction potentials in dipolar aprotic solvents (CH$_3$CN or DMF) from the literature.

The trends for quenching by acceptors (Table VI) are the same as for donors. The quenchers FN, F, and (presumably) DMAD all have smaller reduction potentials (i.e., are better acceptors) than any of the acceptor components of the exciplexes and exhibit near diffusion-controlled rates of quenching in all cases. The moderate acceptors M and cinnamonitrile have reduction potentials in the middle of the range spanned by the acceptor components and show significantly lower rate constants for quenching. Crudely, Table VI shows that thermoneutral electron transfer as calculated by $\Delta E_{1/2}$ leads to rate constants in the range of 1 × 10^9 M^{-1} s^{-1} for these compounds, complementary to the results for electron donor quenching of exciplexes. The presumably weaker acceptors dimethyl maleate and acrylonitrile show even smaller rate constants, but we do not have a reduction potential for the former and the literature value for the latter seems far too low to reflect simple one-electron transfer in the light of the values for the other acceptors.

Table VII presents a study in which the quencher Q_2 is kept constant but the exciplex components are varied. Quenching of a series of substituted cyanophenanthrene···diethylaniline exciplexes shows that the expected trend in k_Q^{Cl} with variation in reduction potential results. Figure 11 plots these five points against the known[31] reduction potentials for the phenanthrene component of the exciplex. The line is drawn schematically to reflect the expected curvature at the diffusion limit. Taking the reduction potential of M as −1.87 V, the CH$_3$CN value, it is apparent that ΔE_Q = 0 corresponds to a rate of 2–3 × 10^9

Table VIII. Quenching[a] of Excited Monomers, M*, and Exciplexes, $(MQ_1)^*$, by Quenchers, Q_2

M* or $(MQ_1)^*$	Q_2	k_Q^{Cl}, M^{-1} s^{-1}	k_Q^M, M^{-1} s^{-1}
P	FN		10^{10}
P-FN	FN	$\lesssim 10^8$	
P	TME		$<10^7$
P-FN	TME	1.6×10^9	
P-F	TME	1.8×10^9	
9CNP	Et_3N		5.7×10^9
9CNP-*t*-An	Et_3N	9.8×10^7	
9CNP	FN		1.5×10^8
9CNP-*t*-An	FN	7.8×10^9	
pyrene[b]	$PhNEt_2$		6.2×10^9
pyrene-pyrene[b]	$PhNEt_2$	5.9×10^7	
pyrene	*trans*-PhCH=CHCN		2.2×10^8
pyrene-pyrene	*trans*-PhCH=CHCN	5.6×10^7	
pyrene-$PhNEt_2$	*trans*-PhCH=CHCN	3.0×10^9	

[a] In benzene, precision ±10%, unless stated otherwise. [b] In absolute ethanol.

M^{-1} s^{-1}, as above, and that $\Delta E_Q \sim +0.1-0.2$ V leads to k_Q^{Cl} approaching diffusion control. The results resemble those for donors and reinforce the ideas that both processes occur by electron-transfer interactions and follow similar ground rules.

The other entries in Table VII refer to a change in the donor component of the exciplex. According to the geometric model presented above, this component is expected to be the one farthest away from the added quencher (diethyl fumarate) in the exciplex. However, it too has an effect (albeit not very large). Presumably it exerts its effect by orbital splitting and alterations in the exciplex polarity, which could be expressed as a ΔE_{LUMO} term if electron affinities were available.

Note that, in Table VII, raising χ_3 by varying substituent in ^{1}(9CP···$PhNEt_2$) raises the rate constant. Raising χ_3 by increasing the polarity of the exciplex in the ^{1}(3,9-CN_2P···βMS) series by substituent variation also raises the rate constant.

Magnitude of the Slopes of the Logarithmic Plots. The correlation of log k_Q^{Cl} with energy parameter of Figure 10 shows a slope ~4 eV^{-1}. The same number applies roughly to the line drawn in Figure 11, though the data are much more sketchy. A slope of about 16 eV^{-1} would correspond to $1/RT$ at room temperature and thus to an exact correspondence of activation free energy to the energetics of complete charge transfer. The value of 4 eV^{-1} thus corresponds to about 25% of complete charge transfer. A still larger value obtains for ^{1}(P···FN) (Figure 8). Clearly, the sensitivity of quenching rate to one-electron transfer parameters is substantial.

Comparison of Monomer and Excimer/Exciplex Quenching. Table VIII gives rate constants for quenching by a common Q_2 of monomers and the excimer exciplexes derived from them. Differences up to two orders of magnitude exist. For the pyrene excimer, the rate constants for quenching by *either* a donor ($PhNEt_2$) *or* an acceptor (PhCH=CHCN) are lower than for pyrene singlet, a result readily rationalized by FMO. By familiar perturbation arguments, we expect χ_2 to be above the pyrene HOMO and χ_3 to be below the pyrene LUMO (cf. Figure 9, center). Electron transfer to χ_2 or from χ_3 will thus be less facile than for the monomer for a common Q_2; the excimer is "stabilized" against electron-transfer quenching. We presume that other excimers would show similar behavior.

For exciplexes, two cases obtain. In the simpler, the second quencher Q_2 is a donor when Q_1 is an acceptor (and vice versa). In such cases, we observe that the exciplex is quenched the faster. By the reasoning above, Q_2 will interact with the frontier orbital of the initially excited monomer. The FMO picture provides a ready rationalization so long as we assume that the electron-electron repulsions discussed above are dominant; cf. Figure 9 (right). If so, χ_2(exciplex) will be lower than χ_2(excited monomer) in (e.g.) ^{1}(P···FN) compared to ^{1}P, and ^{1}(P···FN) is a better acceptor toward donors such as TME than ^{1}P. Analogously, χ_3(exciplex) will be above χ_3(excited monomer) when the acceptor component is the excited one; thus ^{1}(9CNP···*t*-An) is a better donor toward FN than is ^{1}9CNP alone.

In the second case, Q_2 and Q_1 are either both donors or both acceptors. The orbitals of the excited monomer are now not relevant. For example, the interaction of $^1(P^{\delta+}\cdots FN^{\delta-})$ with FN will involve a LUMO predominantly on FN, and the comparison of ^{1}P LUMO with an $FN^{\delta-}$-like LUMO is not meaningful; the $^1(9CNP^{\delta-}\cdots t\text{-}An^{\delta+})$ case quenched by Et_3N would lead analogously to a comparison of a 9CNP HOMO with a $t\text{-}An^{\delta+}$ HOMO. The observations that, when Q_1 is a donor, forming $^1(M\cdots Q_1)$ stabilizes ^{1}M against quenching by another donor Q_2, and, when Q_1 is an acceptor, forming $^1(M\cdots Q_1)$ stabilizes against further quenching by acceptors, are, however, intuitively reasonable.

Summary

The rate data presented herein can all be rationalized simply. Excited complex quenching by a donor (acceptor) will occur with high rate constant only when it is roughly as oxidizable (reducible) as the excited complex. When electron transfer would be exothermic by ca. 0.2-0.3 eV, the quenching rate constant will be close to diffusion controlled.

The problem of determining the exciplex oxidation potential (i.e., the energy of χ_2 in Figure 9) or reduction potential (the energy of χ_3) remains. Energies of χ_2 and χ_3 are determined by three factors: (a) the energy of the HOMO of the donor component for χ_2 or the LUMO of the acceptor component for χ_3; (b) orbital splitting, which is particularly significant for excimers in raising χ_2 relative to the monomer HOMO and lowering χ_3 relative to the monomer LUMO; (c) electron repulsion effects within the components, significant only for polar exciplexes, which lower the energy of χ_2 and χ_4 (donor based) and raise the energy of χ_1 and χ_3 (acceptor based). Our results suggest that good predictions of quenching rate result from consideration of ΔE_Q alone, i.e., properties of monomers and quenchers, where ΔE_Q = IP(donor component) − IP(donor quencher) or − E_{red}(acceptor component) + E_{red}(acceptor quencher). Thus *for moderately polar exciplexes,* $\Delta E_Q \gtrsim +0.2-0.3$ *V will lead to diffusion-controlled exciplex quenching, with* $\Delta E_Q = 0$ *affording ca.* 10^9 M^{-1} s^{-1}. In fact, for some highly polar exciplexes, it appears that diffusion-controlled rates of quenching can even result for negative ΔE_Q.

For excimers and rather nonpolar exciplexes, $\Delta E_Q = 0$ *affords rates* $\lesssim 10^7$ M^{-1} s^{-1}, *and* $\Delta E_Q \gtrsim +0.5-0.6$ *V is required for quenching rates* $\gtrsim 10^9$ M^{-1} s^{-1}.

Finally, the success we have obtained with our correlations with IP and E_{red} provides strong evidence for the generality of quenching from the donor side by donor quenchers, (Q_D···D···A) instead of (D···A···Q_D), and of quenching from the acceptor side by acceptor quenchers, (D···A···Q_A) instead of (Q_A···D···A), as first shown by Beens and Weller.[18] We believe that this geometry may be suggestive of chemistry deriving from exterplexes.

Experimental Section

Materials. AR benzene was extracted with concentrated H_2SO_4 until no further discoloration of the acid occurred, washed (H_2O, then saturated $NaHCO_3$), dried (anhydrous Na_2SO_4), distilled off Na/Pb alloy, and stored over 4A molecular sieves. Absolute ethanol was used as received. Phenanthrene (Eastman Kodak, EK) was purified as described previously;[10] (EK) pyrene and 9-cyanophenanthrene (Aldrich) were treated in boiling absolute ethanol with Norit A and recrystallized three times from absolute ethanol. Anthracene (EK blue-violet fluorescent) was used as received. The other substituted phenanthrenes were prepared and purified as previously described.[9] Fumaronitrile (Aldrich) and dimethyl fumarate (EK) were recrystallized twice from hexane-benzene and benzene, respectively. Diphenylamine and triphenylamine were recrystallized twice from aqueous ethanol following treatment with Norit A. *trans*-β-Methylstyrene and dimethyl maleate were purified by fractional distillation under reduced pressure using a Teflon-coated spinning band column. Fractions containing <1% (by GLC on Carbowax 20M) of the wrong isomers were used. *trans*-Anethole was distilled at water pump pressure (12-18 mm) through a 15-cm Vigreux column; fractions containing <1% by GLC of the cis isomer were used. *N,N*-Diethylaniline was distilled once at water pump pressure off granulated zinc through a Vigreux column. Triethylamine, 2-methyl-2-butene, 2,3-dimethyl-2-butene (Aldrich), dihydropyran, ethyl vinyl ether, and acrylonitrile were all distilled at atmospheric pressure. Styrene, α-methylstyrene, and cinnamonitrile were purified by simple distillation under reduced pressure. Diethyl fumarate was distilled at water pump pressure through a 15-cm Vigreux column; a fraction containing <1% of the cis isomer by GLC was used. All liquid samples were stored under N_2 and over 4A molecular sieves at 0-5 °C in the dark. *N,N,N′,N′*-Tetramethyl-1,4-diaminobenzene was prepared from an aqueous solution of its hydrochloride by addition of aqueous KOH. The crude product was filtered and recrystallized from aqueous ethanol. The product from recrystallization was dissolved in benzene and dried over Na_2SO_4 and the solution passed through basic alumina (to remove oxidation products) just prior to use. The concentration of the resulting solution was determined by evaporation (water pump) of an aliquot of the solution and weighing the residue to constant weight. 4-Methyl-*trans*-β-methylstyrene was prepared as follows. Reaction of ethylmagnesium iodide with *p*-tolualdehyde afforded 1-(4-methylphenyl)propanol, purified by distillation at water pump pressure. The alcohol was dehydrated by treatment for 20 min with a trace of *p*-toluenesulfonic acid in refluxing benzene. The crude product was distilled at water pump pressure through a 15-cm Vigreux column. A fraction containing <1% of the cis isomer (by GLC) was used. The compound has satisfactory NMR and UV spectra. *p*-Isobutenylanisole was prepared in like fashion from *p*-anisaldehyde and 2-bromopropane as previously described.[9]

Methods. Fluorescence spectra were recorded on a Farrand MKI ratio recording spectrofluorometer using a Houston Instruments Omnigraphic X-Y recorder.

Sample Preparation and Exciplex Quenching. Spectra of air-saturated benzene solutions (3 mL) were obtained in standard 10-mm quartz or Pyrex cuvettes. Generally the concentration of M was $10^{-3} \rightarrow 10^{-4}$ M and of Q_1 0.02 → 0.2 M. The exciplex quenchers (Q_2) were added either as neat liquids or for solids as solutions of known concentration in benzene, using Hamilton syringes. We find under these conditions using benzene only that up to 200 → 300 μL of liquid can be added to the sample (3 mL) without significantly ($\lesssim$2-3%) affecting the fluorescence intensity. However, correction to [Q_2] for dilution by Q_2 at each addition has been made. Outgassed samples were prepared in 13- or 16-mm o.d. Pyrex tubes. The samples were outgassed by three freeze (liquid N_2)-pump-thaw cycles (to $<10^{-3}$ mmHg) and then sealed off. All spectra were obtained at 22-25 °C.

Exciplex Lifetimes by the Indirect, O_2 Quenching Method. Argon was bubbled for 10 min through solutions of M + Q_1 contained in 10-mm path length Pyrex cuvettes closed with a rubber septum. The fluorescence spectrum was recorded, the septum removed, and air bubbled through the solution until no further drop in fluorescence intensity could be observed. Exciplex lifetimes τ_{C1} were obtained from the I_{argon}/I_{air} ratios as described in the Methods and Results section.

Exciplex Lifetimes by Nanosecond Flash Spectroscopy. For these measurements samples were outgassed by the freeze-pump-thaw method as described above and sealed in Pyrex tubes. Concentrations of M were chosen so that the optical densities at 337 nm were in the range 0.1 → 0.5. The samples were excited at 337.1 nm by 20-40 pulses s^{-1} (fwhm $\simeq$ 8 ns) from a homemade N_2 laser. Fluorescence emission passed through a Spex 1704 monochromator to either an RCA 1P28 or Hamamatsu R446 photomultiplier. The PM output was analyzed using a Princeton Applied Research 152 boxcar integrator equipped with a Model 164 processor module. Scanning of the boxcar aperture delay afforded the time dependence of the emission. The time base was calibrated with a 50-MHz crystal oscillator whose output signal was also passed through the boxcar integrator. The boxcar output was recorded on a Houston Instruments Omnigraphic X-Y recorder. In general, lifetimes were determined by deconvolution.

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