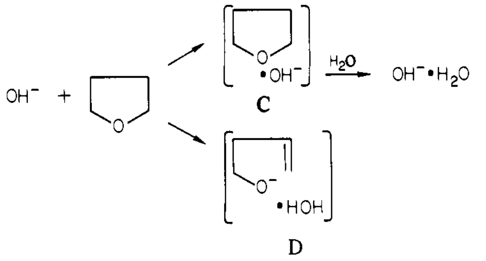
the reaction time was increased, the detected OH^- current initially increased substantially before beginning to decrease. For all of these reactions, a major ionic product appeared at a mass corresponding to addition of the reactants. These products are rapidly destroyed by traces of water vapor, carbon dioxide, or other impurities to produce $OH^-(H_2O)$, HCO_3^-, or other corresponding species. We view this process as occurring by the mechanism in eq 22. The adduct (most likely a simple cluster C but conceivably a cluster D in which elimination has occurred) is weakly bound, and a large fraction of these species collisionally dissociate to regenerate reactants. This phenomenon produces an increase in detected OH^- signal since the more rapidly diffusing OH^- species is temporarily replaced in the flow tube by a larger, more slowly diffusing adduct; the diffusive loss of ions is thereby lessened.[18] Addition of water rapidly and quantitatively destroys the adducts. There is evidence that at least some of the addition product exists in form D. When OH^- is allowed to react with perdeuteriotetrahydrofuran, both OD^- and $OD^-(H_2O)$ are generated; these species must originate from decomposition and a switching reaction, respectively, of complex D in which elimination has occurred.



(22)

Similar unusual kinetic behavior occurs for reaction of NH_2^- with oxetane, and a mechanism similar to eq 22 is therefore implicated. The adduct in this case is expected to be very weakly bound, and, in fact, only traces of this ion are observed. Alternatively, for oxetane the initial substitution product $[H_2NCH_2CH_2CH_2O^-]$ may fragment by an exothermic but "invisible" process

$$[H_2NCH_2CH_2CH_2O^-] \rightarrow NH_2^- + CH_2CH_2 + CH_2O \qquad (23)$$

This mechanism would also explain the slow rates of reaction of NH_2^- and OH^- with oxetane.[19] The reactions of amide with tetrahydrofuran, tetrahydropyran, and 3-methyltetrahydrofuran, in contrast to those of hydroxide, are well behaved and easily measured and only small amounts of adduct formation are observed.

In conclusion we have observed that most cyclic ethers undergo rapid β-elimination reactions with NH_2^- and OH^- in the gas phase. Strained ethers which react by ring opening may generate ions with sufficient internal energy to allow further fragmentation, usually of the reverse-aldol type. Indeed, even unstrained ethers may fragment upon ring opening, and reversible, and hence hidden, fragmentation may be a common phenomenon in gas-phase reactions of anions.

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Registry No. **1**, 109-99-9; **2**, 2167-39-7; **3**, 142-68-7; **4**, 13423-15-9; **5**, 96-47-9; **6**, 503-30-0; **7**, 930-22-3; **8**, 646-06-0; **9**, 123-91-1; **10**, 21490-63-1; NH_2^-, 17655-31-1; OH^-, 14280-30-9.

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Long-Distance Fluorescence Quenching by Electron Transfer in Rigid Solutions[1]

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Abstract: Fluorescence of aromatic molecules in solid solutions at room temperature and low temperature is quenched by addition of strong electron donors. The efficiency of quenching correlates well with calculated energetics for electron transfer (ET) from the added donors to the excited molecules, $D + A^* \rightarrow D^+ + A^-$. The quencher (D) always had a substantially higher-lying excited state than did A to prevent electronic energy transfer (e.g., Förster transfer). The A* fluorescence decreased exponentially with D concentration, being halved by addition of about 0.1 M D in cases with favorable energetics for electron transfer. These quenching measurements are interpreted as indicating electron transfer over distances up to 15 Å (center to center). These maximum quenching distances are in excellent agreement with electron tunneling distances measured for ion-molecule reactions by pulse radiolysis. Formation of donor-acceptor complexes during sample preparation is a possible alternate interpretation, but several features of the data provide evidence against this alternative.

Introduction

Intermolecular electron transfer (ET) has long been recognized as an efficient mechanism for fluorescence quenching in fluid solutions.[4-9] The energetics of the ET steps can be described in terms of the singlet excitation energy ($E(S_1)$) of the excited molecule, the oxidation potential ($E(D/D^+)$) of the donor (D),

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(3) Undergraduate Research Participant from the University of Chicago; see note 2.

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and the reduction potential ($E(A/A^-)$) of the acceptor (A).[4,10] It is worth noting that the excited molecule may function as either A or D, depending on the energetics of the system. The well-known equation 1 serves to estimate free energy changes and

$$-\Delta G^\circ_{\mathrm{E,}t} = E(S_1) - E(D/D^+) + E(A/A^-) + e^2/\epsilon R$$
$$= E(S_1) - \Delta G^\circ(D^+\cdot A^-) + e^2/\epsilon R \qquad (1)$$

contains as the last term a correction for the Coulomb energy changes associated with charge separation. Since fluorescence quenching by ET has to compete with the normal fluorescence decay, it can be used to obtain rates of ET processes and to establish correlations between rates and energetics.[4-9] The reverse process, the formation of excited states from chemically prepared radical ions, has also been studied.[11]

If D and A are randomly dispersed in rigid matrices, a new dimension is added. One may ask at which distances ET by photoexcited molecules is possible within the constraint of a limited excited-state lifetime. The answer to this question is important for many reasons. For example, charge separation in photosynthesis involves ET from an excited chlorophyll species through an array of acceptors held at relatively fixed distances. It is desirable to understand this process to the point where molecular systems can be designed performing similar energy-storing functions. These same processes are also critical to operation of organic, solid-state photoimaging systems.

Fluorescence quenching of organic molecules in cryogenic glasses by polychlorinated hydrocarbons has been previously reported.[13-16] The unusual kinetics of fluorescence decay as measured by nano- and picosecond spectroscopy strongly support an ET mechanism for the quenching in these systems. From a study of the quencher concentration dependence an ET distance of 9.8 Å was deduced. Unfortunately, these systems are ill-suited for a systematic study because the energetics of these processes are not well understood.

Previous studies in this laboratory have been directed toward increasing ET distances in ground-state radical ion–neutral molecule pairs, described by eq 2.[17-24] In favorable cases ET

$$D^- + A \rightarrow D + A^- \qquad D + A^+ \rightarrow D^+ + A \qquad (2)$$

distances of 15–18 Å were measured to be spanned in 10^{-8} s, a typical fluorescence lifetime. Of course, in these cases, much longer distances have been observed at longer times (e.g., 35 Å at 10^2 s) because any competing processes are very slow. Pulse radiolysis experiments in progress indicate that these electron transfer distances are not subtantially decreased by large tunneling barrier heights.[20] We therefore expected that ET by photoexcited molecules should be possible at 15–18-Å distances. We now wish to report that this expectation has been confirmed for aromatic molecules excited by visible light in rigid matrices at room temperature (and above) and at 77 K.

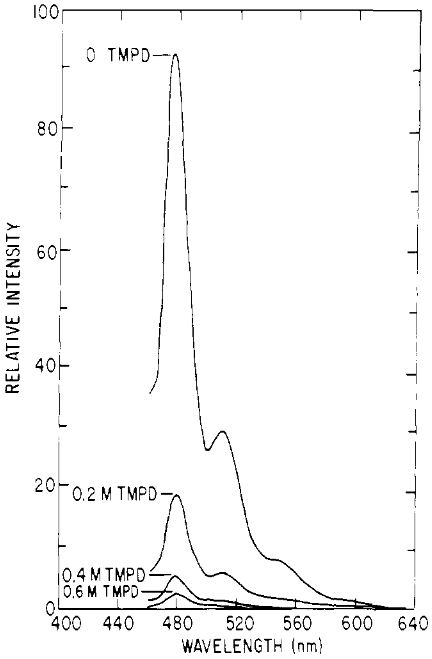

Figure 1. Fluorescence spectra of perelyene in rigid decalindiol (DD) at 295 K. The fluorescence is partly quenched in samples containing varied concentrations of the electron donor TMPD.

Experimental Section

Materials and Sample Preparation. Most of the chemicals were used as received from Aldrich and Eastman. *trans*-1,5-Decalindiol (DD) and *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) were sublimed. When melted at >150 °C and recooled to room temperature (24 ± 2 °C), DD yielded a clear, colorless rigid matrix (d = 1.128 g/mL). Its glass transition is probably a few degrees below room temperature, and it devitrifies over several days. Subsequent tests showed that molecular mobility is unimportant in fluorescence quenching experiments in DD up to at least 90 °C. Tetrakis(dimethylamino)ethylene (TMAE) from RSA Corp. was distilled (bulb to bulb) twice under vacuum. MTHF (2-methyltetrahydrofuran) was distilled from lithium aluminum hydride.

All samples were degassed and sealed off under vacuum. The samples contained a concentration of the fluorescer molecule (A) sufficient to give an absorbance of about 1.5 at a prominent low-energy absorption band (usually the 0–0 band), plus varied concentrations of the quencher (D). In all cases reported here, the acceptor (A) was excited. Some of the fluorescent acceptors, most notably rubrene, were unstable to photochemical decomposition in solution. Sample preparation was therefore carried out in a darkened room. In rigid DD at room temperature no decomposition was observed. Solid DD, fluorescer, and quencher in evacuated cells were melted together at 200 °C and quenched to room temperature by immersion in water.

TMAE reacts with O_2 yielding chemiluminescence. For samples containing TMAE, vacuum-sublimed DD was transferred to a glovebox without exposure to air. The cells were filled in an N_2 atmosphere, capped, and transferred to the vacuum line for outgassing and sealing.

Fluorescence yields were measured by using a Perkin-Elmer Model 44B spectrofluorimeter equipped with a differential correction unit. Low-temperature measurements were made in cylindrical, 3-mm i.d., quartz cells which fitted into the tail of a Dewar. Room-temperature measurements were made in 3 × 9 mm i.d. Pyrex cells placed at a 45° angle to excitation and emission beams. Higher-temperature measurements on DD samples were performed by immersing the fluid samples at 200 °C into a Dewar in the Fluorimeter containing hot water at the desired lower temperature.

Results

Figure 1 shows fluorescence spectra typical of those measured in this study. The fluorescence intensity decreased close to exponentially with the quencher (TMPD) concentration:

$$I/I_0 = \exp(-cv) \qquad (3)$$

where I_0 is the fluorescence intensity without quencher, c is the

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(10) We will neglect the small energy $e^2/a\epsilon$ which corrects for forming ions at a finite distance a, where ϵ is the dielectric constant.

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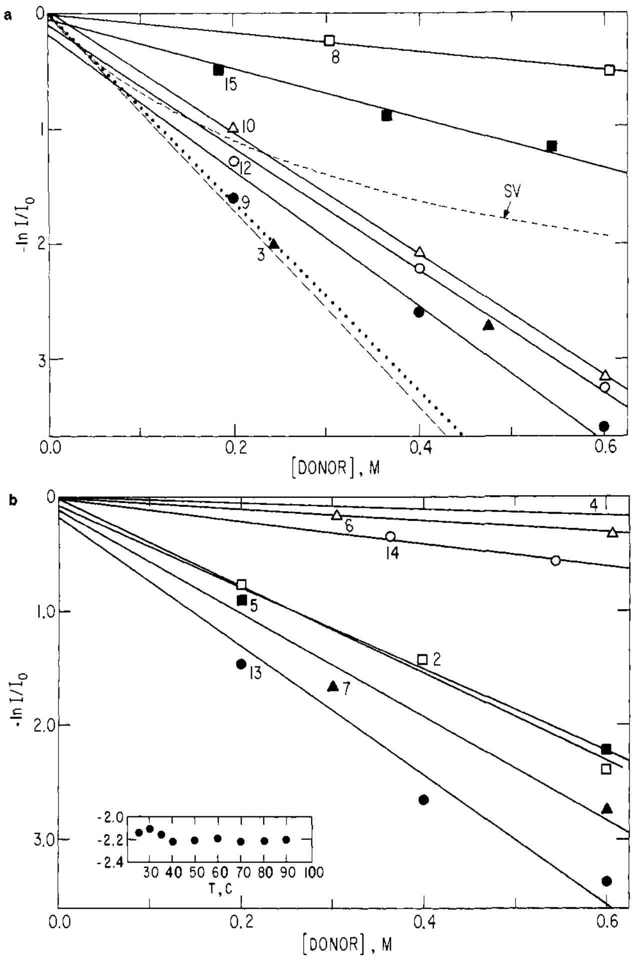

Figure 2. Relative fluorescence intensities, I/I_0, measured as a function of quencher concentration in DD at 295 K. The solid lines are least-squares fits to the data using eq 5. The numbers identify the fluorescer-quencher pairs in Table I. In part a the dotted line (and tangential straight, dashed line) shows slight departures from linearity caused by the range of excited-state lifetimes,[29] and the dashed line labeled SV shows Stern-Volmer kinetics (eq 11), which fail to fit the data. The inset in part b shows the lack of temperature dependence for quenching of excited 9-methylanthracene by 0.4 M TMPD in DD.

quencher concentration (number/volume units), and v is the quenching volume discussed below. This exponential dependence is illustrated in the semilog plots of Figure 2. The dotted line in Figure 2a shows Stern-Volmer kinetics, typical for fluorescence quenching in fluids, which do not hold for this solid-state quenching process. The inset in Figure 2b shows a test for temperature dependence from room temperature to 90 °C for the system 9-methylanthracene (9MA) + TMPD in DD. No temperature dependence was observed although DD changes from a solid to a very viscous liquid over this range. This clearly indicates that diffusional processes are not important for quenching in DD, even at 90 °C.

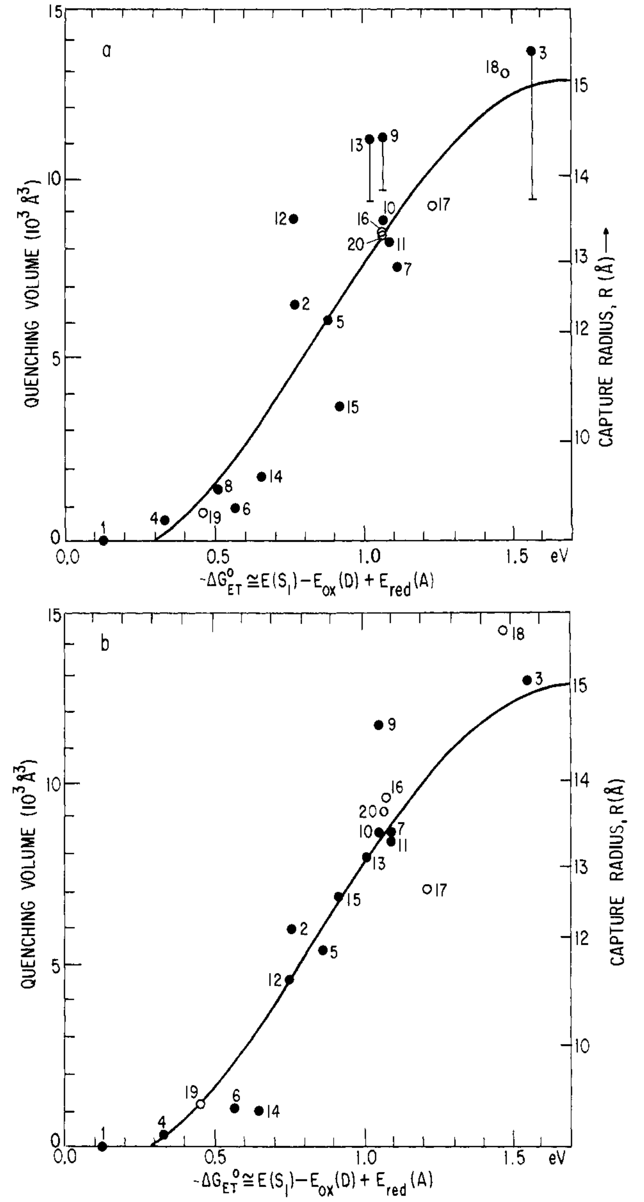

Figure 3. (a) Measured quenching efficiencies expressed as quenching volumes (eq 5) and radii (eq 6) vs. exothermicity for the excited-state electron transfer reaction. The line assumes that electron transfer rates show Gaussian dependence on exothermicity (see text). (b) The same data, with the quenching radii (and therefore volumes) adjusted to compensate for variations in fluorescence lifetimes, τ_f, using eq 8 with a = 0.75 Å. The radii were adjusted to the values that they would have if all the τ_f's were changed to 10 ns.

Table I reports the observed quenching volumes for all the systems studied, along with data from the literature giving energetics of the ET process (eq 1). For four of the systems showing strongest quenching, departure from exponential quenching kinetics is noticeable. In these cases our measure of quenching efficiency, the quenching volume v of eq 3, is not uniquely defined. For these cases we reported v from the best fit to eq 3 from $\ln(I/I_0) = 0$ to -2.0 (over the first 87% quenching) to give a quenching volume typical of the average. The lines shown in Figure 2 are from linear regression on the data points for ln I including zero quencher concentration. Uncertainties to 80% confidence ranged from ±15% for the cases with more scatter and/or fewer points to ±3%, excepting systems 3 and 9, where we estimate ±25% and ±40% uncertainty. For system 9, which showed very weak quenching, the only data point was at 0.909 M, $\ln(I/I_0) = -0.26$. Figure 2 just shows a line drawn to this point. Figure 3 shows the dependence of the quenching volume on the energetics of the ET reaction (eq 1). Error bars extend down to quenching volumes obtained if all the data are fitted.

The absorption and emission spectra of the glasses showed no features not characteristic of either D or A alone with the exception of one system, acridine + DEA. With 0.546 M DEA added in DD, the acridine fluorescence peaking at 420 nm decreased by about a factor of 5 and a new emission appeared. The new emission, which was broad and structureless, extended to about 650 nm. It indicates the probable presence of an electron donor-acceptor (EDA) complex. The absence of new emissions in all the other systems is consistent with, but does not prove, the hypothesis that significant amounts of charge transfer complexes are not present in the other systems.

Discussion

We will interpret the observed fluorescence quenching in terms of long-distance (up to 15 Å) electron transfer, but two other

Table I. Measured Quenching Volumes (ν) and Radii (R) with Energy Parameters for Electron Transfer Fluorescence Quenching Energetics in Polar Liquids

acceptor, τ_f[a]	donor[b]	$E(S_1)$[c]	$\Delta G(D^+ \cdot A^-)$[d]	$-\Delta G_{ET}$[d,e]	$10^{-3}\nu$,[f] Å^3	R,[g] Å
1. rubrene, 16.5	DEA	2.29	2.17	0.12	0	0
2. rubrene	TMPD	2.29	1.65	0.76	6.4	12.7
3. rubrene	TMAE	2.29	0.74	1.57	13.6[h]	15.5[h]
4. tetracene, 22.6	DEA	2.60	2.28	0.32	0.6	7.9
5. tetracene	TMPD	2.60	1.74	0.86	6.0	12.1
6. 9,10-dinaphthylanthracene, 5.5	DEA	3.16	2.60	0.56	0.9	9.0
7. 9,10-dinaphthylanthracene	TMPD	3.16	2.06	1.10	7.6	13.3
8. perylene, 7.5	DEA	2.85	2.35	0.50	1.4	8.2
9. perylene	TMPD	2.85	1.81	1.04	11.2[h]	14.4[h]
10. 9-methylanthracene, 4.6	TMPD	3.19	2.14	1.05	8.8	13.5
11. 9,10-diphenylanthracene, 9.4	TMPD	3.16	2.08	1.08	8.0	13.1
12. coronene, 380[i]	TMPD	2.95	2.20	0.75	8.8	13.5
13. benzo[*ghi*]perylene, 107	TMPD	3.10	2.08	1.02	11.1[h]	14.4[h]
14. fluoranthene, 53	DEA	3.14	2.47	0.67	1.7	9.1
15. acridine, 0.4[j]	DEA	3.19	2.28	0.91	(3.6)[h]	10.6[h]
	In Ethanol (E) or MTHF (M) at 77 K					
16. 9-methylanthracene (E)	TMPD	3.19	2.14	1.05	8.4	13.3
17. fluoranthene (E), 53	TMPD	3.14	1.93	1.21	9.2	13.6
18. acridine (E), 5[j]	TMPD	3.19	1.74	1.45	13.6	15.3
19. 9-methylanthracene (M)	DEA	3.19	2.73	0.46	0.8	8.1
20. 9-methylanthracene (M)	TMPD	3.19	2.14	1.05	8.2	13.2

[a] Fluorescence lifetimes, τ_f, in nanoseconds. Unless otherwise noted the values are from ref 21. [b] DEA = *N,N*-diethylaniline; TMPD = *N,N,N',N'*-tetramethyl-*p*-phenylenediamine; TMAE = tetrakis(dimethylamino)ethene. [c] First excited singlet energy in electron volts. Except for rubrene, all values are taken from ref 11. [d] $\Delta G(D^+ \cdot A^-) = E_{ox}(D) - E_{red}(A)$, in electron volts, where E_{ox} and E_{red} are oxidation and reduction potentials measured in *polar fluids*. The actual values in our rigid solvents are probably somewhat greater (see text). Values are taken from ref 11 with the correction for polarity removed. [e] Standard free energy change in electron volts for the ET reaction *polar fluids* using eq 2 with the Coulombic term e^2/ER omitted. [f] Measured quenching volume using eq 5. [g] Radius if quenching volume is spherical, using eq 6 with R_0 estimated from molecular models as 7 Å except for reactions of rubrene and dinaphthylanthracene where $R_0 = 8$ Å was used. [h] These quenching plots showed substantial curvature. The quenching volume reported is the average over the 90% quenching. [i] G. Porter and M. R. Topp, *Proc. R. Soc. London, Ser. A*, 315, 163–84 (1970). We took the value in rigid PMMA. [j] Acridine fluorescence lifetimes are very sensitive to temperature and the nature of the solvent. We took values in ethanol from S. L. Shapiro and K. R. Winn, *J. Chem. Phys.*, 73, 5958–62 (1980).

plausible mechanisms must be considered. They are electronic energy transfer by the Förster or exchange mechanism, and formation of donor–acceptor complexes before the matrix becomes rigid.

Of these, the energy transfer mechanism is the easiest to eliminate. The D/A pairs have been chosen so that the quencher excited singlet state lies substantially higher than that of the fluorescer. In the most favorable case for energy transfer, 9-methylanthracene + TMPD in DD energy transfer would be endothermic by 0.38 eV or 15 times kT at room temperature. The resulting Boltzmann factor of $\leq 3 \times 10^{-7}$ makes any energy transfer negligible.

In some of the cases studied, energy transfer to the triplet state may be energetically allowed, but the rates are negligible due to spin restrictions. This can be expected to slow singlet-to-triplet ET by as much as a factor of 10^8 in hydrocarbons. Furthermore, the triplet states of the quenchers used (TMPD, 2.8 eV;[24] DEA ~3.3 eV[25]) lie above the fluorescent states of many of the molecules studied.

Having dismissed energy transfer as a possible mechanism for the observed quenching, we now will examine whether formation of electron donor–acceptor (EDA) complexes might be the cause of the reduced fluorescence. Any possible EDA complexes will have to be formed while the samples are still fluid so that the donor and acceptor can diffuse together to make the complex. The association constant K_a given by

$$K_a = [DA]/([D][A]) \tag{4}$$

always increases with decreasing temperature.[38] In the solid samples used in this study the equilibrium will be frozen in at the admittedly ill-defined fluid–glass transition temperature. The complex can be expected either to be nonfluorescent or to fluoresce with a new band at lower energy. Hence, only uncomplexed molecules will fluoresce with a spectrum of the quencher-free solutions and the relative fluorescence yield is expected to show Stern–Volmer concentration dependence.

$$I/I_0 = \frac{[A]}{[A] + [DA]} = (1 + K_a[D])^{-1} \tag{5}$$

It is interesting to notice that this Stern–Volmer kinetics for static quenching by complexation arises in a different way than does the usual Stern–Volmer kinetics for dynamic quenching in fluid solutions.

In addition to Stern–Volmer concentration dependence, there are some other features expected of the complexing mechanism, setting it apart from the ET mechanism. For example, complexing is favored for easily oxidized donors and easily reduced acceptors and therefore should correlate inversely with the $\Delta G(D^+ \cdot A^-)$ values listed in Table I. Complexing should be quite sensitive to steric effects and to the temperature at which the fluid becomes a rigid matrix. As long as ET is reasonably exothermic, the quenching efficiency should not depend on the excitation energy $\Delta E(S_1)$ or on fluorescence lifetimes, τ_f, in the complexing mechanism.

Next, we discuss the ET mechanism, examine predictions that can be made, and then give a detailed comparison of the exper-

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imental findings with the predictions made for the two mechanisms.

Of central importance in the ET mechanism is the quenching volume v introduced in eq 3 of the Results section. The simplest possible interpretation of the quenching volume is analogous to the capture volume model used in another context by Perrin.[26] Surrounding each fluorescer molecule is a volume v the size of which is defined operationally. If a quencher lies within this volume, the fluorescence will be quenched, otherwise not. If, for simplicity, we assume v to be spherical, an unrealistic assumption (see discussion below), then

$$v = (4\pi/3)(R_q^3 - R_0^3) \tag{6a}$$

$$R_q = [(3v/4\pi) + R_0^3]^{1/3} \tag{6b}$$

R_0, which is defined as the center-to-center distance when D and A are in contact, corrects for the fact that D and A cannot occupy the same space.

Pulse radiolysis experiments in solids showed that ET rates for reactions of radical ions or trapped electrons depend exponentially on distance[17-20,27,28] and can be approximated by eq 7. The

$$k_{ET}(R) = \nu \exp[-(r - R_0)/a] \tag{7}$$

frequency factor ν is proportional to a Franck–Condon weighted density of states, which depends on the exothermicity, $-\Delta G°_{ET}$, of the electron transfer reaction. It reaches a maximum value of $10^{13\pm1}$ s^{-1} when $\Delta G°_{ET}$ equals the total rearrangement energy, λ, typically 0.5–1 eV. In eq 7 the range parameter, a, determines the steepness of the rate–distance dependence. A typical value determined from electron transfer in random matrices[20] is a = 0.75 Å giving a rate decrease of 1 order of magnitude for each ~1.7-Å increase in distance.

An exact mathematical model of fluorescence quenching by a process obeying eq 7 was derived by Inokuti and Hirayama.[29] Although they were concerned with energy transfer, their results apply equally here. They found a very complicated solution which could be recast in the simple form of eq 3 with good accuracy when $R_q \gg a$. R_q is then to good approximation[29] the distance at which the ET quenching rate equals the normal fluorescence decay rate and is given by

$$R_q = R_0 + a \ln \nu\tau_f \tag{8}$$

R_q thus depends on τ_f and all of the molecular parameters which control the dependence of the ET rate on distance and reaction energetics. In contrast to the simple Perrin model R_q and v are recognized to be average quantities, although the average is over a narrow range if $R_q \gg a$. Setting $\tau_f = 10^{-8}$ s, a = 0.75 Å, R_0 = 6 Å, and $\nu = 10^{13\pm1}$ s^{-1}, we estimate the maximum quenching radius (for $-\Delta G°_{ET} = \lambda$) to be 15.6 ± 1.7 Å. For ET quenching with less favorable exothermicity, R_q will be smaller.

It is worth noting that the treatment given above contains a number of simplifying assumptions. Specifically, dispersion in singlet-state lifetimes, dispersion in solvation energies of D and A, and orientation effects have all been ignored. When taken into account, a dispersion of R_q can be expected to cause deviation from the exact exponential form of eq 3. Inokuti and Hirayama[29] calculated exactly the effect of the dispersion of the excited-state lifetimes. The effect of this correction is remarkably small and is plotted as the lower dashed line in Figure 2a. The remaining two simplifications are more difficult to correct for and in the absence of reliable models no attempts have been made to estimate their effect. However, it is safe to say that the neglect of orientation effects and dispersion of solvation cannot lead to major errors because the large body of data collected in pulse radiolysis of random matrices gives a fairly good correlation with the simplified model.

In summary, long-distance ET quenching should display the following features: (1) fluoroescence yield decrease should have a close to exponential dependence on quencher concentration; (ii) the quenching efficiency should depend on $-\Delta G°_{ET}$ and should be at a maximum at 0.5–1 eV; (iii) the maximum radius observable should be ~15 Å so the fluorescence yield should be halved by 0.07 M quencher and reduced by a factor of 10 at ~0.22 M; (iv) the quenching efficiency should depend on τ_f, but only weakly so because 1 order of magnitude change in τ_f will change R_q only by ~1.7 Å; (v) for the most efficient quencher ($-\Delta G°_{ET} = \lambda$) the quenching efficiency should be nearly temperature independent.[31]

We will now discuss the data in more detail and show that they are entirely consistent with the predictions made for the ET mechanism while serious discrepancies exist between the data and predictions made for the complexing mechanism.

First, the quenching efficiency as a function of the donor concentration shows a nearly exponential dependence, while a Stern–Volmer plot gives a very poor fit as shown in Figure 2a. Next, the dependence of the quenching efficiency on $-\Delta G°_{ET}$ also strongly favors the ET mechanism. The observed dependence of the quenching volume on $-\Delta G°_{ET}$ is shown in Figure 3 and is that expected for the ET mechanism. The scatter apparent in Figure 3a is reduced by correcting for difference among the fluorescence lifetimes of the various fluorescers (Figure 3b). Quenching becomes ineffective for $-\Delta G°_{ET}$ of less than 0.5 eV. The simplest possible theoretical formulations of the ET rates give a Gaussian dependence[30,31] of the frequency factor ν in eq 9. This simple

$$\nu = \nu_0 \exp[-(\Delta G°_{ET} + \lambda)^2/(4\lambda kT)] \tag{9}$$

Gaussian form is expected[31-37] to be inadequate in the highly exothermic region ($-\Delta G°_{ET} > \lambda$), but we have no data in the highly exothermic region. The curve in Figure 3 was computed by substituting into eq 6a R_q calculated by eq 10, with a = 0.75 Å,

$$R_q = R_0 + a \ln \nu_0\tau_f - a[(\Delta G°_{ET} + \lambda)^2/(4\lambda kT)] \tag{10}$$

λ = 1.7 eV, and the maximum quenching radius, $R_0 + a \ln \nu_0\tau_f$ = 15 Å. Equation 10 was obtained by substituting eq 9 into eq 8. The unusual shape of the curve in Figure 3 occurs because the ordinate is our observable, quenching volume, which is not simply proportional to the ET rate constant. For example, with a = 0.75 Å, a factor of 2 reduction in quenching volume corresponds to a factor of 45 reduction in ET rate constant. The 1.7 eV value of λ is probably too high because the $\Delta G°_{ET}$ values used are taken from measurements in polar fluids containing electrolytes and will be too large for our conditions. Electrostatic effects which we cannot esimate accurately will also give small changes in both $\Delta G°_{ET}$ and λ with distance. In general, however, the dependence on $-\Delta G°_{ET}$ is that expected for the ET mechanism while the complexation mechanism requires a different dependence. While the association constants K_a do depend on $-\Delta G$ of the reaction, $-\Delta G°_{ET}$ contains the excitation energy which should not influence K_a. The data by contrast do show a strong dependence on $\Delta E(S_1)$. For example, fluorescence of perylene is much more efficiently quenched by TMPD than is fluorescence of tetracene, although $\Delta G°(D^+ \cdot A^-)$ is more favorable for complexing of tetracene.

Several similar examples can be found by examining Table I. If the quenching efficiency were (inversely) correlated with $\Delta G°(D^+ \cdot A^-)$ as expected for complexing, then the efficiencies (as measured by quenching volumes) for quenching by TMPD should be in the order rubrene > tetracene > perylene > 9,10-dinaphthylanthracene > 9,10-diphenylanthracene ≈ benzo[*ghi*]perylene > 9-methylanthracene > coronene. Instead the observed quenching volumes are in the order perylene > benzo[*ghi*]perylene > 9-methylanthracene = coronene > 9,10-diphenylanthracene > 9,10-dinaphthylanthracene > rubrene > tetracene. The two compounds with best complexing energetics, rubrene and tetracene, show in fact the weakest quenching, in accord with their relatively small values of $-\Delta G°_{E}$t.

Another observation in disfavor of the complexing mechanism is the relative insensitivity of the quenching volume on the temperatures at which the sample becomes rigid. The high temperatures of sample preparation in decalindiol (DD) are very unfavorable to complex formation. Much more efficient complexing would be expected in the low-temperature glasses (EtOH) and (MTHF) where the equilibria are probably frozen at ~−150 vs. ~50 °C in DD. Yet the data show similar quenching volumes in DD and the low-temperature glasses for pairs with similar ET energies.

Similar arguments can be based on steric effects which can be expected to influence complex formation but should have no effect in the ET mechanism. One of the most effective quenching molecules is TMAE, which does not form complexes with several aromatic acceptors tested by Hammond,[39] because of severe steric hindrance. Also, rubrene and diphenylanthracene are sterically hindered by their phenyl substituents, yet they are quenched with efficiencies similar to those of unhindered molecules having similar ET energetics. Lishan, Hammond, and Yee[42] showed that dimethylaniline formed exciplexes much more effectively with anthracene than with 9,10-diphenylanthracene. The ratio of the quenching rate constants $k_q(\mathrm{A})/k_q(\mathrm{DPA})$ was 20 in benzene and 200 in cyclohexane. Ion formation is energetically unfavorable in these low-dielectric solvents. By contrast, our data show no such steric effects, as expected in long-distance ET.

The small but significant effect of excited-state lifetime on quenching efficiency also argues for the ET mechanism. Coronene with 390-ns excited-state lifetime is quenched by TMPD much more efficiently than other molecules having similar energetics. The lifetime effect is also reflected in reduced scatter of the data points after corrections for lifetime differences have been made. With the assumption that every complexed molecule will be completely quenched, there should be no lifetime dependence for the complexing mechanism. The scatter remaining in Figure 3b after correction for fluorescence lifetimes may be due in part to variations in λ, which depends on such factors as the size of a charge distribution in D^+ and A^- ions.

Finally, we failed to detect any new absorptions or emissions in the systems with one exception (acridine–DEA). Of course, this is only negative evidence because it is commonly observed that complexing leaves absorption bands unaltered.[38] The absence of charge transfer emissions suggests either that complexes are not formed or that the complexes fluoresce too weakly to be detected.

In conclusion, we believe that several lines of experimental observation are strongly supportive of the long-distance ET mechanism of fluorescence quenching and that the complexing mechanism, if in operation at all, contributes only to a very minor extent.

Having decided in favor of the ET mechanism, there are a few experimental findings that deserve further discussion. From the data listed in Table I it appears that maximum quenching is observed for systems with $-\Delta G°_{\mathrm{ET}} \sim 1.7$ eV. This is somewhat misleading, because the $\Delta G°_{\mathrm{ET}}$ values used here apply strictly to polar liquids (e.g., acetonitrile, $\epsilon = 37$) in which redox potentials of the compounds were measured. The dielectric constants of the rigid matrices used here are certainly much smaller, especially on the short time scale ($\sim 10^{-8}$ s) of fluorescence quenching. They might be similar to dielectric constants of some polymers such as polyesters and cellulose derivatives which range from 2.8 to 7.[43] Using a value of 5 for ϵ, $-\Delta G°_{\mathrm{ET}}$ would be reduced by about 0.43 eV and maximum quenching would occur at 1.3 eV. For $\epsilon = 3.3$ the maximum would occur at 1.0 eV. These estimates are based on the simple Born formula for polarization energies and include also the opposing effect of Coulombic attraction, $e^2/\epsilon r$ in eq 1, for ET quenching at 15 Å. Because the Coulombic term depends on the ET quenching distance, the $-\Delta G°_{\mathrm{ET}}$ scale in Figure 3 not only would be shifted but also would be somewhat compressed if corrections for the dielectric constant were made. Having no specific information on the dielectric properties of our matrices, we attempted no such correlation in plotting quenching efficiency vs. ET energetics.

In classical theories[30] of ET rates, strongly temperature-dependent ET rates are expected in the weakly exothermic region $-\Delta G°_{\mathrm{ET}} \ll \lambda$. Quantum formulations predict a much weaker temperature dependence,[33-37] particularly if the distribution of oscillators contributing to λ peaks at fairly high energies. A puzzling feature of the present data is that little difference is seen between quenching in DD at $\approx$295 K and in EtOH or MTHF at 77 K. A study of quenching in a weakly exothermic reaction covering a wide temperature range in a single solvent would be desirable[44] and would be expected to show temperature dependence. The absence of strong temperature dependence for the 9MA + TMPD reaction (Figure 2b) is not surprising because $-\Delta G°_{\mathrm{Et}} \approx \lambda$ for this reaction, and eq 10 predicts only a 9% increase in the quenching volume. The increase could be partially cancelled by a decrease of τ_f with increasing temperature.

ET distances up to 15 Å at $\approx 10^{-8}$ s are indicated in this study. It should be emphasized that these are center-to-center distances. For the pair rubrene–TMAE at 15.5 Å (center to center), at no orientation are the nearest edges of the π systems[45] further than 12 Å apart, and they are as close as 6 Å in some orientations. It is probable that the quenching volumes are quite nonspherical and depend on the orientations of both the fluorescer and the quencher. Further orientation effects will arise from the symmetry properties of the wave functions. Orientation effects might be responsible, in part, for departures from exponential dependence of quenching or quencher concentration observed in some cases.

The large ET distances of fluorescent molecules we infer from this data stand in contrast to most data in the literature. Picosecond spectroscopy results of Mataga's[46] and Eisenthal's[47] groups on aromatics bonded by $(\mathrm{CH_2})_n$ chains can be interpreted by assuming that ET requires a collision or very near collision of the reactants. We suggest that different results indicating long-distance ET can be obtained if more exothermic reactions are studied. Fluorescence quenching by ET at even longer distances ($k_{\mathrm{ET}} = \tau_f^{-1}$ at 20 Å, with slight quenching measureable to 29 Å) was reported by Möbius[48] in experiments with monolayer assemblies. Our ET distances in $\sim 10^{-8}$-s fluorescence times are then smaller than those found in monolayer assemblies, similar to those found for radical ions in glasses by pulse radiolysis, and larger than those inferred from other experiments.

Conclusions similar to those of this paper have been reached by Guarr and McLendon.[49] They found $\approx$15-Å maximum quenching distances for electron transfer from excited ruthenium complexes by electron acceptors.[49,50] Their results have been briefly described in an abstract[51] as have ours.[52] Very recently we have found evidence for quenching of long-lived ($\approx$6 s) triplet excited states by electron transfer over 25-Å distances.[53]

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Registry No. DEA, 91-66-7; TMPD, 100-22-1; TMAE, 996-70-3; rubrene, 517-51-1; tetracene, 92-24-0; 9,10-dinaphthylanthracene, 43126-71-2; perylene, 198-55-0; 9-methylanthracene, 779-02-2; 9,10-diphenylanthracene, 1499-10-1; coronene, 191-07-1; benzo[*ghi*]perylene, 191-24-2; fluoranthene, 206-44-0; acridine, 260-94-6.

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