Singlet Energy Transfer to Azoalkanes

Paul S. Engel,[1a] Laurence D. Fogel,[1b] and Colin Steel*[1b]

Contribution from the Departments of Chemistry, Rice University,
Houston, Texas 77001, and Brandeis University, Waltham, Massachusetts 02154.
Received June 22, 1973

Abstract: The rate constants for the transfer of singlet energy from a variety of aromatic donors to azoalkanes are reported. In a number of cases it can be shown that exchange interactions predominate and, for these, estimates can be made of the exchange interaction energy, U_e. For the trans-azoalkanes $U_e = 20 \pm 10$ cm^{-1} and for the cis-azoalkanes $U_e = 50 \pm 20$ cm^{-1}.

To date the most thoroughly explored mechanism of singlet energy transfer is the coulombic-induced or Förster transfer.[2,3] However, as the oscillator strengths of the donor emission and acceptor absorption bands decrease, the importance of coulombic-induced transfer diminishes and exchange-induced transfer may become significant.
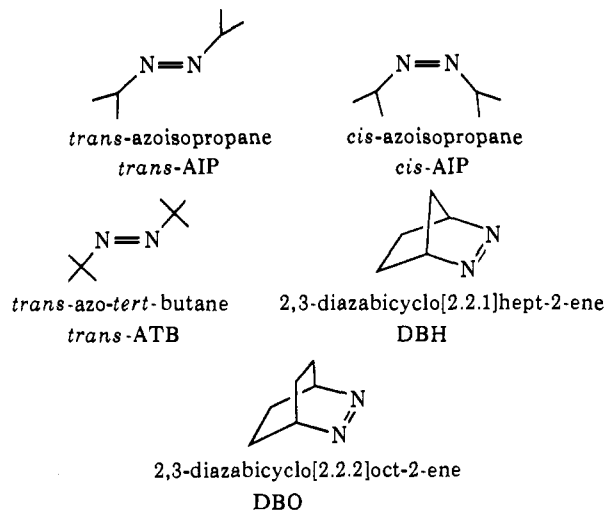
$$^1D^* + {}^1A \xrightarrow{k_q{}^e} {}^1D + {}^1A^* \qquad (1)$$
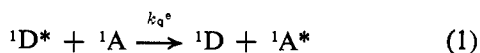
Aliphatic azo compounds fall into this latter category because of their low extinction coefficient n–π^* bands (Figure 1). Moreover, the absence of nearby bands allows one to observe the rare but theoretically predictable fall-off in transfer rate when the singlet energy of the donor greatly exceeds that of the acceptor. Some preliminary data in this field have been reported.[4-6] In this paper, we shall consider these data together with a body of results for a variety of aromatic hydrocarbon donors and azoalkane acceptors in light of current theories of energy transfer.

Experimental Section

Materials. The preparations of the azo compounds shown below have already been reported.[7-11] Before use, trans-AIP and

cis-AIP were purified by preparative gas chromatography and trans-ATB by spinning band distillation; their purities were checked

trans-azoisopropane
trans-AIP

cis-azoisopropane
cis-AIP

trans-azo-tert-butane
trans-ATB

2,3-diazabicyclo[2.2.1]hept-2-ene
DBH

2,3-diazabicyclo[2.2.2]oct-2-ene
DBO

by analytical vpc. DBH and DBO were purified by sublimation. The solid aromatic hydrocarbons were purified either by vacuum sublimation or by zone refining. Benzene and m-xylene were distilled carefully and the center cut employed. In all cases the purity of the hydrocarbons was checked before use by comparison of their absorption and emission spectra with that given in the literature.[12,13] The spectrograde solvents, cyclohexane, acetonitrile, isooctane, and hexane, were used without further purification.

Quenching Studies. Steady-state emission spectra of degassed solutions were measured on a Farrand spectrofluorimeter (C. S. and L. F.) and on a Perkin-Elmer Hitachi spectrofluorimeter (P. E.). Absorption spectra were recorded on a Cary 14R spectrophotome-

(1) (a) Rice University; (b) Brandeis University.

(2) (a) T. Förster, "Modern Quantum Chemistry," O. Sinanoglu, Ed., Academic Press, New York, N. Y., 1965, pp 93-137; (b) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley, New York, N. Y., 1970.

(3) R. G. Bennett and R. E. Kellogg, Progr. React. Kinet., 4, 215 (1967).

(4) K. R. Naqvi and C. Steel, Chem. Phys. Lett., 6, 29 (1970).

(5) P. S. Engel, J. Amer. Chem. Soc., 91, 6903 (1969).

(6) P. S. Engel and P. D. Bartlett, J. Amer. Chem. Soc., 92, 5883 (1970).

(7) R. Renaud and L. C. Leitch, Can. J. Chem., 32, 545 (1964).

(8) I. I. Abram, G. S. Milne, B. S. Solomon, and C. Steel, J. Amer. Chem. Soc., 91, 1220 (1969).

(9) S. G. Cohen and R. Zand, J. Amer. Chem. Soc., 83, 2895 (1961).

(10) S. G. Cohen and R. Zand, J. Amer. Chem. Soc., 84, 586 (1962).

(11) J. Stowell, J. Org. Chem., 32, 2360 (1967).

(12) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1971.

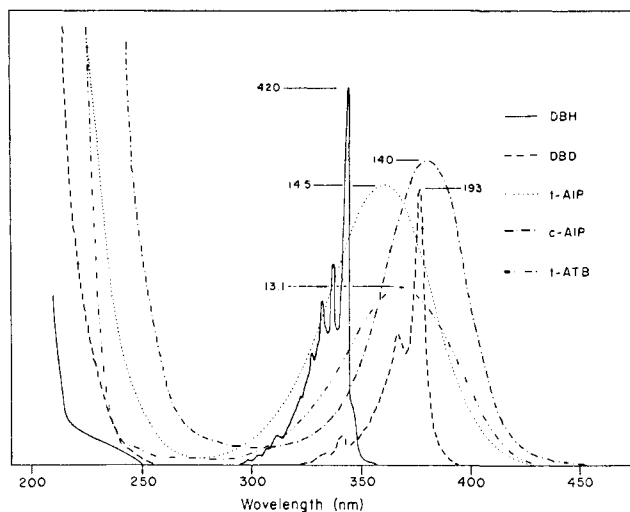(13) E. J. Bowen and B. Brocklehurst, J. Chem. Soc., 3875 (1954).

Figure 1. Absorption spectra of azo compounds in cyclohexane. The numbers refer to the extinction coefficients (M^{-1} cm^{-1}) at the absorption maxima of the n → π* bands: (——) DBH; (- - - -) DBO; ($\cdots\cdots$) trans-AIP; (— · —) cis-AIP; (—— · ——) trans-ATB.

ter. The rate constant, k_q, for the quenching of the aromatic hydrocarbon donor (D) fluorescence by the azoalkane acceptor (A) was determined by measuring the steady-state emission intensities of D in the absence (I_0) and in the presence (I) of A. I was always

$$I_0/I = 1 + \tau_D k_q[A]$$

corrected for trivial absorption by the acceptor.[14] Except for coronene, the lifetimes (τ_D) of the various donors were taken from ref 2b and 12. The coronene singlet lifetime was determined by exciting a degassed cyclohexane solution with an air-spark flash (1/e time = 0.13 × 10⁻⁶ sec; 0.005 μf capacitors) and by monitoring the emitted light with the photomultiplier-oscilloscope circuit previously described.[15] A lifetime of 0.35 × 10⁻⁶ sec was obtained, in good agreement with that reported by Kropp and Dawson for coronene in a solid matrix.[16] Direct evidence that the quenching of aromatic hydrocarbons occurs by energy transfer as represented by eq 1 is the fact that the fluorescence of DBO can be effected by exciting naphthalene–DBO in regions where only naphthalene absorbs.[4] Good indirect evidence is the fact that the experimental quenching constant falls off rapidly when the singlet energy of the donor is less than the singlet energy of the acceptor (see, for example, Figure 5) and that singlet sensitization results in the same photochemistry as direct n → π* irradiation.[17]

Theory

General treatments of both coulombic- and exchange-induced energy transfer have been given.[2a,18] In this section some of the major results which are important in the interpretation of the experimental data will be presented. In particular, the rate constant for exchange-induced transfer will be expressed in such a manner that its formal similarity with coulombic-induced transfer is apparent. This form also leads to a simple method for estimating exchange energies from experimental data.

Coulombic Interactions. It can be shown that the first-order rate constant for coulombic-induced transfer

(14) C. A. Parker, "Photoluminescence of Solutions," Elsevier, New York, N. Y., 1968, p 222. Right angle illumination was used. Under these conditions log I_0/I = log $(I_0/I)_{exptl}$ − ΔD_{exc}^A − ΔD_{em}^A, where ΔD_{exc}^A is the absorbance, for $l = \frac{1}{2}$ cell length, of A at the exciting wavelength and ΔD_{em}^A is the corresponding absorbance at the wavelength where the emission is monitored.

(15) C. Steel and T. F. Thomas, *Chem. Commun.*, 900 (1966).

(16) J. L. Kropp and W. R. Dawson, "Molecular Luminescence," E. C. Lim, Ed., W. A. Benjamin, New York, N. Y., 1969, p 39.

(17) P. S. Engel and C. Steel, *Accounts Chem. Res.*, **6**, 275 (1973); *cf.* ref 8.

(18) D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953).

of electronic energy from a donor D to an acceptor A separated by a distance R is given by

$$k_t{}^c(R) = \frac{4\pi^2}{h} U_c{}^2 \int f_D(\bar{\nu})\bar{\epsilon}_A(\bar{\nu})d\bar{\nu} = \frac{4\pi^2}{h} U_c{}^2 J \quad (2)$$

In eq 2 subscript t stands for transfer. If the transfer is specifically coulombic induced, the superscript c is used. For exchange-induced transfer, the superscript is e. The subscript q is used in eq 1 since the constant is often measured by studying the quenching of ¹D* fluorescence by A. $\bar{\epsilon}_A(\bar{\nu})$ is the normalized extinction coefficient of the acceptor absorption at wave number $\bar{\nu}$ (cm⁻¹), that is $\int \bar{\epsilon}_A(\bar{\nu})d\bar{\nu} = 1$; $f_D(\bar{\nu})$ is the similarly normalized fluorescence intensity at $\bar{\nu}$ of the donor. Thus, the integral J in the above expression is a measure of the Franck–Condon overlap of the donor emission and acceptor absorption bands. U_c is the matrix element $\langle \psi_{D*}\psi_A | V_c | \psi_D\psi_{A*}\rangle$ for the coulombic interaction energy, where V_c is the coulombic potential arising from interaction between the protons and electrons of D with the charges on A. Equation 2 is in fact a form of the Förster equation; however, in the latter $\epsilon_A(\bar{\nu})$ is usually left unnormalized. We choose to incorporate the oscillator strength of A into U_c leaving $\bar{\epsilon}_A(\bar{\nu})$ as a normalized term in the F–C integral. This preserves the formal similarity with exchange-induced transfer, as seen in eq 5.

The field arising from a complex arrangement of positive and negative charges can be analyzed as the sum of fields arising from a dipole (d) plus a quadrupole (q) plus an octapole (o) and so on. Provided $R \gg \sigma$ (the diameter of the molecules concerned), V_c can be expressed as a series in increasing powers of $1/R$. Moreover, under these conditions the leading term in the series $(V_c{}^{d-d})$ will dominate.[19] $V_c{}^{d-d}$ represents the

$$V_c{}^{d-d} = \frac{1}{n^2 R^3}\left\{\mathbf{m}_D \cdot \mathbf{m}_A - \frac{3}{R^2}(\mathbf{m}_D \cdot R)(\mathbf{m}_A \cdot R)\right\} \quad (3)$$

interaction between $\mathbf{m}_D$, the dipole moment associated with D, and $\mathbf{m}_A$, the dipole moment associated with A. Neglecting higher terms, $U_c{}^2$ becomes

$$U_c{}^2 = \frac{K^2|M_{D*\to D}|^2|M_{A\to A*}|^2}{n^2 R^6} \quad (4)$$

where K^2 is an orientation factor (about 0.66), n is the solvent refractive index, $M_{D*\to D}$ is the mean electronic transition moment for the transition D* → D, and $M_{A\to A*}$ is the corresponding moment of the transition A → A*.

For smaller values of R, $R \sim \sigma$, there is of course still a coulombic interaction but V_c can no longer be expressed as a power series in R. However, by constructing models for typical dipoles and quadrupoles and numerically evaluating $V_c(R)$ at $R \sim \sigma$, the following can be deduced: (a) for d–d interaction, eq 3 is not in error by more than a factor of 2; (b) d–q and q–q interactions, though of the same order, are still smaller than d–d interactions. Thus, eq 3 will give the correct order of magnitude for the coulombic interaction and the Förster equation will still be a reasonable approximation for the rate of coulombic-induced energy transfer.

(19) W. Kauzmann, "Quantum Chemistry," Academic Press, New York, N. Y., 1957, p 504.
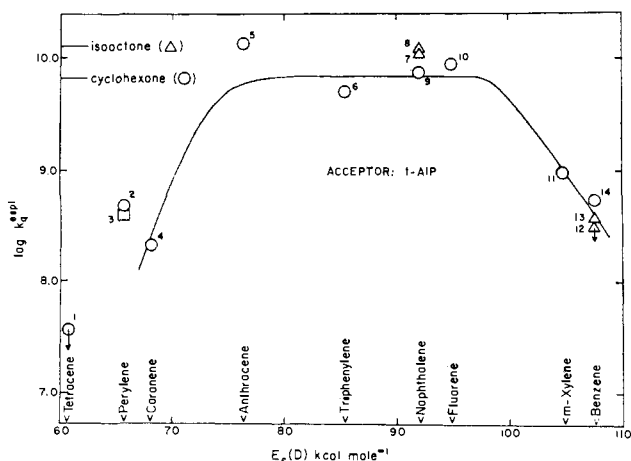
Figure 2. Rate constants for the quenching of the fluorescence of aromatic compounds by *trans*-AIP as a function of aromatic singlet energy. Solvent: acetonitrile (□), isooctane (△), and cyclohexane (○). The horizontal lines on the top left of the diagram refer to the values of the diffusion-controlled constant (k_d) calculated from eq 9. The viscosities are to be found in ref 23. Points 7 and 12 from ref 1. In some cases the quenching was so small that only upper limits to k_q could be given; these points are shown with arrows.
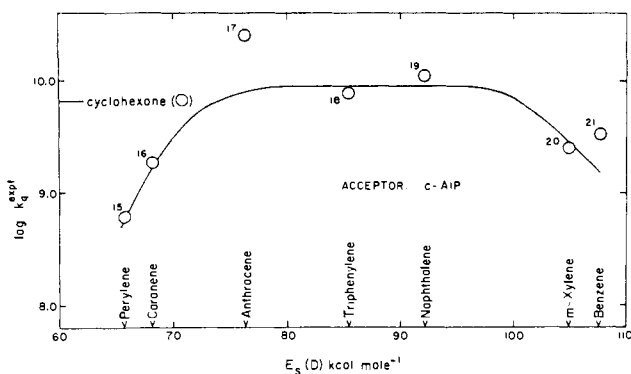

Figure 3. Rate constants for fluorescence quenching by *cis*-AIP.

Exchange Interactions. For $R \sim \sigma$, one must also consider the fact that the electrons of D and A may now exchange. This perturbation results in exchange-induced energy transfer[4] (eq 5), where U_e is the ex-

$$k_t{}^e(R) = \frac{4\pi^2}{h}U_e{}^2 \int f_D(\bar{\nu})\bar{\epsilon}_A(\bar{\nu})\mathrm{d}\bar{\nu} = \frac{4\pi^2}{h}U_e{}^2J \quad (5)$$

change-interaction energy. Unfortunately, unlike U_c, U_e cannot be expressed in terms of experimentally observable quantities so that its evaluation becomes a formidable quantum mechanical problem for all but the very simplest of systems.[18,20]

Relationship of Transfer Constants to Quenching Rate Constants. Consider an energy transfer process that requires a close encounter, say $R_{enc} \sim \sigma$. The rate constant for formation of (D*, A) pairs is equal to the familiar second-order diffusion constant

$$k_d = 4\pi ND\sigma/1000 \quad (6)$$

where D is the sum of the diffusion coefficients of the donor (D_D) and of the acceptor (D_A). The probability that energy transfer will occur during an encounter will equal $k_t(\sigma)/(k_t(\sigma) + k_{-d})$, where $k_t(\sigma)$ is the first-order rate constant for energy transfer of (D*, A) pairs

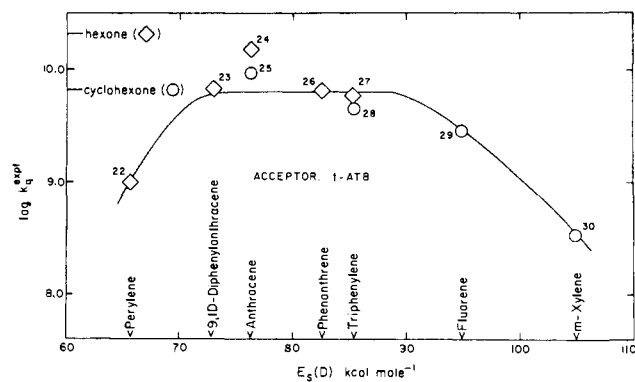(20) J. N. Murrell and G. Shaw, *J. Chem. Phys.*, **49**, 4731 (1968).

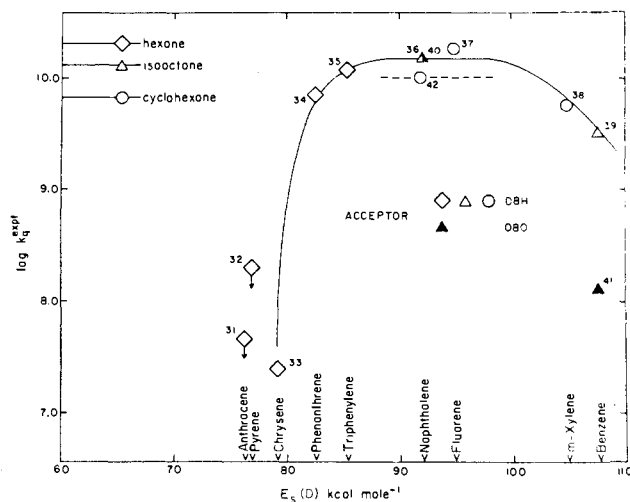Figure 4. Rate constants for fluorescence quenching by *trans*-ATB. Points 22-24, 26, and 27 from ref 6.

Figure 5. Rate constants for fluorescence quenching by DBH (open points) and by DBO (closed points). Points 31-35 from ref 5; points 36 and 39-41 from ref 4.

at the encounter distance σ, and k_{-d} is the first-order rate constant for diffusion of D* and A out of the encounter cage. An approximate formula for the latter is[21]

$$k_{-d} = 6D/\sigma^2 \quad (7)$$

We should therefore have

$$k_q = \frac{4\pi ND\sigma}{1000} \frac{k_t(\sigma)}{k_t(\sigma) + (6D/\sigma^2)} \quad (8)$$

where k_q is the second-order constant associated with reaction 1.

In the Förster equation, a critical transfer distance R_0 is defined such that $k_t{}^c(R_0)$ equals the reciprocal of the fluorescence lifetime of the donor in the absence of quencher (τ_D). It should be pointed out that $R_0 \sim \sigma$ does not imply that quenching by coulombic interaction is necessarily efficient. Fluorescence lifetimes of many donors lie in the range 5–50 nsec[2b,12] so that $k_t{}^c(R_0) \sim 10^8$ sec^{-1}. But for most solvents at room temperature $k_{-d} \sim 10^{10}$ sec^{-1}, so that under these circumstances, by eq 8, $k_q \ll k_d$.

Results and Discussion

Exchange-Interaction Dominant. (a) The Diffusion-Controlled Region. In Figures 2–5 the experimental

(21) P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, **90**, 2232 (1968).

Engel, Fogel, Steel / Singlet Energy Transfer to Azoalkanes

Table I. Comparison of $k_t^c(\sigma)$ with k_{-d} for Diffusion-Controlled Energy Transfer to Azo Compounds

Donor	Acceptor	Solvent	$10^{-10}k_t^c(\sigma)$,[a] sec^{-1}	$10^{-10}k_{-d}$,[b] sec^{-1}	$10^{-10}k_q$exptl, M^{-1} sec^{-1}	$10^{-10}k_d$,[c] M^{-1} sec^{-1}
Triphenylene	DBH	Hexane	0.020	13.2	1.2[d]	2.1
Naphthalene	DBH	Cyclohexane	0.34	4.2	1.0	0.66
Naphthalene	DBH	Isooctane	0.34	8.2	1.5[e]	1.3
Naphthalene	DBO	Isooctane	0.055	8.2	1.5[e]	1.3
Triphenylene	cis-AIP	Cyclohexane	0.30	4.2	0.78	0.66
Naphthalene	cis-AIP	Cyclohexane	0.075	4.2	1.1	0.66
Triphenylene	trans-AIP	Cyclohexane	0.031	4.2	0.61	0.66
Naphthalene	trans-AIP	Cyclohexane	0.019	8.2	0.77	0.66
Naphthalene	trans-AIP	Isooctane	0.019	4.2	1.2[e]	1.3

[a] Calculated from the Förster equation[2a] setting $\sigma = 5$ Å. [b] k_{-d} was calculated from eq 7 setting $\sigma = 5$ Å. D at 20° was obtained from $D = 2kT/3\pi\sigma\eta$ using experimental values of η. [c] Calculated from eq 9. [d] Reference 5. [e] Reference 4.
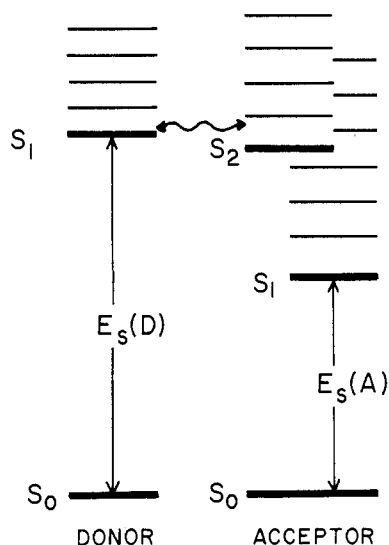

Figure 6. Energy levels involved in energy transfer when the singlet energy of the donor is considerably greater than the singlet energy of the acceptor.

quenching constants of various azo compounds for a series of donors are given. The original experiments reported in ref 4–6 were carried out using isooctane and hexane as solvents. Cyclohexane was used in this work because most lifetime studies[2b,12] and many kinetic measurements have been reported in this solvent. The horizontal lines in the figures give the values of k_d calculated from the equation[22]

$$k_d = 8RT/3000\eta \tag{9}$$

where η is the solvent viscosity.[23] It is apparent from eq 4 that in order to minimize coulombic effects one must choose (D, A) pairs in which the D → D* and A → A* transitions have low extinction coefficients. Some of the pairs which satisfy this criterion and yet have diffusion-controlled quenching constants have been tabulated in Table I. It can be seen that in all cases the coulombic term $k_t^c(\sigma)$ as calculated from the Förster equation is much smaller than k_{-d}, so that coulombic terms cannot account for the high rates. In these cases exchange interaction must dominate.

(b) Franck–Condon Factors. Even if U_c or U_e is

(22) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 626.
(23) "Handbook of Chemistry and Physics," 53rd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1972, pp F37, F40; "International Critical Tables," Vol. III, McGraw-Hill, New York, N. Y., 1930, p 218; J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Vol. I, Elsevier, New York, N. Y., 1950, p 94.

large, $k_t(R)$ will become small if the overlap integral J is small. This will occur either if the singlet energy of the donor $E_s(D)$ is significantly less than or greater than the singlet energy of the acceptor $E_s(A)$.

The first situation is especially familiar for triplet energy transfer where the fall-off in k_q when $E_T(D) < E_T(A)$ can be used as a method of locating the triplet of A. The second situation is less familiar because in general, when $E_s(D)$ (or $E_T(D)$) $\gg E_s(A)$ (or $E_T(A)$), higher levels of the acceptor overlap with the donor resulting in favorable transfer to these higher levels (see Figure 6). In the case of aliphatic azo compounds, the S_1–S_2 gap is large (see Figure 1) and one can observe the fall-off in k_q as one goes to the donors of higher energy where J is small. Thus, $E_s(D) > E_s(A)$ is a necessary but not sufficient condition for efficient energy transfer. This can be seen in Figures 2–5 where the high energy singlet donors, m-xylene and benzene, have quenching constants significantly less than diffusion controlled. The reason why the quenching constant for benzene–cis-AIP lies above that for m-xylene–cis-AIP will be discussed in the next section.

(c) Exchange-Interaction Energies. For conditions where exchange is dominant, one has a particular case of eq 8 with $k_t(\sigma) = k_t^e(\sigma)$. Two subcases may be considered. (i) In the diffusion-controlled region $k_q$exptl $\sim k_d$, so that by eq 8 $k_t^e(\sigma) > 6D/\sigma^2$. Therefore, from eq 5 and the above inequality one may estimate a lower limit of the exchange interaction energy U_e. (ii) In the region where $k_q$exptl $< k_d$, $k_t^e(\sigma) < 6D/\sigma^2$; from eq 8

$$k_t^e(\sigma) \approx \frac{6D}{\sigma^2\left(\dfrac{k_d}{k_q^{exptl}} - 1\right)}$$

Since D, σ, k_d, and $k_q$exptl are all known or can be estimated, $k_t^e(\sigma)$ can be determined. This value is then substituted into eq 5 to obtain U_e. The above inequalities will hold when J is sufficiently small. As pointed out above, this condition can be experimentally obtained in the singlet manifold but has not yet been realized in the triplet where the electronic energy levels tend to lie close together. Moreover, J values are difficult to evaluate at present for the triplet manifold since accurate determinations of the positions of the electronic levels and the Franck–Condon envelopes are in general not known. Thus, although triplet is much more common than singlet exchange-induced transfer, the latter affords the better method for experimentally evaluating exchange energies.

Table II. Exchange-Interaction Energies (U_e) for Various Donor–Acceptor Pairs

Point no.	Donor	Acceptor	Solvent	$10^{-10}k_q^{exptl}$, $M^{-1}\,sec^{-1}$	$10^{-10}k_d$,[a] $M^{-1}\,sec^{-1}$	$10^7 J$,[b] cm	U_e, cm^{-1}
34	Phenanthrene	DBH	Hexane	0.70	2.1	152	61
36	Naphthalene	DBH	Isooctane	1.50	1.3	2620	>16
38	m-Xylene	DBH	Cyclohexane	0.58	0.66	246	99
39	Benzene	DBH	Isooctane	0.32	1.3	101	47
40	Naphthalene	DBO	Isooctane	1.5	1.3	683	>32
41	Benzene	DBO	Isooctane	0.013	1.3	2	55
18	Triphenylene	cis-AIP	Cyclohexane	0.78	0.66	2019	>13
19	Naphthalene	cis-AIP	Cyclohexane	1.08	0.66	620	>18
20	m-Xylene	cis-AIP	Cyclohexane	0.25	0.66	192	34
21	Benzene	cis-AIP	Cyclohexane	0.34	0.66	247	41
6	Triphenylene	trans-AIP	Cyclohexane	0.60	0.66	1791	>14
9	Naphthalene	trans-AIP	Cyclohexane	0.77	0.66	1274	>17
8	Naphthalene	trans-AIP	Isooctane	1.2	1.3	1274	>23
11	m-Xylene	trans-AIP	Cyclohexane	0.098	0.66	103	25
14	Benzene	trans-AIP	Cyclohexane	0.057	0.66	44	27
13	Benzene	trans-AIP	Isooctane	0.039	1.3	44	22
27	Triphenylene	trans-ATB	Hexane	0.56	2.1	1725	>25
28	Triphenylene	trans-ATB	Cyclohexane	0.46	0.66	1725	>14
30	m-Xylene	trans-ATB	Cyclohexane	0.033	0.66	143	>11

[a] Calculated from eq 9. [b] Corrected donor emission spectra from ref 12. Acceptor absorption spectra from Figure 1.

Table III. Constants for Coulombic-Induced Energy Transfer $(k_t^c(\sigma))$ for Donors with High Extinction Coefficients

Donor	Acceptor	R_0,[a] Å	$10^{-10}k_t(\sigma)$,[b] sec^{-1}	$10^{-10}k_{-d}$,[c] sec^{-1}	$10^{-10}k_q^{exptl}$,[d] $M^{-1}\,sec^{-1}$
Anthracene	cis-AIP	13.6	8.4	6.3	2.51
Anthracene	trans-AIP	8.4	0.44	6.3	1.37
Anthracene	trans-ATB	10.1	1.3	6.3	1.07
Fluorene	trans-AIP	8.4	0.23	6.3	0.90
Fluorene	trans-ATB	7.9	0.17	6.3	0.29
Fluorene	DBH	25.5	17.5	6.3	1.83

[a] Calculated from the Förster equation.[2a] [b] See Table I footnote a. [c] See Table I footnote b. [d] Solvent cyclohexane. From eq 9, k_d has the value $0.66 \times 10^{10}\,M^{-1}\,sec^{-1}$.

It is also interesting to note that in the second region since

$$k_q \approx k_d \frac{k_t(\sigma)}{k_{-d}} = \frac{4\pi N\sigma^3}{6000}k_t(\sigma) \qquad (10)$$

the quenching constants should become independent of solvent viscosity. The slower migration of the species toward each other is exactly counterbalanced by the longer time they spend in encounter. Of course if the viscosity is increased sufficiently so that $6D/\sigma^2 < k_t(\sigma)$, then we no longer satisfy the condition for the second region and the rates will become viscosity dependent.

In Table II, the values of U_e calculated by the above methods are tabulated. In all cases the donors have low transition moments, $M_{D\rightarrow D^*}$, thus minimizing coulombic effects. It can be seen that cis-azo compounds have interaction energies in the range 50 ± 20 cm^{-1}, while the values for the trans compounds lie in the range 20 ± 10 cm^{-1}. It should also be noted that the experimental quenching constant is not necessarily a smooth function of $E_s(D)$. For example, comparison of the data for cis-AIP with m-xylene and benzene shows that the overlap with benzene is somewhat greater than that with m-xylene because the second absorption band of cis-AIP (see Figure 1) appreciably overlaps the emission band of benzene. Thus, the quenching constant does not decrease in going from m-xylene–cis-AIP to benzene–cis-AIP as it does for the other azo compounds.

Coulombic Effects. If the data for the "plateau" regions in Figures 2–5 are examined, it will be seen that,

in general, most points lie rather close to the values calculated from eq 9. However, some points do lie somewhat higher. The two most obvious in this category are anthracene–cis-AIP (point 17, Figure 3) and fluorene–DBH (point 37, Figure 5). In both of these cases the aromatic donor has a large extinction coefficient for the $S_0 \rightarrow S_1$ transition. In Table III we have gathered together all the data for donors lying in the "plateau" regions which have high extinction coefficients. It will be noticed that the two points mentioned above are those which have values of $k_t^c(\sigma)$ comparable to k_{-d} and R_0 values significantly greater than σ.

The determination of an explicit theoretical equation for the coulombic-induced quenching constant, k_q^c, in the viscosity region where diffusional effects are important is a problem that has been considered by several authors.[24–26] The complete equations are very complex and cannot be solved exactly.[25] However, Yokota and Tanimoto have given a treatment which seems to be in fair agreement with experiment. They show that under certain limiting conditions

$$k_q^c(M^{-1}\,sec^{-1}) = \frac{0.514\pi NR_0^{3/2}D^{1/4}}{1000\tau^{1/4}}$$

where R_0 is in centimeters, D in square centimeters per second, and τ in seconds. If one makes a plot of the experimental data for a series of donor–acceptor pairs

(24) M. Yokota and O. Tanimoto, *J. Phys. Soc. Jap.*, 22, 779 (1967).
(25) Y. Elkana, J. Feitelson, and E. Katchalski, *J. Chem. Phys.*, 48, 2399 (1968).
(26) J. B. Birks and M. S. S. C. Leite, *Proc. Phys. Soc., London (At. Mol. Phys.)*, 3, 513, (1970), and references cited therein.

for which coulombic-induced transfer has been involved,[24,26,27] most of the points, except those of anthracene, lie fairly close to the theoretical line for $k_q{}^c$ vs. $R_0{}^{1/2}D^{3/4}/\tau^{1/4}$. Using the Yokota-Tanimoto line, one estimates for fluorene–DBH ($R_0 = 25.5$ Å) in cyclohexane a $k_q{}^c$ of 2.0×10^{10} M^{-1} sec^{-1}; the experimental value is 1.83×10^{10} M^{-1} sec^{-1}. In the case of anthracene, it seems best to plot Ware's experimental values[27] of k_q vs. $R_0{}^{1/2}D^{3/4}/\tau^{1/4}$ and interpolate the value of k_q at $R_0 = 13.6$ Å. The value so obtained is $k_q{}^c = (1.9 \pm 0.6) \times 10^{10}$ M^{-1} sec^{-1}. The experimental value for anthracene–cis-AIP is 2.51×10^{10} M^{-1} sec^{-1}.

Conclusions and Problems

This study shows that the influence of coulombic and exchange interactions on the rate of singlet energy transfer can often be separated to a good degree of approximation. The data allow estimates to be made for U_e. Since U_c can be determined directly from spectral data, eq 2, 5, and 8 allow a reasonably good estimate to be made for the quenching constant (k_q) of any aromatic–azo pair.

There are, however, problems that remain. Although the diffusion-controlled quenching constants do depend upon solvent viscosity in the expected manner, the points for hexane do not differ from those for cyclohexane as much as one would expect from eq 9 (see Figure 4). Since the hexane data were taken from a different study,[6] there is always the possibility of a small

systematic error. The reason why the k_q for fluorene–trans-ATB lies below that for fluorene–trans-AIP (Table III) is also puzzling. It should not be due to a steric effect since we ran the quenching of triphenylene by azo-trans-octane, a very bulky azo compound, and obtained a k_q of 3.5×10^9 M^{-1} sec^{-1}, which is close to that of triphenylene–trans-ATB. Finally, we should mention the perylene–trans-AIP point (Figure 2). Perylene has a very high extinction coefficient (ϵ_{max} 39,500 M^{-1} cm^{-1}) but its Franck–Condon overlap integral with trans-AIP is vanishingly small. Therefore, both coulombic-induced and exchange-induced transfer should be precluded; nevertheless, the quenching constant is significant. Leonhardt and Weller[28] reported that aniline (IP = 7.7 eV) quenches perylene fluorescence with $k_q = 7.7 \times 10^9$ M^{-1} sec^{-1} in acetonitrile and with $k_q = 1.6 \times 10^7$ M^{-1} sec^{-1} in benzene. Since it seemed possible that the IP for trans-ATB could be low,[29] a charge-transfer complex could account for the high quenching constant for perylene–trans-AIP. We ran this pair in acetonitrile and also in cyclohexane, but as can be seen from Figure 2, the data afford no support for the idea of a charge-transfer complex.

(27) W. R. Ware, J. Amer. Chem. Soc., 83, 4374 (1961).

(28) H. Leonhardt and A. Weller, "Luminescence of Organic and Inorganic Materials," H. P. Kallman and G. M. Spruch, Ed., Wiley, New York, N. Y., 1962, p 74.

(29) E. Haselbach and E. Heilbronner, Helv. Chim. Acta, 53, 684 (1970).

Concerning the Role of Steric Factors in the Quenching of Alkylbenzene Fluorescence by Dienes[1,2]

Peter M. Froehlich and Harry A. Morrison*

Contribution from the Department of Chemistry, Purdue University, Lafayette, Indiana 47907. Received June 22, 1973

Abstract: The quenching of alkylbenzenes fluorescence by cis-piperylene has been studied for benzene and 22 mono- and polyalkylated benzenes. Rate constants, k_q, have been obtained from Stern–Volmer slopes and independently measured singlet lifetimes. The k_q values seem to be relatively independent of the number and size of the alkyl substituents, changing only significantly when two or three tert-butyl groups are appended to the ring. It is proposed that in the exciplex the interplanar distance between quencher and quenchee is 4.0 to 5.5 Å.

There has been considerable recent interest in the possible role of steric factors in bimolecular "photophysical" processes involving contact or near contact between partners.[3–6] The quenching of fluorescence

(1) Organic Photochemistry. XXVI. Part XXV: F. Scully, J. Grutzner, and H. Morrison, J. Amer. Chem. Soc., 95, 5100 (1973).

(2) Abstracted from the doctoral dissertation of P. Froehlich, Purdue University, August 1971; presented, in part, at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971.

(3) P. J. Wagner, J. M. McGrath, and R. G. Zepp, J. Amer. Chem. Soc., 94, 6883 (1972).

(4) A. Yekta and N. J. Turro, Chem. Phys. Lett., 17, 31 (1972).

(5) J. C. Dalton, D. M. Pond, and N. J. Turro, J. Amer. Chem. Soc., 92, 2173 (1970).

(6) K. Janda and F. S. Wettack, J. Amer. Chem. Soc., 94, 305 (1972).

of aromatic hydrocarbons by dienes is believed to be such a process, occurring via a transitory complex (exciplex) of the lowest excited singlet of the aromatic hydrocarbon with the ground state of the diene.[7] The suggested fate of the exciplex is outlined in eq 1, where

$$A^* + Q \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (AQ)^* \overset{k_2}{\longrightarrow} A_v + Q_v \qquad (1)$$
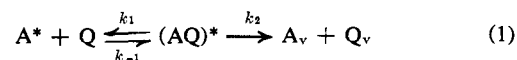
A* is the aromatic hydrocarbon in its electronically excited singlet state, Q is the quencher, (AQ)* is the

(7) (a) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, J. Amer. Chem. Soc., 88, 3665 (1966); (b) D. A. Labianca, G. N. Taylor, and G. S. Hammond, ibid., 94, 3679 (1972), and reference therein.