environments to the extent that the external virials exerted by the neighboring fragments remain unchanged.[20] When a fragment does exhibit changes in its properties in different systems, *e.g.*, (B) in BH_3, BF_3, the changes may be directly related to changes in the electrostatic fields exerted on the fragment and the effect they have on its virial and charge distribution.

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[20] R. F. W. Bader and G. Runtz, unpublished results.

Role of Charge Transfer Interactions in the Quenching of 1,4-Dimethoxybenzene Fluorescence[1,2]

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Abstract: The fluorescence of 1,4-dimethoxybenzene (DMB) in acetonitrile is quenched by a number of organic compounds having lowest lying excited singlets higher in energy than that of DMB. The rate constants show a structure-reactivity pattern that seems to implicate charge transfer as an integral part of the quenching process. The group as a whole does not show a linear correlation of log k_q with quencher reduction potentials, even though a limited relationship of this kind appears in selected subseries. The results suggest that charge transfer provides the binding energy of the exciplex, while the internal conversion of electronic excitation involves a vibronic mechanism not strongly dependent on the reduction potentials of the quenchers.

The fluorescence of electronically excited molecules is often quenched by compounds having no excited singlet states lying low enough to be populated by transfer of electronic energy available in the quenchee. In particular, the quenching of naphthalene fluorescence by conjugated dienes,[5] aliphatic[6,7] and aromatic amines,[7] and strained hydrocarbons[8,9] has been investigated in our laboratory and in others.

The role of charge-transfer interactions in singlet quenching is still in dispute. We have suggested that while charge transfer is the dominant pathway of electronic deexcitation in the quenching of naphthalene fluorescence by aliphatic amines,[6] charge transfer is not entirely responsible for the quenching of naphthalene fluorescence by conjugated dienes.[5] Others, however, have concluded that charge transfer interactions are the source of fluorescence quenching in these cases as well.[10,11]

Recently we reported that the fluorescence of indole, *N*,*N*-diethylaniline, anisole, 2-methoxy- and 2,6-dimethoxynaphthalenes, and other "electron-rich" aromatic molecules was quenched by methyl chloroacetate and 2-chloroacetamide and that the ordering of quenching rate constants suggested charge transfer from the excited molecule to the quencher.[12] We have extended this study by determining the rate constants for the quenching of 1,4-dimethoxybenzene (DMB) fluorescence by several groups of organic compounds, and report results which yield additional insight into the quenching mechanism.

Experimental Section

Materials. Acetonitrile (Matheson Coleman and Bell, Spectroquality) was used as received. The 1,4-dimethoxybenzene (Aldrich) was recrystallized twice from hexane. Chloroacetonitrile (Matheson Coleman and Bell) and chloromethyl methyl ether (Aldrich) were distilled from phosphorus pentoxide and a center cut was taken. The benzyl acetates were synthesized by treating the corresponding benzyl alcohols (commercial materials) with acetic anhydride in pyridine; the products were distilled and a center cut was taken. Benzyl chloride (Matheson Coleman and Bell) and the para-substituted benzyl chlorides (Aldrich), allyl acetate (Eastman), allyl chloride (Matheson Coleman and Bell), and ethyl trifluoroacetate (Calbiochem) were distilled and center cuts were taken. Methyl chloroacetate was distilled twice; a center cut was taken each time. 2-Chloroacetamide was recrystallized twice from water. Acetic anhydride (Baker) and trifluoroacetic anhydride (Matheson Coleman and Bell) were used as received. The mesylates were prepared from the corresponding alcohols by the procedure of Hudson and Withey[13] except that the sodium hydroxide was omitted from the reaction mixture. Comparable yields were obtained. Allyl mesylate was vacuum distilled and benzyl mesylate was purified by bulb to bulb vacuum distillation. *p*-Chlorobenzyl mesylate, a solid, decomposed upon attempted vacuum sublimation. The material used was recrystallized repeatedly from 30:70 benzene: hexane and had a melting point of 48–53°.

Measurements. Relative fluorescence intensities were measured with an Aminco-Bowman spectrophotofluorometer. Samples were prepared in duplicate or triplicate in 13 × 100 mm Pyrex test tubes using 3-ml solutions of *ca.* 1.5×10^{-2} *M* DMB and varying concentrations of quencher. The tubes were degassed by three freeze pump thaw cycles at $\leq 5 \times 10^{-4}$ Torr.

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[3] National Science Foundation Predoctoral Fellow, 1969–present.

[4] National Institutes of Health Postdoctoral Fellow, 1969–1970.

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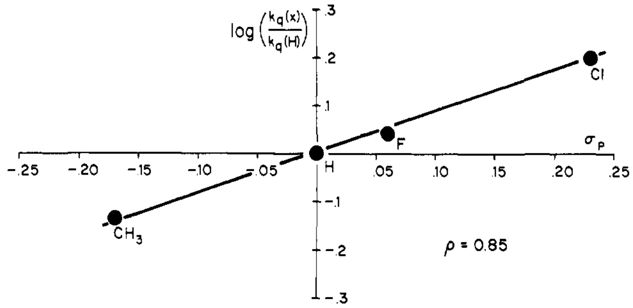

Figure 1. Hammett correlation in the quenching of DMB fluorescence by p-$XPhCH_2Cl$.

Reduction potentials were determined in the laboratory of Professor F. L. Lambert of Occidental College, Los Angeles, Calif. The solvent was doubly distilled *N,N*-dimethylformamide (Eastman) containing 0.01 *M* tetraethylammonium perchlorate as the supporting electrolyte. Potentials were recorded on a Beckman Electroscan 30 with reference to a saturated calomel electrode. A carbon electrode supplied by Topai Electrode Manufacturing Co. (Tokyo, Japan) was used in this study.[14] Control experiments in which the reduction potentials of selected quenchers were determined at the carbon electrode in acetonitrile containing 0.01 *M* tetraethylammonium perchlorate as supporting electrolyte or at the dropping mercury electrode in DMF containing the same concentration of tetraethylammonium perchlorate ruled out significant solvent or electrode effects as important factors in determining relative values of the reduction potentials.

Results and Discussion

Table I shows the rate constants (k_q) for quenching DMB fluorescence in degassed acetonitrile solution by a number of organic chlorides. As evidenced by their absorption spectra, all the quenchers studied had lowest lying excited singlets higher in energy than that of DMB. The k_q values were calculated from the slopes of Stern–Volmer plots of relative fluorescence intensity which are accurate to within ±10%. In all cases, the unquenched portion of the fluorescence had the same spectral distribution as that observed in the absence of quencher. No new emission was detected in either acetonitrile or benzene solution.

Table I. Rate Constants for the Quenching of 1,4-Dimethoxybenzene Fluorescence by Organic Chlorides[a]

Quencher	k_q, M^{-1} sec^{-1}
$Cl\text{-}CH_2CN$	9.6×10^9
p-$ClC_6H_4CH_2\text{-}Cl$	8.9×10^9
p-$FC_6H_4CH_2\text{-}Cl$	6.2×10^9
$C_6H_5CH_2\text{-}Cl$	5.6×10^9
p-$CH_3C_6H_4CH_2\text{-}Cl$	3.1×10^3
$ClCH_2COOCH_3$	4.1×10^9
$CH_2CHCH_2\text{-}Cl$	2.0×10^9
$ClCH_2CONH_2$	8.9×10^8
$ClCH_2OCH_3$	1.2×10^8
$ClCH_2CH_2CH_3$	$<10^6$ [b]

[a] Determined from relative fluorescence intensities in degassed acetonitrile solution. τ_s for DMB is 2.7 ± 0.5 nsec. [b] No fluorescence quenching was detected. This is our estimate of the upper limit of k_q.

The k_q's for the para-substituted benzyl chlorides yield a linear correlation with σ_p as shown in Figure 1. The value of ρ calculated from this plot is 0.85.

We have also found that a carbon–chlorine bond is not a requirement for efficient quenching. Table II lists the rate constants for quenching DMB fluorescence by additional organic compounds. The k_q values for the para-substituted benzyl acetates also show a linear Hammett correlation, with ρ equal to 5.2. We were able to prepare only benzyl and p-chlorobenzyl mesylates in sufficient purity for quenching measurements. While there is no certainty that a linear Hammett plot would be obtained with mesylates, the value of ρ calculated from these two points is 0.14. The dependence of k_q on para-substitution for the three benzyl systems investigated here is summarized in Table III.

Table II. Rate Constants for the Quenching of 1,4-Dimethoxybenzene Fluorescence[a]

Quencher	k_q, M^{-1} sec^{-1}
p-$ClC_6H_4CH_2OAc$	4.1×10^9
$C_6H_5CH_2OAc$	3.7×10^8
p-$FC_6H_4CH_2OAc$	5.2×10^8
p-$CH_3C_6H_4CH_2OAc$	3.0×10^7
CH_2CHCH_2OAc	1.0×10^7
p-$ClC_6H_4CH_2OMs$	6.2×10^9
$C_6H_5CH_2OMs$	4.4×10^9
CH_2CHCH_2OMs	7.4×10^8
Acetic anhydride	1.5×10^9
Trifluoroacetic anhydride	1.0×10^{10}
Ethyl trifluoroacetate	1.6×10^9

[a] Determined from relative fluorescence intensities in degassed acetonitrile solution.

Table III. Substituent Effects on Quenching by p-$XC_6H_4CH_2\text{-}Y$

	$X = CH_3, H, F, Cl$
Y	ρ
OAc	5.2
Cl	0.85
OMs	0.14[a]

[a] Determined for X = H, Cl only.

These results are in at least qualitative agreement with our hypothesis that charge transfer from the excited molecule to the quencher is a significant factor in determining reactivity. A positive value of ρ in a Hammett plot is usualy considered evidence for some degree of negative charge accession to the benzyl system at the transition state of the rate-determining step of the reaction under consideration. We hesitate, however, to derive mechanistic implications from the relative magnitudes of the ρ values in Table III.

While it seems clear that charge transfer is important in the quenching of DMB fluorescence, we have not defined precisely the nature of the interaction. We envision two possible modes of charge transfer influence in the quenching process: (1) an effect on the binding energy of the exciplex or (2) an effect on the radiationless decay processes of the exciplex. These effects are related kinetically to the rate constants k_1 (and k_{-1}) and k_2, respectively, in eq 1 and 2 below. We have previously written this scheme as the simplest kinetic formulation of fluorescence quenching.[5] In the gen-

$$A^* + Q \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{exciplex}}{(AQ)^*} \qquad (1)$$

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(14) The experimental techniques used with this electrode system will be described elsewhere: F. L. Lambert, to be submitted for publication.

$$\begin{tikzcd} (AQ)^* \arrow[r] & A^{*(vib)} \arrow[d] & + & Q^{*(vib)} \arrow[d] \\ & A & & Q \text{ or other products} \end{tikzcd} \qquad (2)$$

eral case, the exciplex is characterized by contributions from the resonance forms

$$(AQ)^* \equiv A^*Q \longleftrightarrow AQ^* \longleftrightarrow A^+Q^- \longleftrightarrow A^-Q^+$$

In this formulation, the experimental rate constant for quenching would have the significance shown in eq 3.

$$k_q = k_1k_2/(k_{-1} + k_2) \qquad (3)$$

As we have previously noted,[5] if k_2 is much larger than k_{-1}, the relation for k_q reduces to the form shown in eq 4. In other words, the experimental k_q will be

$$k_q \approx k_1 \qquad (4)$$

governed by factors which determine k_1, regardless of the nature of the radiationless decay step, k_2. On the other hand, if k_2 is slow relative to k_1 and k_{-1}, the relation for k_q reduces to the form shown in eq 5.

$$k_q = (k_1/k_{-1})k_2 = Kk_2 \qquad (5)$$

That is, the radiationless decay of the electronic excitation will be attenuated by the equilibrium constant K. If eq 4 holds, we may attribute the effect of charge transfer on variations of k_q to corresponding variations of k_1. If eq 5 holds, we might expect to observe charge transfer effects on either or both K and k_2.

In this discussion we have remained purposely vague in the use of the term "charge-transfer interaction." Other workers, however, have been quite specific in using the term charge transfer to mean the irreversible formation of a cation–anion radical pair.[7,10,11] Weller,[7] in particular, has proposed this pathway for a number of quenching interactions. He has shown kinetically that in a solvent of low viscosity and high dielectric constant (such as acetonitrile) the rate limiting step is the formation of the radical ion pair. In that case, k_q is a function of the potential energy of formation of the ion pair, and it can be shown that for the quenching of one excited molecule by a series of quenchers which act as electron acceptors, there should emerge a linear correlation between log k_q and quencher reduction potential, as shown in eq 6.[15]

$$\log k_q = c_1 + c_2E_{1/2} \qquad (6)$$

If charge transfer leads to a radical ion pair in the fluorescence quenching we are studying here, we should see a correlation in the form of eq 6. We emphasize, however, that although a radical ion pair mechanism demands the relationship shown in eq 6, the converse is not true. A similar correlation could arise from distinctly different interactions (*vide infra*).

To test the kinetic formulations for quenching DMB fluorescence, we have determined the reduction potentials of the quenchers used in this study. Table IV lists the results for the chlorides, acetates, and mesylates studied here, and Figure 2 shows a plot of log k_q *vs.* quencher reduction potential. It is clear that for all the types of quenchers there is not a linear correlation. Within the various series (chlorides, mesylates, or acetates) linear correlations do appear. The points generally describe three straight lines. The points which fall off the lines will be discussed below. (The leveling effect as k_q approaches the diffusion-limited encounter rate, k_D, is to be expected.) These results are clearly inconsistent with the relation of eq 6 and suggest that formation of a radical cation–radical anion pair is not a necessary step in the quenching of DMB fluorescence by the quenchers reported here.

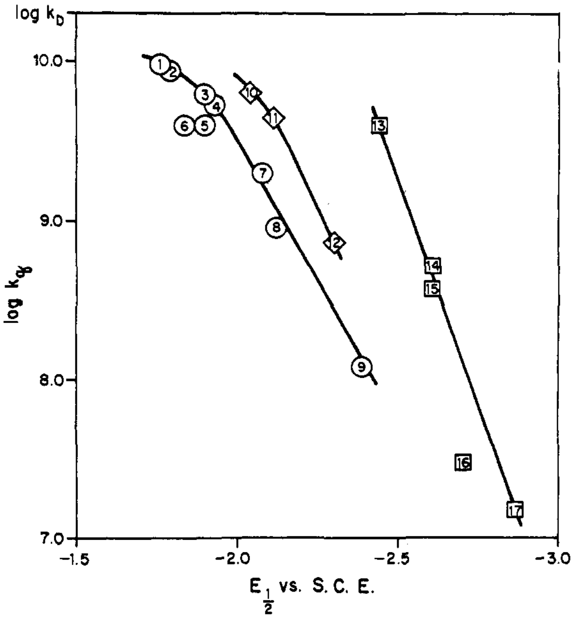

Figure 2. Correlation of log k_q with quencher reduction potential.

Table IV. Reduction Potentials of Quenchers Used in This Study

Quencher no.	Quencher	$E_{1/2}$ *vs.* sce, V
1	$ClCH_2CN$	−1.76 ± 0.03
2	*p*-$ClC_6H_4CH_2Cl$	−1.79 ± 0.03
3	*p*-$FC_6H_4CH_2Cl$	−1.90 ± 0.03
4	$C_6H_5CH_2Cl$	−1.93 ± 0.03
5	*p*-$CH_3C_6H_4CH_2Cl$	−1.90 ± 0.03
6	$ClCH_2COOCH_3$	−1.84 ± 0.03
7	CH_2CHCH_2Cl	−2.08 ± 0.03
8	$ClCH_2CONH_2$	−2.12 ± 0.03
9	$ClCH_2OCH_3$	−2.39 ± 0.10
10	*p*-$ClC_6H_4CH_2OMs$	−2.03 ± 0.03
11	$C_6H_5CH_2OMs$	−2.11 ± 0.03
12	CH_2CHCH_2OMs	−2.30 ± 0.03
13	*p*-$ClC_6H_4CH_2OAc$	−2.44 ± 0.05
14	*p*-$FC_6H_4CH_2OAc$	−2.61 ± 0.03
15	$C_6H_5CH_2OAc$	−2.60 ± 0.03
16	*p*-$CH_3C_6H_4CH_2OAc$	−2.70 ± 0.03
17	CH_2CHCH_2OAc	−2.86 ± 0.05

The results shown in Figure 2 seem more compatible with the viewpoint we have taken in discussing the quenching of naphthalene fluorescence by conjugated dienes.[5] That is, fluorescence quenching is a result of enhanced radiationless decay of the excited molecule with certain vibrational modes in the quencher being specifically involved in the internal conversion process. Electronic interactions are necessary both to bind the components of the exciplex and to establish

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(15) This relationship is the analog of the linear correlation expected between log k_q and quencher ionization potential when one excited compound is quenched by a series of electron donors.[10,11] It follows directly from the equation for log k_q in the general charge transfer case[5,7,10,11] if the Coulombic term is constant for the series of radical ion pairs. Weller[7] has shown this to be true for charge transfer complexes which show ranges of molecular dimensions and charge transfer exothermicity at least as great as for those complexes which might be generated in the present study.

communication between excited electrons in the quenchee and the vibrating nuclei in the quencher.

The origin of this study was a report by Witkop and coworkers[16] on the photocyclizations of some bichromophoric molecules analogous to systems we have now studied in intermolecular quenching. We have observed very low quantum yields of product formation in at least one bimolecular quenching study.[12] These results suggest that the C–Cl, C–OMs, and C–OAc bonds are involved in the quenching process. We suspect that the vibrational modes of the C–Cl bond, for example (coupled with the molecular vibrational modes), provide a convenient sink for the energy of the electronic excitation and that coupling of the excited molecule with these modes in an exciplex provides a facile pathway for radiationless decay of the exciplex. Some support for this view may be found in the work of Ogata, *et al.*, whose results suggest carbon–halogen bond homolysis upon the direct irradiation of ethyl haloacetates.[17] Furthermore there is a possible relationship between our work and that of Berenfel'd and Krongauz, who studied the fluorescence of a series of substituted benzyl systems and concluded that intramolecular charge transfer plays a role in determining the probability of their radiationless transitions.[18] These results are consistent with the type of exciplex radiationless decay interactions we are considering here.

If coupling of the vibrational modes of the C–Cl, etc., bond is important in the radiationless decay mechanism, we might expect it to be roughly the same within a series of chlorides, acetates, or mesylates. In that case the rates k_2 would be roughly constant within a series of chlorides, acetates, or mesylates.

While the decay rates for the exciplexes derived from DMB and the quenchers we have studied here may be invariant for a series of chlorides, etc., the equilibrium constants K need not be identical. The straight lines in Figure 2 suggest a relationship between K and the quencher reduction potential. In particular, if binding of the exciplexes is due only to resonance charge transfer from the excited molecule to the quencher, as shown below, then we would expect K to be a function of the change in free energy of formation of the charge transfer

$$(AQ)^* \equiv A^*Q \longleftrightarrow A^+Q^- \qquad (7)$$

species exactly as was predicted for k_q in the radical ion pair formulation discussed above. Just as in that situation, we would then expect log K to be a linear function of the quencher reduction potential.

If we take the logarithm of eq 5 and substitute the right-hand side of eq 6 for the log K term, then we have the relationship shown in eq 8. The data shown in

$$\log k_q = c_1 + c_2E_{1/2} + \log k_2 \qquad (8)$$

Figure 2 are entirely consistent with this formulation.

We should emphasize that the type of charge transfer resonance we propose for the exciplexes of DMB is in some respects different from the irreversible formation of cation–anion radical pairs. Although it seems clear that such species are formed in some types of fluorescence quenching,[19] there is no compelling evidence for their intermediacy in all cases. In fact, in the case of fluorescence quenching of naphthalene and related compounds by conjugated dienes, which has been proposed to occur by a radical ion pair pathway, Taylor has observed emission from the exciplexes formed from 1-cyanonaphthalene and a number of electron-rich monoolefins, with spectral distributions which indicate the exciplex to be much less polar than those derived from naphthalene and triethylamine.[9] It seems likely that exciplexes derived from less electron-rich olefins and less electron-poor naphthalenes would have even less polar character.

Further support for this difference between exciplex charge transfer resonance and radical ion pair formation can be seen in those points which fall off the lines in Figure 2. One such point is *p*-methylbenzyl chloride. The electrochemical reduction potentials for substituted benzyl chlorides have been reported by Streitwieser,[20] who found that all substitutents made the reduction potential more positive, *i.e.*, a linear Hammett correlation was not obtained. The relative values of the reduction potentials of the benzyl chlorides reported in this study are in good agreement with those of Streitwieser. Streitwieser concluded that in the transition state for reduction the benzyl system had both anionic and radical character. The polar effect, which is measured by σ, affects **2**, but radical stabilization

$$\mathrm{ArCH_2Cl} \xrightarrow{e^-} \underset{\mathbf{1}}{\mathrm{ArCH_2\cdot Cl^-}} \longleftrightarrow \underset{\mathbf{2}}{\mathrm{ArCH_2{}^-Cl\cdot}}$$

effects, which are in no way measured by σ, influence **1**. If this explanation is correct, then there is clearly a distinction between the electrochemical reduction of the compounds used as quenchers in this study and the type of charge transfer involved in the exciplexes they form.

Although we have found the reduction potential of *p*-methylbenzyl acetate to be more negative than that of benzyl acetate, the $E_{1/2}$ values do not yield a linear Hammett plot. We suggest that effects such as those proposed by Streitwieser for the electrochemical reduction of benzyl chlorides may also be operating, though to a lesser degree, in the reduction of the benzyl acetates.

It is noteworthy that, had we used only chlorides in this study, the correlations with Hammett parameters and reduction potentials would have been compatible with a simpler explanation of structure–reactivity relationships than is demanded by inclusion of acetates and mesylates. For example, a correlation based upon only the reduction potentials of the chlorides would predict that acetates should have virtually no quenching reactivity. The present results indicate the need for caution in interpretation of correlations between rate constants for quenching and molecular properties.

Acknowledgments. This work was supported by the Directorate of Chemical Sciences of the Air Force Office of Scientific Research under Contract No. AF OSR-71-1958. We wish to thank Professor F. L. Lambert of Occidental College for the use of facilities and for many helpful discussions.

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