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# SINGLET-QUENCHING OF PHOTOEXCITED AROMATICS BY CARBONYL COMPOUNDS

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Considerable interest exists today in the study of energy transfer mechanisms. The general features of the various modes of transfer have been documented[1]; in dilute solution electronic-energy transfer can occur via a long-range dipole-dipole or via a Dexter-type collisional energy transfer mechanism. Both processes have been shown to occur between photoexcited aromatics and carbonyl compounds. Lamola et al[2] demonstrated the existence of intramolecular dipole-dipole energy transfer between naphthalene and benzophenone which were present as nonconjugated chromophores in the same compound. Lee et al[3] advanced a similar mechanism to explain the intermolecular quenching of benzene fluorescence by acetone. Dubois and coworkers[4] have also demonstrated that naphthalene fluorescence can be quenched by biacetyl via the Dexter mechanism. In the above cases, of course, the $S_1$ level of the ketone is lower in energy than the quenched aromatic and, further, there exists a region of spectral overlap between the excited donor fluorescence and acceptor absorption. We now wish to report results which indicate that a third mechanism, quite distinct from, and possibly competitive with, energy transfer can operate to deactivate the $S^1$ state of aromatics by certain carbonyl compounds.

In Table I are examples of the quenching of aromatic fluorescence by benzophenone, benzaldehyde and acetophenone. The quenching constants, $k_q$, listed in column 5, were obtained from Stern-Volmer experiments together with literature value fluorescence lifetimes.[5] As seen by comparing columns two and four, the energy of the lowest excited singlet state of the quencher is higher in energy than the lowest excited singlet of the corresponding aromatic. Therefore, it is unlikely that the fluorescence quenching is due to classical electronic-energy transfer as seen in the above cases. Quenching via the formation of a ground-state complex can be ruled out on the evidence that: (a) the UV/visible spectra of the aromatic-carbonyl mixtures revealed no new absorption bands; (b) For the tetracene-benzophenone system Stern-Volmer experiments utilizing fluorescence lifetime measurements were in agreement with fluorescence intensity measurements.[6]

We believe that quenching is occurring via a charge-transfer (CT) stablized exciplex, similar to that found by Nesta and Ricci for the fluorescence quenching of indole by carboxylic acids.[7] In the present study, the photoexcited aromatic serves as the charge donor to the highly electronegative carbonyl quencher,

TABLE I

Fluorescence Quenching of Aromatic Hydrocarbons by Carbonyl Compounds[10]

| | D | $S_1$ (Kcal/mole) | A | $S_1$ (Kcal/mole) | $k_q \times 10^{-9}$ $M^{-1}sec^{-1}$ | $E^{\frac{1}{2}}(D,D^*)$[10] | $-E^{\frac{1}{2}}(A,A^-)$[12] | $-\Delta G_q$ (Kcal/mole) |
|---|---|---|---|---|---|---|---|---|
| 1 | 9-10-DMA* | 71 | Benzophenone | 76 | 16 | .87 | 1.26 | 24 |
| 2 | 9-10-DMA | 71 | Benzaldehyde | 77 | 13 | .87 | 1.34 | 22 |
| 3 | Perylene | 66 | Benzophenone | 76 | 5.3 | .85 | 1.26 | 19 |
| 4 | 9-10-DMA | 71 | Acetophenone | 80 | 11 | .87 | 1.48 | 19 |
| 5 | Perylene | 66 | Benzaldehyde | 77 | 3.9 | .85 | 1.34 | 18 |
| 6 | Tetracene | 61 | Benzophenone | 76 | 3.8 | .77 | 1.26 | 16 |
| 7 | Tetracene | 61 | Benzaldehyde | 77 | 1.8 | .77 | 1.34 | 14 |
| 8 | Perylene | 66 | Acetophenone | 80 | 0.95 | .85 | 1.48 | 14 |
| 9 | Tetracene | 61 | Acetophenone | 80 | 0.20 | .77 | 1.48 | 11 |
| 10 | Coronene | 68 | Benzophenone | 76 | 0.38 | 1.32 | 1.26 | 11 |
| 11 | Coronene | 68 | Benzaldehyde | 77 | 0.24 | 1.32 | 1.34 | 9 |
| 12 | Coronene | 68 | Acetophenone | 80 | 0.09 | 1.32 | 1.48 | 6 |
| 13 | Rubrene | 54 | Benzophenone | 76 | 0.020 | .61 | 1.26 | 14 |
| 14 | Rubrene | 54 | Benzaldehyde | 77 | 0.013 | .61 | 1.34 | 11 |
| 15 | Rubrene | 54 | Acetophenone | 80 | 0.007 | .61 | 1.48 | 9 |

*9-10-Dimethylanthracene

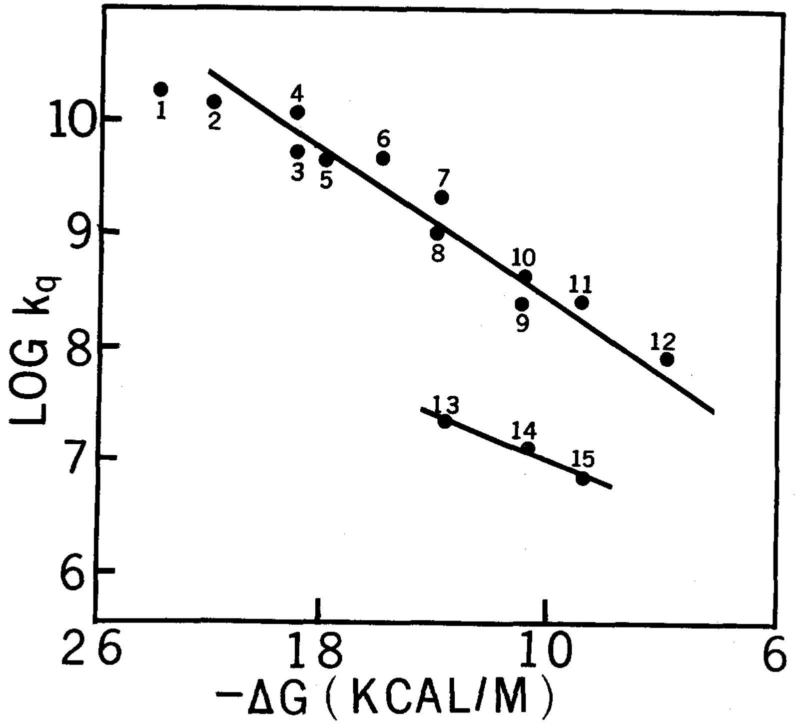

Fig. 1. Plot of the log of the quenching constant, $k_q$, versus the free energy change.

$$D^* + A \rightleftarrows [D^+ A^-] \longrightarrow \text{quenched}$$

where $D^*$ represents the fluorescent donor aromatic; A, the carbonyl; and $[D^+ A^-]$, an encounter complex. From a knowledge of the oxidation potential of the donor, and the reduction potential of the acceptor, the singlet excitation energy of the donor, and the free energy gained by bringing the ions to the encounter distance ($\approx 7$Å), we can estimate the free energy change accompanying CT quenching from the equation,[8,9]

$$\Delta G_q = (E^{\frac{1}{2}}\ D^+/D) - {}^1\Delta E_{oo}(D) - (E^{\frac{1}{2}}\ A^-/A) - \frac{e_o^{\ 2}}{r}\ . \qquad (1)$$

The changes in free energy are listed in column 8 of Table I. Clearly, the free energy changes are negative, indicating that quenching via CT is spontaneous. Further, the observed rate constants $k_q$, decrease from the near diffusion-controlled value in case 1 to values below the sensitivity of our instrument.

In similar quenching studies thought to involve a CT exiplex mechanism a linear relationship has been found between log $k_q$ and $\Delta G$.[9,13] Such a relationship can be seen in Fig. 1. The numbers in the figure refer to the entries in Table 1. The main body of the kinetic data does, in fact, correlate rather well with the energy term.

The three points lying below the major correlation line all represent the quenching of rubrene fluorescence. The reduced quenching ability of the carbonyl compounds in this case we attribute to the presence of steric hindrance. The tetracene backbone of rubrene is flanked by a group of four benzene rings positioned at 90° to the fused ring system. These benzene groups prevent the quencher from approaching to the optimum distance for exciplex formation thereby reducing the efficiency with which the process occurs.

Though the quenching is clearly sensitive to univalent charge-transfer energetics it is difficult to estimate quantitatively the degree to which it actually controls quenching efficiency. For example, acetone has a reduction potential of 1.65 volts, Fig. 1 predicts that this carbonyl compound would quench 9-10-dimethylanthracene with a rate constant of $\approx 10^9$ ($K_{sv} \approx 5$). In fact, acetone is a non-quencher which indicates that charge-transfer energetics alone do not control quenching efficiency. One could speculate that perhaps in addition to favorable charge-transfer energetics, a conjugated system capable of frontier orbital overlap with the aromatic fluorescer is necessary and the function of the carbonyl group is to provide the proper electron withdrawing properties. Interpreted in this way the quenchers used in this study are similar to dicyanobenzene which Weller et al[14] has found to be an excellent quencher of aromatic fluorescence.

In the case of the photoexcited naphthalene-benzophenone system eq. 1 predicts an estimated free energy change of -29 kcal/mole accompanying CT-exciplex formation. Accordingly, one might expect a highly efficient quenching manifold via exciplex formation. Lamola et al did, in fact, observe in the low temperature emission spectrum of 1-(1-naphthyl)-3-(4-benzoylphenyl) propane an anomalous fluorescence band which was subsequently linked to exciplex fluorescence.[15] Our studies confirm this explanation.

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