# Mechanism of Fluorescence Quenching by Quadricyclene

By BARTON S. SOLOMON, COLIN STEEL,* and ALBERT WELLER

(*Department of Chemistry, Brandeis University, Waltham, Massachusetts 02154*)

Summary The fluorescence quenching of aromatic hydrocarbons by quadricyclene is believed to proceed *via* a charge-transfer complex and not by a transfer of vibrational energy.

RECENTLY Murov and Hammond[1] have reported that quadricyclene (I) is a very effective quencher of the fluorescence of aromatic hydrocarbons. They have suggested that the electronic energy of the aromatic hydrocarbon is efficiently transferred to vibrational energy of the quadricyclene, and that the latter may then isomerise to norbornadiene (II). However, most molecules of moderate com-

(I)   (II)   (III)
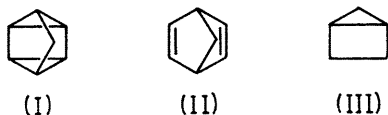
plexity have a wide range of vibrational modes and it is hard to see on the basis of this model why most hydrocarbons would not also be rather effective quenchers. Bicyclo[2,1,0]pentane (III) which has obvious structural similarities to (I) is quite ineffective as a quencher (Table).

For these reasons we feel that a more specific quenching mechanism has to be involved. Murov and Hammond could obtain no correlation between their quenching constants and variables such as electron affinities, ionisation potentials, and energies of the electronic transitions. However, a correlation does emerge when we plot their data against parameters similar to those used previously by one of us[3] in studies of fluorescence quenching through the formation of molecular complexes which possess considerable charge-transfer character. Stephenson *et al.*,[4] in discussing the factors which influence singlet quenching by hydrocarbons, have discussed the possibility of charge-transfer stabilisation of the complex.

A and D represent an acceptor and donor in an electron-transfer process. A left superscript gives the multiplicity of the state while an asterisk represents an electronically excited molecule. The right subscripts, g = gas and s = solution, give the phase. For the process ${}^1A^* + D_g \rightarrow {}^1(A^-, D^+)_g$

$$\Delta F \approx -{}^1\Delta E_A + IP_D - EA_A - C$$

where the four terms on the right are, respectively, the singlet excitation energy of A, the ionisation potential of D, of electron affinity of A, and the coulombic energy gained

Fluorescence quenching in iso-octane at room temperature

	τ^a (nsec.)	${}^1\Delta E_A$ (ev)	$\epsilon(A^-/A)$ vs. S.C.E. (ev)	Quadricyclene $k_q\tau$ (M⁻¹)	Quadricyclene $k_q \times 10^{-7}$ (M⁻¹ sec.⁻¹)	Piperylene $k_q \times 10^{-7}$ (M⁻¹ sec.⁻¹)	Bicyclopentane $k_q \times 10^{-7}$ (M⁻¹ sec.⁻¹)
1-Cyanonaphthalene	26	3·83	−2·00	286	1100	490	
Naphthalene	96	3·95	−2·58	320	330	10	0·225
1-Methoxynaphthalene	49	3·83	−2·65	10·2	21	3·8	

a Determined by the oxygen quenching technique see "Handbook of Fluorescence Spectra of Aromatic Molecules" by I. B. Berlman, Academic Press, New York, 1965, p. 35.

Furthermore, from unimolecular theory[2] the lifetime of vibrationally excited (I) possessing a 90 kcal. mole⁻¹ excess of vibrational energy, the maximum available, is still sufficiently long (*ca.* 10⁻⁹ sec.) for collisional deactivation to be the predominant fate of such a species in solution.

in bringing A⁻ and D⁺ from infinity to within a distance a of each other. For the equivalent reaction in solution

$${}^1A_s + {}^1D_s \rightarrow {}^1(A^-, D^+)_s$$
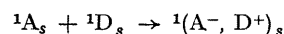
there will be an additional free-energy term representing

the difference between the free energy of solvation of $^1(A^-, D^+)$ and that of $^1A^*$ and ^1D. Electron affinities are in general not accurately known; however, they are related to polarographic redox potentials, $\epsilon(A_s^-/A_s)$, by $EA_A = \epsilon(A_s^-/A_s) + \Delta F_{sg} + const.$, where ΔF_{sg} is the free energy involved in the reaction $A_s + A_g^- \rightarrow A_g + A_s^-$. Therefore, for a series of acceptors, a constant donor, and the same solvent, we may expect, if a is constant,

$$\Delta F = const - [^1\Delta E_A + \epsilon(A_s^-/A_s)]$$

In the Figure we plot the quenching constants of Murov and Hammond against $^1\Delta E_A + \epsilon(A^-_s/A_s)$, and correlation emerges.
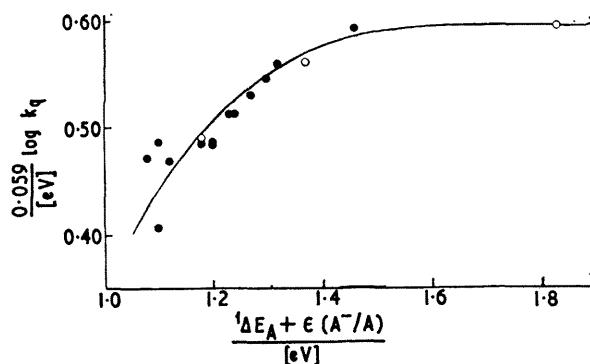

FIGURE. Correlation between rate constants of fluorescence quenching by quadricyclene and electron affinities of the excited molecules. (Black circles: from ref. 1; open circles: this work.)

We also obtained the quenching constants for 1-cyano-naphthalene, naphthalene, and 1-methoxynaphthalene, which have very similar singlet excitation energies ($^1\Delta E_A$) but the redox potentials of which differ significantly. There is a 50-fold change in k_q (Table) in going from the cyano- to the methoxy-compound concomitant with the change in $^1\Delta E_A + \epsilon(A^-_s/A_s)$. Complete electron transfer is probably not necessary for quenching.

Interaction between $^1A^*$ and ^1D results in the formation of an excited complex whose wave-function can be written

$$^1\psi_{complex} = c_1 \, ^1\psi_{A^*,D} + c_2 \, ^1\psi_{A^-,D^+}.$$

For the charge-transfer state to contribute significantly to the complex, its energy cannot be too different from that of (A^*,D). The vertical ionisation potential of (I) in the gas phase[5] is 8·7 ev, the adiabatic ionisation potential[6] may be lower by 0·9 ev. The electron affinity of naphthalene is −0·3 ev, whilst the first excited singlet lies 3·95 ev above the ground state. Thus the process $^1A^*_g + D_g \rightarrow A^-_g + D^+_g$ is endothermic by some 4·15 ev. Bringing the ions close together (ca. 3·5 Å) would produce enough coulombic energy to make the process thermoneutral. In solution there may be further stabilisation of the charge-transfer dipole as a result of polarisation forces.

There is not much change in $k_q\tau$ in going from iso-octane to acetonitrile which has a large dielectric constant. The values of $k_q\tau$ for 1-cyanonaphthalene, naphthalene, and 1-methoxynaphthalene are 202, 238, and 28 M^{-1}, respectively. This might be expected to be the case if rapid electron-transfer takes place between contiguous molecules before free energy can be gained by solvent reorientation around the incipient dipole. However, polarisation stabilisation—which is essentially due to the electronic motion—is possible.

We therefore envisage the quadricyclene moiety in the complex as being considerably distorted from normal quadricyclene and having contributions such as

to its structure. It then becomes apparent why when an electron is eventually "returned" to D^+ either (I) or (II) can be formed. [The mass spectra of (I) and (II) are identical.[5]]

The same order of quenching activity holds (Table) when piperylene is the quencher, so it is possible that charge-transfer stabilisation is significant for quenching by dienes as well. We and others[7,8] have previously observed that the fluorescence of 2,3-diazabicyclo[2,2,2]oct-2-ene is quenched by olefins but not by dienes. However, we have found that quadricyclene is not a particularly good quencher for this azo-compound: k_q(piperylene) $= 3·0 \times 10^7 M^{-1}$ sec.$^{-1}$, k_q(quadricyclene) $= 1·6 \times 10^7 M^{-1}$sec.$^{-1}$ for iso-octane solvent and $\tau = 0·33 \times 10^{-6}$ sec.[7]

Thus quite small changes in IP_D and EA_A may have marked effects on the rate constants of quenching and could well mask the structural effects which have been sought.[4,8]

[1] S. Murov and G. S. Hammond, J. Phys. Chem., 1968, 72, 3797.
[2] D. W. Setser and B. S. Rabinovitch, Canad. J. Chem., 1962, 40, 1425.
[3] H. Beens and A. Weller, Acta Phys. Pol., 1968, 34, 593; D. Rehm and A. Weller, Ber. Bunsenges. phys. Chem., 1969, 73, to be published.
[4] L. M. Stephenson, D. G. Whitten, and G. S. Hammond in "The Chemistry of Ionisation and Excitation," Taylor and Francis, London, 1967, p. 35.
[5] Z. Dolejsek, V. Hanus, and H. Prinzbach, Angew. Chem., 1962, 74, 902.
[6] Norbornadiene (II) whose vertical ionisation potential in the gas phase[5] is 8·6 ev is more stable than (I) by approximately 0·9 ev (R. B. Turner, unpublished results, cited in ref. 1).
[7] B. S. Solomon, T. F. Thomas, and C. Steel, J. Amer. Chem. Soc., 1968, 90, 2249.
[8] A. C. Day and T. R. Wright, Tetrahedron Letters, 1969, 1067.