Formation of Excited Charge-transfer Complexes in the Quenching of Anthracene Fluorescence by Anions

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Summary Halide and pseudohalide ions quench the fluorescence of anthracene, the correlation of quenching rate constants with redox potential of the anion indicating a mechanism involving excited charge-transfer complex formation.

HALIDE and pseudohalide anions quench the fluorescence of electron acceptors by acting as the donor in formation of a ground state charge-transfer complex.[1] Other electron donor and acceptor compounds quench the fluorescence of aromatic hydrocarbons by formation of charge-transfer complexes in their excited states, there being no evidence for ground state complex formation.[2-4] The Table shows data for the quenching of anthracene fluorescence by a series of anions in acetonitrile. There was no evidence from spectrophotometric absorption measurements of any ground-state complex formation.

If these anions derived their quenching ability from external heavy-atom spin–orbit coupling then the quenching constant might be expected to depend on the square of the atomic spin–orbit coupling parameter[5,6] of the heavy atom leading to a predicted order, $I^- > Br^- > CNSe^- > Cl^- > CNS^-$. The observed order is $CNSe^- > I^- > CNS^- > Br^- > Cl^-$ which is the order of the redox potentials. Alternatively formation of an excited-state charge-transfer complex $^1A^* + X^- \rightleftharpoons {}^1(A^-X\cdot)$ may be considered, the stability of this complex to back dissociation to $^1A^*$ and X^- determining the relative quenching ability of the anions. Following Weller,[7] the free energy of the electron transfer step may be expressed as,

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

where $^1\Delta E_A$ is the singlet excitation energy of the acceptor hydrocarbon, IP_D the ionisation potential of the donor anion, EA_A the electron affinity of the acceptor and C a term for the coulombic energy change on forming the complex in its equilibrium configuration. This expression refers to the gas phase and in solution there will be an additional term for the difference in free energies of solvation of $^1(A\text{–}X\cdot)$ and of $^1A^*$ and X^-. For the same acceptor and a series of anions in the same solvent, assuming a constancy for C, then

$$\Delta F = \text{constant} + IP_D$$

The ionisation potentials of the anions will be related to the redox potential for $2X^- \rightarrow X_2 + 2e$. In the Figure we

TABLE

Quenching constants for quenching of anthracene fluorescence (10^{-5} M *in acetonitrile*)

Quencher	$CNSe^-$	I^-	CNS^-	Br^-	Cl^-
$k_y\ \tau$ (M^{-1})	125	66	20	11·7	0·55
k_q[a] ($M^{-1}\ s^{-1}$)	$2·2 \times 10^{10}$	$1·1 \times 10^{10}$	$3·5 \times 10^9$	$1·9 \times 10^9$	$9·5 \times 10^7$
Redox potential (V) ..	0·42[b]	0·54	0·77	1·07	1·36

[a] Taking τ = 5·8 ns: W. Ware, *J. Phys. Chem.*, 1962, **66**, 455.
[b] Estimated value from correlation of redox potential with energy of charge-transfer to solvent absorption band.

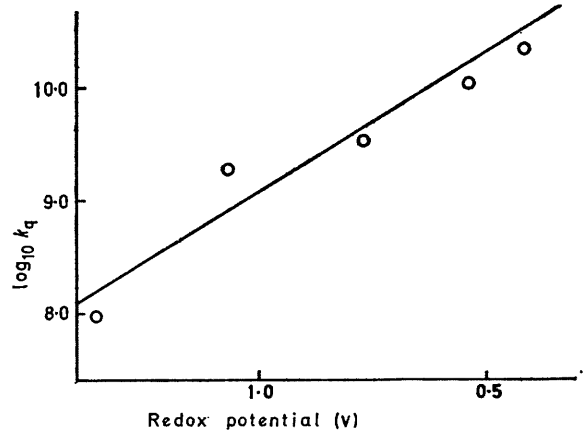

FIGURE. *Plot of* $\log_{10} k_q$, *the quenching rate constant, agains tthe redox potential of the anion for the quenching of anthracene fluorescence in acetonitrile solution.*

plot $\log_{10}k_q$, obtained from relative intensities using the Stern–Volmer relationship, against the redox potential of the anion. A good linear correlation establishes the charge-transfer mechanism.

The quenching constants were much lower for solutions in ethanol. For complexes of this type where the transfer of an electron is from an anion with a highly localised negative charge to the electron acceptor where it will be more delocalised, greater stabilisation of charge on the halide anion would be expected as the polarity of the solvent increases.[8] The quenching constant should therefore increase as the solvent polarity is lowered.

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