Charge-transfer Complexes. Part XI.[1] Quenching of Anthracene Fluorescence by Anions

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The group of simple inorganic anions known to exhibit charge-transfer-to-solvent (C.T.T.S.) absorption bands in solution, have also been found to be effective in the quenching of anthracene fluorescence. Correlation of quenching constants with both the redox potential, when known, and with the energy of the C.T.T.S. absorption band maximum, supports a mechanism involving electron transfer. The data is tentatively interpreted in terms of an excited state charge-transfer complex (' exciplex ') formation, although no emission band due to an exciplex was detected. No detectable change occurred in the absorption band of anthracene on the addition of the quencher.

INORGANIC anions have been found to act as quenchers of the fluorescence of dyes[2] and electron acceptors.[3-5] The mechanism of quenching has been postulated as involving the formation of an excited state charge-transfer complex between the excited state of the fluorescer and a ground state quencher. In a preliminary publication[6] it was shown that, at least for a limited number of inorganic anions for which redox potentials were known, there was a good linear correlation between the rate constant for quenching of anthracene fluorescence and redox potential of the anion, supporting an electron transfer mechanism for the quenching. In this paper we present the results of an investigation into the quenching ability of the group of inorganic anions distinguished by their exhibition of a charge-transfer-to-solvent (C.T.T.S.) absorption band in solution.

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[1] Part X, T. G. Beaumont and K. M. C. Davis, *J. Chem. Soc.* (*B*), 1970, 592.

[2] D. K. Majumdar, *Z. Phys. Chem.*, 1961, **217**, 200.

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[4] G. Briegleb, W. Herre, W. Jung, and H. Schuster, *Z. phys. Chem.* (*Frankfurt*), 1965, **45**, 229.

[5] K. D. Legg and D. M. Hercules, *J. Phys. Chem.*, 1970, **74**, 2114.

[6] R. Beer, K. M. C. Davis, and R. Hodgson, *Chem. Comm.*, 1970, 840.

EXPERIMENTAL

Materials.—De-ionised water was distilled from alkaline permanganate. Other solvents were of fluorimetric grade and were used without further purification. Ultra-pure grade potassium bromide and iodide were used. Other salts were AnalaR grade and were recrystallised before use.

Spectra.—Emission spectra were measured with a Baird–Atomic SF 100 recording spectrofluorimeter. Concentrations of anthracene used were in the region of 10^{-5}M at which concentration the fluorescence intensity (uncorrected) was proportional to concentration. Quencher concentrations were at least a factor of 10 higher than this.

RESULTS AND DISCUSSION

Quenching constants, $K_{\text{S.V.}}$, were obtained using the Stern–Volmer relationship (1) where F_0 and F are the

$$(F_0 - F)/F = K_{\text{S.V.}}[Q] = k_q\tau_0[Q] \qquad (1)$$

uncorrected intensities of fluorescence at a given wavelength in the absence of and presence of a concentration [Q] of the quencher respectively. The quenching rate constant k_q can then be obtained if the singlet state lifetime at infinite dilution, τ_0 is known. Table 1 shows $K_{\text{S.V.}}$ and k_q for the quenching of anthracene fluorescence by a series of inorganic anions in the solvents acetonitrile and ethanol–water (1 : 1). A much wider range of anions could be studied in the latter solvent owing to increased solubility of the salts.

TABLE 1

Quenching constants for the quenching of anthracene fluorescence in acetonitrile and ethanol–water by the potassium salts of various anions

Quencher	$CNSe^-$	I^-	HS^-	$S_2O_3^-$	Br^-	N_3^-	SO_3^{2-}	SCN^-	HSO_4^-	Cl^-	SO_4^{2-}	CNO^-
$k_q\ \tau/\text{M}^{-1}$ in MeCN	125	66			11·7			20		0·55		
$k_q/\text{M}^{-1}\ \text{s}^{-1}$ in MeCN	2·2 $\times 10^{10}$	1·1 $\times 10^{10}$			1·9 $\times 10^{9}$			3·5 $\times 10^{9}$		9·5 $\times 10^{7}$		
$k_q\ \tau/\text{M}^{-1}$ in EtOH–H_2O	20·9	18·5	7·0	3·0	2·8	2·55	2·45	0·7	0·34	0·17	0·17	0·18
$k_q/\text{M}^{-1}\ \text{s}^{-1}$ in EtOH–H_2O	3·6 $\times 10^{9}$	3·2 $\times 10^{9}$	1·2 $\times 10^{9}$	5·2 $\times 10^{8}$	4·8 $\times 10^{8}$	4·4 $\times 10^{8}$	4·3 $\times 10^{8}$	1·2 $\times 10^{8}$	5·9 $\times 10^{7}$	2·9 $\times 10^{7}$	2·9 $\times 10^{7}$	3·0 $\times 10^{7}$
Redox potential (V)	0·42	0·54			1·07			0·77		1·36		
$10^{-3}\ \bar{\nu}_{\text{C.T.T.S.}}$ [a]/ cm^{-1}	38·9	40·8			45·6			41·4		50·8		
$10^{-3}\ \bar{\nu}_{\text{C.T.T.S.}}$ [b]/ cm^{-1}	42·5	44·2	43·5	46·5	50·3	49·3	44	45	>60	54·5	57·14	>55?

[a] In MeCN, from ref. 9. [b] In H_2O, from ref. 9.

Following the treatment due to Weller *et al.*[7] for the process of ' exciplex ' formation (2) involving non-heavy atom containing quenchers we may write the energy of

$${}^1A^* + X^- \rightleftharpoons {}^1(A^{\bullet-}X^{\bullet}) \qquad (2)$$

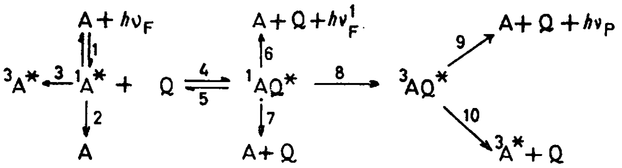
the electron transfer step as (3) where ${}^1\Delta E_A$ is the singlet

$$\Delta F \approx -{}^1\Delta E_A + IP_D - EA_A - C \qquad (3)$$

excitation energy of the acceptor, anthracene, IP_D is the ionisation energy of the donor anion, EA_A is the electron affinity of the acceptor, and C is a term for the coulombic energy change on forming the complex, in its equilibrium configuration, from the components. This expression refers to the gas phase and in solution there will be an additional term for the difference in free energy of solvation of ${}^1(A^{\bullet-}X^{\bullet})$ and of ${}^1A^*$ and X^-. For the same solvent and same acceptor and assuming constancy for the term C then equation (4) holds. This predicts a linear correlation of $\log_{10} k_q$ and IP_D.

$$\Delta F \approx \text{constant} + IP_D \qquad (4)$$

For quenching of pyrene fluorescence by halogen-containing solvents, which is also assumed to proceed *via* ' exciplex ' formation, Thomaz and Stevens[8] have developed a treatment which includes the spin–orbit coupling-induced intersystem crossing to the complex triplet state (Scheme). Here ν_F, $\nu_F{}^1$, and ν_P are the frequencies of fluorescence of the hydrocarbon and complex and phosphorescence of the hydrocarbon respectively. Since $\tau_0 = 1/(k_1 + k_2 + k_3)$ then if γ^0 and γ are the fluorescence yields in the absence and presence of the quencher, Q, then equations (5) and (6) are obtained



SCHEME

$$\frac{\gamma^0}{\gamma} = \frac{F^0}{F} = 1 + k_4[Q]\tau_0\frac{(k_6 + k_7 + k_8)}{(k_5 + k_6 + k_7 + k_8)} \qquad (5)$$

$$= 1 + k_q\tau_0[Q] \qquad (6)$$

The quenching rate constant, k_q, is given by equation (7).

$$k_q = [k_4(k_6 + k_7 + k_8)]/(k_5 + k_6 + k_7 + k_8) \qquad (7)$$

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[7] B. S. Solomon, C. Steel, and A. Weller, *Chem. Comm.*, 1969, 927.

[8] M. F. Thomaz and B. Stevens, ' Molecular Luminescence,' ed. E. C. Lim, Benjamin, New York, 1969, 153.

[9] M. J. Blandamer and M. F. Fox, *Chem. Rev.*, 1970, **70**, 59.

If heavy atom-induced intersystem crossing is considerably faster than the other complex decomposition rate constants, k_6 and k_7, *i.e.* $k_8 \gg k_6 + k_7$, then expression (8) holds.

$$k_q \simeq k_4k_8/k_5 \qquad (8)$$

k_5 May be expressed in terms of its dissociation energy [equation (9)] where $-E_5$ is given by equation (10) whereas k_8 is expressed in terms of the

$$k_5 = A_5 \exp(-E_5/RT) \qquad (9)$$

$$-E_5 \simeq \mathrm{IP_D} - EA_A - \mathrm{C} \qquad (10)$$

atomic spin orbit coupling parameters, ζ, of the heavy atom in the quencher [expression (11)]. Equations

$$k_8 \simeq A_8(\Sigma\zeta_i)^2 \qquad (11)$$

(8)—(11) give the relationship (12).

$$\ln[k_q/(\Sigma\zeta_i)^2] \approx \text{constant} + (EA_A - \mathrm{IP_D})/RT \qquad (12)$$

This predicts for heavy atom quenchers a dependence of k_q on both the stabilisation energy of the complex and on the extent of spin–orbit coupling.

The ionisation potential of the anion will be related to the redox potential for $2X^- \longrightarrow X_2 + 2e$. Unfortunately this data is only available for I^-, Br^-, Cl^-, SCN^-, and $SeCN^-$. A plot of $\log_{10} k_q$ against redox potential gives a good linear correlation as shown in ref. 6 for these ions in acetonitrile as solvent. Another parameter which provides a measure of the ionisation energy of an inorganic anion is the energy of the C.T.T.S. absorption band maximum, as shown in Figure 1.

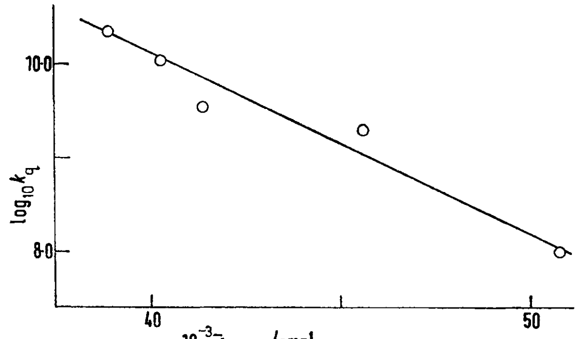

FIGURE 1 Plot of $\log_{10} k_q$, the quenching rate constant against the C.T.T.S. band maximum, $\bar{\nu}_{\text{C.T.T.S.}}$, for the quenching of anthracene fluorescence in acetonitrile

$E_{\text{max.}}$, The energy of the C.T.T.S. band maximum, varies with IP but also depends on the solvent shell–ion distance.[9] This will vary with the ion used and will also affect the energy of formation of the ion–anthracene complex. Thus $\bar{\nu}_{\text{C.T.T.S.}}$ will not be as good a measure of IP as the redox potential. However, we may use $\bar{\nu}_{\text{C.T.T.S.}}$ at least to show the trend of quenching rate with IP. An interesting conclusion may be drawn from Figure 2 concerning the cyanate ion. The transition at >55,000 cm^{-1} observed [9] in aqueous solutions of CNO^- has not been attributed to C.T.T.S. conclusively. If the interpolation of the quenching rate constant for CNO^- is taken on the straight line in Figure 2, a predicted value of *ca.* 57,000 cm^{-1} for a C.T.T.S. band is obtained. This method may be of use in tentatively assigning transitions of unknown origin to C.T.T.S. transitions.

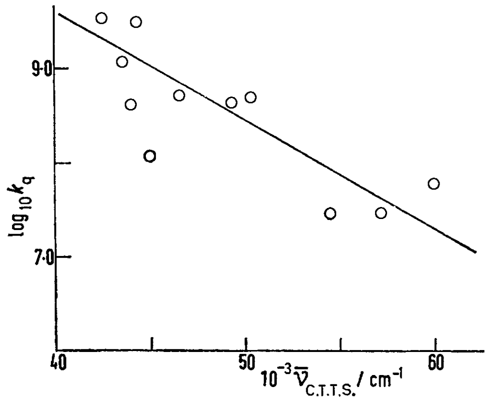

FIGURE 2 Plot of $\log_{10} k_q$, the quenching rate constant against the C.T.T.S. band maximum, $\bar{\nu}_{\text{C.T.T.S.}}$, for the quenching of anthracene fluorescence in ethanol–water

Figure 2 shows a plot of $\log_{10} k_q$ against $\bar{\nu}_{\text{C.T.T.S.}}$ for a wide range of inorganic anions in ethanol–water (1 : 1) as solvent. No correlation emerged when the same quenching data was plotted as $\log_{10} [k_q/(\Sigma\zeta)^2]$ against $\bar{\nu}_{\text{C.T.T.S.}}$ A much better correlation thus emerges using equation (4) rather than equation (11). Thus, although some of the anions used have appreciable atomic spin–orbit coupling parameters, it appears that in this case the assumption that $k_8 \gg k_6 + k_7$ is not valid. Although intersystem crossing will undoubtedly occur, particularly with the heavy atom anions like I^-, $SeCN^-$, and Br^-, it appears that the dominating influence on quenching rate is the resistance to dissociation of the exciplex by process (6), *i.e.* the complex stabilisation energy.

No fluorescence of the exciplex could be detected in any of the systems studied. The correlation of quenching rate with measures of ionising ability of the anions, which is quite good in view of the gross assumptions made, points quite clearly to an electron transfer mechanism for quenching. In view of the electron donor–acceptor nature of the components, such electron transfer is likely to be *via* exciplex formation although in the absence of complex fluorescence, a collisional mechanism cannot be ruled out.

TABLE 2

Effect of counter-ion on the quenching constants for the quenching of anthracene fluorescence by iodide ion

Cation	$k_q\,\tau$ (EtOH–H$_2$O)/ M^{-1}	$k_q\,\tau$ (Bu^{t}PH–H$_2$O)/ M^{-1}
Li^+	12·6	8·3
Na^+	12·7	
K^+	16·7	
Rb^+	18·0	11·8
Cs^+	18·4	12·0
NH_4^+	18·3	

Some dependence of quenching rate on cation was noted and the results are shown in Table 2 for the iodides of a range of cations. Iodides of the heavier cations generally give higher quenching rates. This could be due to heavy atom spin–orbit coupling-induced intersystem crossing, or to the reduced stabilisation of charge on the iodide ion, the increased radius of the cation giving a reduced attraction in the ion pair. In view of the similarity of the quenching constants for Cs^+ and NH_4^+, the latter explanation seems to be favoured.

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