QUENCHING OF EXCITED SINGLET STATES BY METAL IONS

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Bimolecular rate constants, k_q, have been determined for the dynamic quenching of the fluorescence of quinine sulphate, acridine, 2-naphthamide, xanthone and acridone in acidic aqueous solutions at 293 K by eighteen metal cations and four inorganic anions from the dependence of the donor molecule fluorescence lifetime on quencher concentration. The values of k_q are discussed in terms of possible quenching mechanisms.

1. Introduction

The quenching of organic singlet states by inorganic anions has been the subject of numerous investigations [1] and it was generally accepted until recently that charge transfer was likely to be the predominant mechanism. Watkins [2] has however shown that radical species are not always formed in these reactions and has suggested that radiationless transitions from the excited singlet state, mainly to the triplet, may be induced by the proximity of higher lying charge transfer states. Although the quenching of organic triplet states by metal ions and complexes have been widely studied [3] relatively little attention has been given to the quenching of organic singlet states by metal cations. Perhaps the most comprehensive study has been that of Varnes et al. [4], on the quenching of riboflavin fluorescence by metal ions. These workers concluded that electronic energy transfer was probably the most general quenching mechanism but did not reject the possibility of other mechanisms being operative. We have obtained bimolecular quenching rates for the interaction of several different organic singlet states with a wide range of metal ions and discuss these results below in terms of possible quenching mechanisms.

2. Experimental

The donor molecules were recrystallised twice be-

fore use. Donor concentrations of ca. 10^{-5} mol dm^{-3} in acidic aqueous solutions were used in all cases. The acidities of the solutions were made sufficiently high to ensure that the donor molecules were protonated in both the ground and excited singlet states [5]. With the exception of the Ag$^+$ ion, all the potential acceptor metal ions were added as metal sulphates to sulphuric acid solutions of the donor. The halides and pseudohalide ion quenchers were added as the appropriate A.R. grade potassium salt. All metal salts were recrystallised before use if not available as A.R. grade materials. A.R. grade sulphuric and nitric acids and doubly distilled water (off alkaline permanganate) were used.

The fluorescence quenching of all the metal ions was studied using lifetime measurements of the donor fluorescence. Lifetimes were measured using an Applied Photophysics single photon counting nanosecond spectrofluorimeter. The values of the lifetimes, τ, were computed using a least squares regression of the data obtained after the excitation pulse thus allowing τ values of $\geqslant 6$ ns to be obtained directly. With the halides, Ag$^+$ and NCS$^-$ ions, both relative lifetime and quantum yield measurements were made and agreed in all cases within experimental error. The fluorescence and relative quantum yield measurements were made using a Perkin–Elmer Hitachi MPF-2A spectrofluorimeter.

Measurements were made at 293 ± 2 K. The solutions were not degassed and the only case in which this may have led to significant errors in the bimolecular quenching rates, k_q, quoted is that of iodide quenching

where some oxidation to iodine was observed during exposure to ultraviolet radiation. The values of τ_0 remained unchanged after prolonged bubbling of O_2-free nitrogen through the solutions. At least four quencher concentrations were used in each case to obtain the quoted values of k_q.

Absorption spectra of the metal ions were obtained in 0.05 M H_2SO_4 solution at 293 K using a Perkin—Elmer 401 spectrophotometer.

3. Results and discussions

The donor molecules and their fluorescence lifetimes, τ_0, in the absence of added quenchers are given in table 1. As many of the metal ions investigated absorb within the fluorescence emission bands of the donor molecules the dependence of the fluorescence lifetime, τ, on metal ion concentration was measured, rather than fluorescence yield, in order to avoid errors due to inner-filter effects. In all cases the Stern—Volmer rela-

tionship $\tau_0/\tau = 1 + K_{sv}[Q]$, where K_{sv} is the Stern—Volmer quenching constant and $[Q]$ is the quenching ion concentration, was obeyed. The values of the bimolecular quenching rate constants, k_q ($= K_{sv}/\tau_0$), obtained from these results are given in table 1. Values of k_q for the anionic quenchers, Cl^-, Br^-, I^- and NCS^- are also given.

Of the metal ions, the most efficient quenchers are Fe^{3+}, Cr^{3+}, Fe^{2+} and Co^{2+} with k_q values of ca. (1—3) $\times$ 10^9 dm^3 mol^{-1} s^{-1} for all the donor molecules. A second group of metal ions, VO^{2+}, Nd^{3+}, Cu^{2+}, Pr^{3+} and Ni^{2+} may be distinguished with k_q values of 10^8—10^9 dm^3 mol^{-1} s^{-1}. The Mn^{2+} ion showed measurable but less efficient quenching with k_q between 10^7 and 10^8 dm^3 mol^{-1} s^{-1}. With the metal ions, Na^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+}, La^{3+} and Gd^{3+} no significant decrease in τ was observed and on the basis of the maximum ion concentrations used and the values of τ_0 it may be concluded that k_q, if finite, is certainly less than 10^7 dm^3 mol^{-1} s^{-1}.

Values for the bimolecular diffusion rate constants,

Table 1
Bimolecular quenching rate, k_q (dm^3 mol^{-1} s^{-1} $\times$ 10^{-7}), the bimolecular diffusion rate constants, k_d (dm^3 mol^{-1} s^{-1} $\times$ 10^{-7}), calculated from $k_d = 8RT/3000\eta$ and the fluorescence lifetimes of the donors, τ_0

Quenching ion [a]	Donor molecule				
	quinine sulphate 0.05M H_2SO_4	acridine 0.05 M H_2SO_4	2-naphthamide 0.2M H_2SO_4	xanthone 2M H_2SO_4	acridone 3.5M H_2SO_4
	k_q	k_q	k_q	k_q	k_q
I^-	1200	1300	1060	800	490
NCS^-	890	1100	1120	780	410
Br^-	760	1200	880	580	220
Cl^-	630	150	2	380	1
Fe^{3+}	160	300	370	160	190
Cr^{3+}	170	94	140	120	130
Fe^{2+}	100	250	190	310	150
Co^{2+}	140	190	160	190	240
VO^{2+}	43	90	30	80	36
Nd^{3+}	30	100	8	48	34
Cu^{2+}	21	25	54	14	36
Pr^{3+}	21	29	2	30	27
Ni^{2+}	17	14	30	19	15
Mn^{2+}	6	1	3	13	1
k_d	730	730	690	490	360
τ_0(ns)	19.5	37.2	17.2	26.6	23.2

[a] No significant quenching was observed with Na^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+}, La^{3+} and Gd^{3+}.

k_d (table 1), have been calculated for the various con- centrations of sulphuric acid solution used in these in- vestigations from the approximation [6].

$$k_d = 8RT/3000\eta , \qquad (1)$$

where η is the solvent viscosity. Values of η were de- rived from previous results [7]. It may be seen that the experimentally determined k_q values for the anionic quenchers I^- and NCS^- exceed the relevant k_d values while for the metal ion quenchers $k_q < k_d$ in all cases. Eq. (1) is derived from the Stokes–Einstein equation on the assumption that neutral molecules of equal mo- lecular radii are involved. In the present systems the donor and acceptor species are not of equal size and are charged. Although differences in size of the interacting ions need not necessarily lead to large errors in k_d values obtained from (1), allowance should be made for the relative charges. This may be done using the modified [6] Debye expression,

$$k_d' = (8RT/3000\eta)[\sigma/\exp(\sigma) - 1], \qquad (2)$$

with $\sigma = Z_A Z_B e^2 / DKTl$, where Z_A and Z_B are the ionic charges, e is the electronic charge, D the solvent dielectric constant and l the distance of closest approach. Accepting the approximations inherent in eq. (2) it is possible, at least in a qualitative manner, to rationalise the high k_q values with I^- and NCS^- and the lower k_q values of the Fe^{3+}, Cr^{3+}, Fe^{2+} and Co^{2+} ions on the basis that all these quenching reactions are operating at or very close to the diffusion limiting rate. For ex- ample, the values of k_q/k_d for I^- quenching of the donor molecules are 1.64, 1.78, 1.54, 1.63 and 1.36 indicating from use of eq. (2) closest approach distances of ca. 0.6–0.8 nm which are not unreasonable. The ob- served order of anion quenching ability, $I^- \approx NCS^- > Br^- > Cl^-$ is in agreement with previous results [1].

Possible mechanisms which may account for the quenching of the singlet states by metal ions are (a) heavy atom or paramagnetically induced increases in spin–orbit coupling leading to increased intersystem crossing rates in the donor molecules, (b) ground and/ or excited state complexation of the donor to the metal ion, (c) complete or partial charge transfer between the donor and the metal ion – or an induced radiationless process of the type proposed by Watkins [2] and (d) electronic energy transfer from donor to acceptor. Of these possibilities (a) may be discounted as a significant mechanism since there was no observable quenching

either by the diamagnetic La^{3+} ion ($Z = 57$) or by the heavier paramagnetic Gd^{3+} ion. The protonated nature of the donor molecules and the acidity of the solutions should also preclude complex formation between the donor and the metal ions as an important mechanism. In addition, the charge-transfer related mechanisms (c) alone cannot satisfactorily account for the apparent order of quenching ability i.e. Fe^{3+}, Cr^{3+}, Fe^{2+}, Co^{2+} $> VO^{2+}$, Nd^{3+}, Pr^{3+}, Cu^{2+}, $Ni^{2+} > Mn^{2+}$ since this order does not show any obvious correlation with the redox potentials [8] of the metal ions.

Electronic energy transfer, either by a coulombic [9] or an electron-exchange [10] mechanism, requires a finite overlap of the donor emission band and the ab- sorption band(s) of the acceptor. Efficient transfer from an excited singlet state $^1S_1^*$ to an acceptor with ground state $^m A$,

$$^1S_1^* + {^m A} \rightarrow {^1S_0} + {^n A^*}$$

by either mechanism requires that $m = n$, i.e. the ac- ceptor transition is spin-allowed [11]. Energy transfer from excited triplet states [12] is less restricted in this respect. The fluorescence emission spectra of the donor molecules show that, with the exception of the proto- nated 2-naphthamide, $> 95\%$ of the fluorescence yield occurs within the region 400–600 nm. A summary of the absorption characteristics of the metal ion accep- tors is given in table 2. The absorbance spectra of those metal ions listed in table 1 with k_q values $> 10^7$ dm^3 mol^{-1} s^{-1} show that the overlap criterion for elec- tronic energy transfer is met in all cases except possi- bly Fe^{2+}. It is also notable that the metal ions which did not have an observable quenching effect do not absorb in the fluorescence region. The relatively low values of the molar extinction coefficients, ϵ, of the Laporte forbidden transitions of the metal aquo com- plexes in the overlap region in conjunction with the donor lifetimes of < 40 ns favours electron exchange as an energy transfer mechanism in these circumstances since the coulombic type is dependent on the magni- tude of ϵ.

Although there are no a priori reasons for assuming that all metal ions quench singlet excited states by the same, or even a single, mechanism the considerations above suggest that energy transfer, probably electron exchange in nature, may be the predominant mecha- nism in many cases. For example, the spectral overlaps between the absorption spectra of the Co^{2+} and Cr^{3+}

Table 2
Summary of spectroscopic characteristics of quencher metal ions

Metal ion	Electronic configuration	Ground state	Absorption transitions [a]
Fe^{3+}	$3d^5$	^6S	All d–d transitions spin-forbidden. Intense charge-transfer absorption extends into the visible
Cr^{3+}	$3d^3$	^4F	$^4A_{2g} \rightarrow {}^4T_{2g}(575 \text{ nm})$, $^4T_{1g}(F)(405 \text{ nm})$, $^4T_{1g}(P)(270 \text{ nm})$
Fe^{2+}	$3d^6$	^5D	$^5T_{2g} \rightarrow {}^5E_g$ (ca. 1000 nm)
Co^{2+}	$3d^7$	^4F	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ca. 530 nm), $^4T_{2g}(1200 \text{ nm})$
VO^{2+}	$3d^1$	^2D	$\lambda_{max} \approx 800$ nm. Assignment difficult due to strong VO π-bonding component
Nd^{3+}	$4f^3$	^4I	$^4I \rightarrow {}^4G$ transitions in 400–600 nm region
Pr^{3+}	$4f^2$	^3H	$^3H \rightarrow {}^3P$ transitions in 400–600 nm region
Cu^{2+}	$3d^9$	^2D	$^2T_{2g} \rightarrow {}^2E_g$ (ca. 800 nm)
Ni^{2+}	$3d^8$	^3F	$^3A_{2g} \rightarrow {}^3T_{2g}(1180 \text{ nm})$, $^3T_{1g}(F)(685 \text{ nm})$, $^3T_{1g}(P)(395 \text{ nm})$
Mn^{2+}	$3d^5$	^6S	All d–d transitions spin-forbidden. $^6A \rightarrow {}^4T_1$, $^4T_2$, ^4E, $^4A_1$ (G) lie in the 400–600 nm region
Ag^+	$4d^{10}$	^1S	No d–d transitions. Lowest energy transitions are 4d → 5s type at 224 nm, 211 nm and 193 nm

[a] Absorption spectra for many of these ions are shown in ref. [14].

ions and the donor fluorescence spectra are significantly greater than those of the slower quenching VO^{2+}, Cu^{2+} and Ni^{2+} ions irrespective of whether they are calculated on the basis of a coulombic transfer i.e. $\int D(\nu)\, \epsilon(\nu)\, d\nu/\nu^4$, or an electron exchange transfer, i.e. $\int D(\nu) A(\nu)\, d\nu$, where $D(\nu)$ and $A(\nu)$ are normalised emission and absorption spectra respectively and $\epsilon(\nu)$ is the absorption coefficient. Although the spectral overlap is greater with the lanthanoid ions Nd^{3+} and Pr^{3+} than with VO^{2+} and Cu^{2+} the observed k_q values may reflect the decreased orbital overlap between the donors and the well shielded f-electron orbitals of the lanthanoid ions in comparison with the more poorly shielded d-electron orbitals of the transition metal ions. The relatively low k_q values obtained with the Mn^{2+} ion are consistent with the absence of spin-allowed d–d transitions from the ^6S ground state. It is thus possible to rationalise the quenching behaviour of all the metal ions in table 1, except Fe^{2+} and possibly Fe^{3+} (see table 2) in terms of electron exchange energy transfer.

The Fe^{2+} aquo ion has a single d–d transition (table 2) and considerably less overlap with the donor emission bands than, for example, the Cu^{2+} aquo ion. The

Fe^{3+} ion has the same d^5 electronic configuration as the Mn^{2+} ion but charge transfer absorption does extend from the ultraviolet into the visible. This is greatly increased if hydrolysis products are present. The high quenching rates found with these ions in this work and also with riboflavin as a donor [4] cannot be satisfactorily explained in terms of energy transfer involving overlap of d–d absorption bands and fluorescence emission bands. They may however be associated with the relatively low Fe^{3+}/Fe^{2+} reduction potential (0.771 V) and the consequent possibilities of charge transfer related mechanisms. Since the Fe^{3+}/Fe^{2+} reduction potential is almost identical to that of Ag^+/Ag (0.799 V) and the Ag^+ d^{10} ion has no absorption bands at wavelengths >250 nm [13], the quenching ability of the Ag^+ ion was also examined. These measurements were made in nitric acid solutions containing added $AgNO_3$ and linear Stern–Volmer plots of τ_0/τ against $1 + K_{sv}[Ag^+]$ were obtained with all donors. The Ag^+ ion quenches three of the donors at or near the diffusion controlled limit and the other two at slower but measurable rates (table 3). This clearly shows that spectral overlap is not a necessary requirement for quenching

Table 3

Bimolecular quenching rates, k_q, for Ag^+ quencher and donor molecule lifetimes, τ_0, in the absence of quencher

	Donor molecule				
	quinine sulphate 0.1M HNO_3	acridine 0.1M HNO_3	2-naphthamide 0.4M HNO_3	xanthone 4M HNO_3	acridone 7M HNO_3
k_q (dm^3 mol^{-1} s^{-1} $\times 10^{-7}$)	38	430	280	270	1
τ_0 (ns)	20.9	31.2	14.7	18.9	21.8

and indicates that a charge transfer type mechanism may be equally effective. The results do not however give any indication of the precise nature of the "charge transfer" mechanism.

It may be concluded, at least in the absence of ground state complexation, that rapid dynamic quenching of excited singlet states by a metal ion, M^{n+} (say $> 10^8$ dm^3 mol^{-1} s^{-1} in aqueous solution at room temperature) is only likely (a) if M^{n+} is readily reduced or oxidised by a single electron process and/or (b) if there is appreciable overlap between the fluorescence spectrum and spin-allowed absorptions of M^{n+}. Investigations of metal ion quenching of triplet states is usually restricted to solid solutions and therefore not directly comparable with the dynamic singlet quenching discussed above. However Breuninger and Weller [15] have shown that Co^{2+} quenches the phosphorescence yields and lifetimes of naphthalene-d_8 and triphenylene much more effectively than Ni^{2+} (as found for the singlet quenching reported in table 1) and that Ni^{2+} and Mn^{2+} are approximately equally effective quenchers which is consistent with the less restrictive spin requirements for triplet quenching.

Acknowledgement

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