DEACTIVATION OF EXCITED SINGLET AROMATIC HYDROCARBONS BY METALLIC IONS IN ETHANOL–WATER SOLUTION

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Summary

The deactivation of a number of excited polycyclic aromatic hydrocarbons by copper(II), cobalt(II), nickel(II) and chromium(III) in ethanol–water (1:1 by volume) has been investigated. In spite of the fact that most of the processes have very favourable $\Delta G°$ for electron transfer and $\Delta H°$ for energy transfer, the observed rate constants are considerably below the diffusion-controlled limit. The k_Q values measured correlate well with those calculated assuming a dipole–dipole-induced energy transfer mechanism. The slow rates obtained are considered to be the consequence of the large distance of closest approach.

1. Introduction

Excited aromatic hydrocarbon singlets are readily quenched by inorganic ions. Several systematic studies have been carried out employing inorganic anions and the results obtained generally show that the quenching rate constant correlates well with the free energy of the electron transfer process [1 - 5]. However, only a few systematic studies comprising either a number of closely related excited aromatics and a single cation or several related cations and an excited aromatic have been carried out [6 - 10]. In most of these studies, as well as in those regarding the quenching of aromatic triplets by cations and/or their complexes [11 - 16], the results obtained cannot be explained in terms of a single mechanism. Metal ions can quench an excited molecule by a variety of mechanisms: electron transfer [9, 11, 12], electron exchange energy transfer [9, 10, 11, 13 - 15], dipole–dipole energy transfer [9, 17], heavy-atom-assisted intersystem crossing [8, 18, 19], magnetic-field-assisted intersystem crossing [8, 12] and ligand displacement [15]. The variety of available mechanisms for a given donor–acceptor pair makes the interpretation of quenching results in these systems rather complex [8, 9, 15, 20]. In the present work, we report a study of the quenching of several

excited aromatic singlets by hexaaquo complexes of copper(II), nickel(II), cobalt(II) and chromium(III). The results obtained are interpreted in terms of a quenching mechanism dominated by energy transfer induced by a dipole–dipole interaction.

2. Experimental details

Fluorescence intensity measurements were carried out using an LS-5 Perkin–Elmer spectrofluorometer. Fluorescence lifetimes were taken from literature data or measured by following the singlet decay after excitation with a light pulse from a Nitronite nitrogen laser. All measurements were carried out in ethanol–water (1:1 by volume) solutions.

Fluorescence quenching experiments were carried out either by following the change in the donor lifetime or by following the decrease in fluorescence intensity under steady state irradiation. For the steady state experiments, the measurements were made at several emission wavelengths in order to evaluate the contribution of a trivial quenching mechanism. All the reported data were obtained at those wavelengths where fluorescence reabsorption could be disregarded and gave linear Stern–Volmer plots. In one system (perylene–Cr^{3+}) the trivial mechanism was significant at all wavelengths. In this case, the quenching rate constant was derived from double-quenching experiments employing copper(II) as the second quencher.

In the steady state measurements the hydrocarbons were irradiated at wavelengths such that there was no significant absorption by the quencher at the concentration employed. The absorption and emission spectra of the aromatic hydrocarbons were independent of the quencher concentration. The Stern–Volmer plots obtained were independent of the excitation wavelengths.

Phenanthrene (Aldrich), pyrene (Fluka), perylene (Aldrich), biphenyl (Aldrich), fluoranthene (Aldrich), benzene (Merck, pro analysi), chrysene (Fluka), coronene (Aldrich), benzo[a]pyrene (Fluka) and 2-methoxynaphthalene (Aldrich) were employed as received. Their absorption and emission spectra were identical with those reported in the literature. Naphthalene (Aldrich) and 2-cyanonaphthalene (Aldrich) were purified by sublimation under vacuum. Anthracene (Fluka) was purified chromatographically [21].

$CuSO_4$ (Merck), $CrCl_3 \cdot 6H_2O$ (Merck), $NiCl_2 \cdot 6H_2O$ (Merck), $CoCl_2 \cdot 6H_2O$ (Baker), $MnCl_2 \cdot 6H_2O$ (Merck), $Pb(NO_3)_2$ (AnalaR), $CsCl \cdot H_2O$ (Merck) and $BaCl_2$ (Merck) were of the highest purity available and were employed without further purification.

3. Results and discussion

Tables 1 and 2 give the quenching rate constants measured at 20 ± 1 °C. Tables 3 and 4 give all the kinetic, thermodynamic and spectroscopic

TABLE 1

Deactivation rate constants for $Me(H_2O)_6{}^{z+}$ ions

Aromatic	$k_Q(Cu^{2+})$ $\times 10^{-9}$ $(M^{-1} s^{-1})$	$k_Q(Cr^{3+})$ $\times 10^{-9}$ $(M^{-1} s^{-1})$	$k_Q(Ni^{2+})$ $\times 10^{-9}$ $(M^{-1} s^{-1})$	$k_Q(Co^{2+})$ $\times 10^{-9}$ $(M^{-1} s^{-1})$
Anthracene	6.8	7.90	2.00	1.24
Benz[a]anthracene[a]	1.5	0.78	0.16	0.12
Phenanthrene	1.5	0.44	0.14	0.09
Naphthalene	3.1	1.07	0.04	0.07
2-Cyanonaphthalene	4.6	2.00	0.64	0.25
2-Methoxynaphthalene	3.7	1.2	0.09	0.10
Pyrene[a]	1.7[b]	0.27	0.13[c]	0.14[d]
Benzo[a]pyrene[a]	1.2	0.73	0.08	0.16
Perylene	4.1	4.90[e]	1.96	1.48
Chrysene[a]	1.5	1.30	0.21	0.24
Coronene[a]	0.6	0.17	0.06	0.06
Fluoroanthene[a]	0.16	0.33	0.02	0.33
Biphenyl	4.5	2.65	0.2	0.17

[a]Obtained from fluorescence decay.
[b]2.8×10^9 in ref. 9.
[c]2.5×10^8 in ref. 9.
[d]1.2×10^8 in ref. 9.
[e]Obtained from double-quenching experiments.

TABLE 2

Deactivation rate constants for heavy or highly paramagnetic ions

Ion	k_Q ($\times 10^9 M^{-1} s^{-1}$)			
	Naphthalene	Anthracene	Pyrene	Benz[a]- anthracene
Mn^{2+}	0.003	0.16	—	—
Cs^{1+}	0.1	0.1 - 1.0	—	—
Ba^{2+}	0.01	0.1	—	—
La^{3+}	0.01	0.1	—	—
Pb^{2+}	—	1.0	0.1	0.16

data required for a quantitative interpretation of the measured rate constants. Analysis of the k_Q values reported in terms of the data gathered in Tables 3 and 4 leads to the following conclusions regarding the quenching by copper-(II), chromium(III), cobalt(II) and nickel(II) hexaaquo ions.

(i) Paramagnetic-induced and/or heavy-atom-assisted intersystem crossing does not contribute significantly to k_Q.

(ii) The quenching rates are slower than the diffusion-controlled limit in spite of very favourable free energy changes for electron transfer and for electronic energy transfer.

TABLE 3

Spectroscopic and thermodynamic data of the donors

Hydrocarbon	E_S (kcal mol^{-1})	$E_{1/2}$(ox) (V(SCE))	$E_{1/2}$(red) (V(SCE))	τ_S (ns)	ϕ_F[a]
Perylene	65.8	0.85[b]	−1.73[c]	4.6	0.76
Pyrene	77.0	1.61[b]	−2.19[b]	153.0[d]	0.47
Naphthalene	92.0	1.54[b]	−2.63[b]	60.0	0.12
Phenanthrene	82.9	1.50[e]	−2.46[c]	48.0	0.12
Anthracene	76.3	1.09[b]	−2.07[b]	3.8	0.24
Coronene	66.7	1.23[b]	−2.04[f]	133.0[d]	0.10
Biphenyl	99.0	1.82[c]	−2.58[f]	13.0	0.15
Benz[a]anthracene	75.1	1.18[b]	−2.11[b]	33.0[d]	0.17
Benzo[a]pyrene	78.1	1.27[b]	−2.22[b]	36.0[d]	0.33
2-Cyanonaphthalene	—	—	—	14.0	—
2-Methoxynaphthalene	—	—	—	11.7	0.41
Fluoranthene	79.8	1.45[b]	−1.73[b]	43.5[d]	0.18
Chrysene	79.2	1.35[b]	−2.25[f]	20.0[d]	0.12

[a]Values obtained using as reference those determined in ethanol [22].
[b]From ref. 23.
[c]From ref. 24.
[d]Directly measured from the fluorescence decay.
[e]From ref. 25.
[f]From ref. 26.

TABLE 4

Spectroscopic and thermodynamic data of the quenchers

Ion	Atomic weight (g mol^{-1})	Magnetic moment (BM 300 K)	$E(X^{+n} \rightarrow X^{+n+1})$ (V(SCE))	$E(X^{+n} \rightarrow X^{+n-1})$ (V(SCE))	E(d–d) (cm^{-1})	f oscillator
Cu^{2+}	63.54	1.91[a]	−1.8[b]	0.158[c]	12500[d]	2.3 × 10^{-4} [d]
Cr^{3+}	52.00	3.84[a]		−0.408[c]	24000[d]	2.6 × 10^{-4} [d]
Ni^{2+}	58.71	3.23[a]			25300[d]	7.0 × 10^{-5} [d]
Co^{2+}	58.93	1.81[a]	−1.842[c]		21600[d]	1.8 × 10^{-5} [d]
Mn^{2+}		5.92[a]				
Cs^{1+}	132.91					
Ba^{2+}	137.34					
La^{3+}	138.91					
Pb^{2+}	207.19					

[a]From ref. 27.
[b]From ref. 28.
[c]From ref. 29.
[d]From ref. 30.

(iii) There is no clear relationship between the k_Q values and the ΔG for ion pair formation, the exothermicity of the electronic energy transfer process or the normalized overlap integral. This lack of correlation applies to

data obtained employing a donor and several acceptors as well as to those obtained employing different donors and a single quencher.

(iv) The data can be best explained in terms of a dipole–dipole-induced energy transfer mechanism.

The first conclusion was reached by a comparison of the quenching rates of the hexaaquo ions considered and those obtained for ions of atoms with higher atomic weights (caesium, calcium or lanthanum) and/or greater magnetic momenta *e.g.* manganese. It is particularly interesting that such relatively low values of k_Q should be obtained since in several of the systems there are four processes that could lead to diffusion-controlled rates: electron transfer from the excited aromatic to the cation, electron transfer from the cation to the excited aromatic, dipole–dipole interactions and energy transfer by an exchange mechanism. This implies that $\Delta G^{\ddagger}(o)$ and/or k_o for both electron transfer [18] and energy transfer by an exchange mechanism [31] must be particularly unfavourable. Similar results have been found in many other systems involving transfer from excited species to metal ions [9, 20] or complexes [14, 16, 32] and have been rationalized in terms of significant distortion of the excited states (large $\Delta G^{\ddagger}(o)$) [31, 32] or in terms of poor spatial overlap between the donor orbitals and the acceptor (metal centred) orbitals leading to a small k_{en}^o [16, 31].

In order to determine whether the low rates are a consequence mainly of low pre-exponential factors [16] or of large activation enthalpies [32], we measured the values of k_Q for pyrene deactivation at different temperatures (in the temperature range 20 - 60 °C). Pyrene was chosen because its lifetime can be monitored easily and the values of k_Q are relatively low, the expected effects thus being larger. The apparent activation energies and pre-exponential A factors obtained are given in Table 5. This table shows that the Arrhenius activation energies are low and that there is no clear relationship between the rates of the processes and their activation energies. Low activation energies, which are frequently even lower than expected for the case of diffusion control, are more the rule than the exception in quenching processes involving metallic complexes [15, 16, 20, 33]. These data can be explained in terms of the mechanism
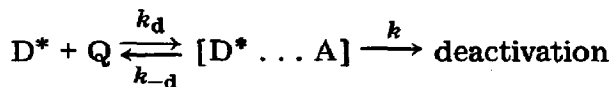
$$D^* + Q \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} [D^* \ldots A] \overset{k}{\longrightarrow} \text{deactivation}$$

TABLE 5

Arrhenius parameters in the quenching of pyrene by ions

Quencher	E_a (kcal mol^{-1})	log A[a]
Cu(II)	3.0 ± 0.5	11.6
Cr(III)	2.0 ± 0.5	10.5
Ni(II)	4.0 ± 0.5	11.4

[a]A is in M^{-1} s^{-1}.

where k is slow because of the large distance separating the relevant orbitals involved in the process. Under these conditions it might be expected that the mechanism that determines the value of k_Q must be that which is least sensitive to distance. When excited singlet quenching is considered, this process could be the dipole–dipole-induced electronic energy transfer. If this mechanism were operative, the quenching rate could be expected to be proportional to the overlap integral between the fluorescence band of the donor and all the absorption bands of the quencher, and to the fluorescence constant of the donor:

$$k_Q \propto (k_F)_{\text{donor}} J_{\text{overlap}}$$

In order to test this hypothesis, values of $k_F J$ were obtained for the present systems from the donor fluorescence, the absorption spectra of the acceptors and the k_F. The overlap integral in the coulombic interaction mechanism has the form:

$$J = \int\limits_0^\infty F_D(\bar{\nu}) \epsilon_A(\bar{\nu}) \frac{d\bar{\nu}}{\bar{\nu}^4}$$

where $F_D(\bar{\nu})$ is the normalized spectral distribution of the emission and $\epsilon_A(\nu)$ (cm^{-1}) is the molar extinction coefficient of the acceptor at the frequency $\bar{\nu}$.

This quantity was calculated by means of a FORTRAN IV program which works through the following steps: input of intensities at equally spaced wavelength intervals; reproduction of the absorption and emission spectra, changing the units from nanometres to reciprocal centimetres; measurement of area and normalization of fluorescence spectra; calculation of the overlap integral.

The k_F values were obtained from fluorescence yields and singlet lifetimes:

$$k_F = \frac{\phi_{fl}}{\tau_S}$$

Log k_Q is plotted against log $k_F J$ in Fig. 1. This figure shows that there is a fair correlation between the experimental values and the spectroscopic parameters. Chromium(III), cobalt(II) and nickel(II) behave similarly, while k_Q for copper(II) is larger than the k_Q measured for the other ions. This plot appears to indicate that dipole–dipole-induced energy transfer is the main mechanism leading to the quenching of excited aromatic singlets by the hexaaquo complexes. The fact that copper(II) appears to be a better quencher can be explained in terms of the closer approach for this compound (and/or its more extended orbitals). The dispersion of the present data, together with previous data which showed partial aromatic triplet production during the quenching process [9], may indicate that other mechanisms can operate in parallel with the dipole–dipole-induced energy transfer. Nevertheless, we consider that dynamic quenching by a Förster-type mechanism, which is strongly favoured because of the large value of the overlap
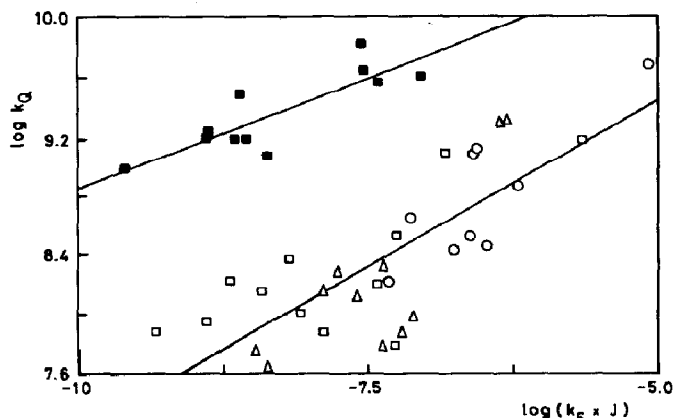
Fig. 1. Experimental value of k_Q as a function of $k_F J$ (see text): ■, copper (II); ○, chromium(III); □, cobalt(II); △, nickel(II).

integral but is hindered by the water ligand molecules which preclude close contact between the donor and the acceptor, explains the main features of the data obtained in the present work.

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