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ELECTRON TRANSFER QUENCHING OF DYE TRIPLETS BY NO_2^- AND N_3^-. A SPIN–ORBIT COUPLING EFFECT ON THE RADICAL YIELD

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Triplet quenching of 3-methyllumiflavin, thionine and thiopyronine by electron transfer from NO_2^- and N_3^- in acetonitrile, methanol and water was investigated by flash spectroscopy. The radical yield is systematically lower for N_3^- than for NO_2^-, explicable by the different spin–orbit coupling properties of the inorganic radicals produced.

1. Introduction

Electron transfer between electronically excited states and electron donors or acceptors in the ground state has been established as an important mechanism for the quenching of excited states. The paper of Rehm and Weller [1], demonstrating for several aromatic excited singlets and numerous aromatic quenchers in acetonitrile a clear-cut correlation between the quenching rate constant k_q and the free enthalpy change ΔG_{et}^0 of the electron transfer between excited molecule and quencher, represented a landmark in the understanding of this mechanism. In the meantime Rehm–Weller-type correlations have been shown to be valid also for reactions of excited triplet states [2–4] and excited transition-metal complexes [5,6]. Such correlations are now widely applied in the interpretation of excited-state quenching data to assess the role of electron transfer in the quenching process.

With organic molecules as quenchers in polar solvents the electron-transfer mechanism is generally corroborated by the detection of radical ions whenever the Rehm–Weller correlation ($\log k_q/\Delta G_{et}^0$) is observed. The situation is less clear when using inorganic ions, generally in the role of potential electron donors, as quenchers [7–9]. Although correlations of $\log k_q$ with ΔG_{et}^0 have been found in these cases too, stressing the importance of a charge-transfer interaction, observation of radical formation in the quenching reaction is rather exceptional. Instead the anions seem to induce physical quenching via charge-transfer catalyzed intersystem crossing ($S_1 \rightarrow T_1$ or $T_1 \rightarrow S_0$).

In our previous investigations on the mechanism of dye triplet quenching by organic electron donors, we found many examples where the factors determining quenching rate constant and radical yield appeared to be rather independent [10–12]. These results could be satisfactorily explained by a mechanism (cf. scheme I below) where the quenching step proper is an electron transfer and the radical yield is determined by the competition between two processes: the dissociation of the primary electron transfer product (radical-pair-like exciplex) into free radicals and the electron retransfer leading to the singlet ground state of the donor–acceptor pair and therefore involving an intersystem crossing process. Such a mechanism explains why in the case of triplet quenching the radical yield depends critically on the strength of spin–orbit coupling in the primary electron-transfer product rather than on the rate of formation of this intermediate.

In this paper we report some flash spectroscopic experiments using NO_2^- and N_3^- ions as quenchers of the dye triplets 3-methyllumiflavin (MLf), thionine (TH^+) and thiopyronine (TP^+) in the solvents

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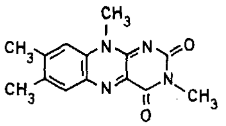
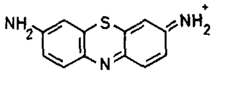
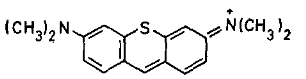
acetonitrile, methanol and water. In these systems the observation of radical formation proves the electron-transfer nature of the quenching and the trends in quenching rate constants (k_q) and radical yields (Φ_r) can be qualitatively understood by the mechanistic principle described above (cf. scheme I).


3-methyllumiflavin (MLf)


thionine (TH⁺)


thiopyronine (TP⁺)

2. Experimental

The flash apparatus used was the same as described recently [12]. The solutions investigated were deaerated by flushing with nitrogen for 30 min.

3-methyllumiflavin was synthesized and purified as described by Hemmerich [13], thionine (Merck) was purified according to ref. [14]. The preparation and purification of thiopyronine was recently described in ref. [12]. The optical absorption spectra of the dyes, their corresponding triplets and semiquinone radicals can be found in ref. [10] (thionine) and ref. [12] (thiopyronine). 3-methyllumiflavin with its intermediates is spectroscopically very similar to lumiflavin which has been spectrally characterized with its photochemical intermediates in refs. [15,16]. The inorganic quenchers were applied as sodium salts, $NaNO_2$ (Merck, reagent grade), NaN_3 (Merck, pure grade) doubly recrystallized from water.

Solvents used were water, doubly distilled, methanol (Merck, reagent grade) and acetonitrile (Merck, reagent grade). Aqueous solutions were buffered at $pH = 5$ using 0.104 M citric acid and 0.196 M NaOH (Merck Titrisol solution) and at $pH = 8$ using 0.112 M H_3BO_3, 0.056 M NaOH and 0.044 M HCl (Merck Titrisol solution). Methanol solutions, if necessary, were buffered at $pH = 8.6$ [17] using 0.015 M phenylacetic acid (Fluka $\geq$ 99%) and 0.005 M sodium methylate, freshly prepared from pure sodium.

The rate constants of triplet quenching were determined by applying a Stern–Volmer analysis to the triplet lifetime as a function of the quencher concentration, whereby the triplet decay was monitored at a suitable wavelength of triplet absorption (680, 780 and 810 nm for MLf, TH^+ and TP^+, respectively). Typical dye concentrations were $(1–2) \times 10^{-5}$ M.

The radical yields, extrapolated to infinite donor concentration, were determined either by measuring the semiquinone formation as described in ref. [10], which requires that the protolytic form of the semiquinone radical be exactly defined, or by observing the fraction of dye molecules returning from the triplet to the ground state during the quenching reaction [10]. The methods applied in the different cases are summarized in table 1. Whereas different protolytic forms of the dye semiquinone radicals were used in

Table 1
Data pertinent to determination [a] of radical yield Φ_r [b]

	MLf	TH^+	TP^+
ACN	G(440 nm)	– [c]	G(563 nm)
MeOH	$pH = 8.6$ R($MLfH^{\cdot}$ 560 nm) [d]	unbuffered R($TH^{\cdot}$ 410 nm)	unbuffered R($TP^{\cdot}$ 425 nm)
H_2O	$pH = 5$ R($MLfH^{\cdot}$ 560 nm) [d]	$pH = 8$ R($TH_2^{\cdot +}$ 780 nm) [d]	$pH = 8$ R($TP^{\cdot}$ 425 nm)

[a] G(... nm) indicates ground-state depopulation method [10] at given wavelength, R($X^{\cdot}$ ... nm) indicates radical absorption method [10], radical $X^{\cdot}$ observed at given wavelength.

[b] Extrapolated to complete triplet quenching.

[c] No measurement since dye ground state was deprotonated by NO_2^- and N_3^-.

[d] Radicals produced in electron transfer were protonated before observation, for $MLfH^{\cdot}$ cf. ref. [18] for $TH_2^{\cdot +}$ cf. ref. [12].

Table 2
Quenching constants k_q and radical yields Φ_r for dye triplet quenching by NO_2^- and N_3^-

		NO_2^-		N_3^-	
		$k_q (M^{-1} s^{-1})$	Φ_r	$k_q (M^{-1} s^{-1})$	Φ_r
^{3}MLf	ACN	6.3×10^9	0.92	4.5×10^9	0.21
	MeOH	1.5×10^9	1.0	2.9×10^9	0.21
	H_2O	1.5×10^9	1.0	4.3×10^9	0.09
$^3TH^+$	MeOH	2.8×10^8	0.90	1.6×10^9	0.22
	H_2O	6.8×10^6	> 0.7 a)	1.8×10^8	0.03
$^3TP^+$	ACN	2.0×10^{10}	0.97	2.5×10^{10}	0.12
	MeOH	3.5×10^8	0.90	4.5×10^8	0.11
	H_2O	5.0×10^6 b)	> 0.7 a)	7.0×10^4	– a)

a) Due to small k_q the radical yield could not be extrapolated exactly to complete triplet quenching.
b) Stern–Volmer plot was curved, maximum slope 5×10^6 $M^{-1} s^{-1}$ at small NO_2^- concentrations.

the measurements, the protolytic forms of the reacting triplets were in all cases ^{3}MLf, $^3TH^+$ and $^3TP^+$, respectively.

The absorption of the oxidized anions ($NO_2^{\cdot}$ [19] and $N_3^{\cdot}$ [20]) is negligible with respect to the absorption of dye semiquinone or ground state at the wavelengths of observation.

3. Results

In all cases investigated, the semiquinone radicals of the dyes could be detected as the direct products of the triplet quenching by NO_2^- and N_3^-. The quenching constants and radical yields observed for the different systems are listed in table 2. Acetonitrile could not be used in the case of thionine, since in this solvent the dye was deprotonated by the anions.

4. Discussion of the quenching constants

Since, from the formation of the semiquinone radicals it is clear that the triplet quenching is due to electron transfer from the anions to the triplets, it should be possible to understand the quenching rate constants on the basis of the Rehm–Weller correlation established for this type of reactions. In the cases considered the electron transfer reaction is of the type

$$^3A^z + D^- \rightarrow A^{z-1} + D^{\cdot}, \qquad (1)$$

where A^z and D^- denote acceptor (dye triplet, charge z) and donor (anion) respectively. The standard free enthalpy change for this reaction is given by

$$\Delta G^0_{et} = E_0(D^-/D^{\cdot}) - E_0(A^{z-1}/A^z) - E(^3A^z) + ze_0^2/\epsilon a, \qquad (2)$$

where the E_0 denote standard redox potentials, $E(^3A^z)$ is the triplet energy of the acceptor and the final term accounts for the Coulomb interaction in the reacting donor–acceptor pair, $-e_0$, ϵ and a being the electronic charge, dielectric constant of the solvent and the separation of the reacting molecules in the electron-transfer reaction, respectively. Due to the high dielectric constants of the solvents used, the Coulomb term contributes less than 0.1 eV in the cases considered and is neglected in the qualitative discussion to follow.

For the sum of the terms contributed by the acceptor to ΔG^0_{et} which we denote as $\Delta G^0_{A^z}$, the following values are in use: lumiflavin −1.44 V [2], thionine −1.21 V [2] and thiopyronine −1.13 V [12] (all versus SCE in H_2O). For the anions NO_2^- and N_3^-, there are no experimentally determined values of $E_0(D^-/D^{\cdot})$ in the literature. For NO_2^- an estimate of $E_0(NO_2^-/NO_2^{\cdot})$ of 0.76 V versus SCE was reported [21]. Adopting a value of this order of magnitude and using the $\Delta G^0_{A^z}$ values given above, one obtains negative ΔG^0_{et} values, indicating that fast electron-transfer reactions are indeed to be expected for $NO_2^{\cdot}$. As for N_3^-, there is evidence that it is a comparably good electron donor as NO_2^-. Recently threshold energies of photoelectron emission by NO_2^- and N_3^- in aqueous solutions have been determined [22]. For NO_2^- 7.57 eV was obtained, and for N_3^- there was some ambiguity whether 7.35 or 7.66 eV is the correct result, which in any case is close to the NO_2^- result.

Although sufficient data are not available for an exact calculation of ΔG^0_{et}, eq. (2) may be used to give a qualitative explanation for the observed *variation* of the quenching constant when using different dye triplets and different solvents.

According to the Rehm–Weller correlation, the rate constant of an electron-transfer reaction approaches the diffusion controlled limit as ΔG^0_{et} decreases in its negative region. The rate constant drops when ΔG^0_{et} passes through zero and log k_q approaches a limiting slope of $-\Delta G^0_{et}/RT$ when ΔG^0_{et} increases in its positive region. Hence it follows that in the positive or weakly negative region, only a sensitivity of k_q towards changes of ΔG^0_{et} can be expected.

Comparing the rate constants of triplet quenching by NO_2^- and N_3^- for the three dye triplets in water, where ΔG^0_{et} is more positive than in the other solvents (see below), its is observed that there is a general decrease in the order MLf > TH$^+$ > TP$^+$. This is just what is expected from the $\Delta G^0_{A^z}$ values given above.

Discussing the solvent effect on k_q one should be mainly concerned about the solvent dependence of $E_0(D^-/D^\cdot)$ and $E_0(A^{\cdot z-1}/A^z)$. Their changes are determined by the free enthalpy changes of transferring the corresponding redox pair from water into the solvent considered. Since we are concentrating on the major effects it is sufficient to consider only the ionic species. In general the free energy of solvation increases in the series water, methanol, acetonitrile, whereby the effect is much more pronounced for small ions. Values published for the free enthalpy change of NO_2^- transfer from water to methanol and acetonitrile are 0.11 and 0.32 eV respectively [23]. Thus the anions contribute strongly to a decrease of ΔG^0_{et} in the series water, methanol, acetonitrile. This effect is supported by the contribution of the acceptor ions TH$^+$ and TP$^+$ since these, as NO_2^- and N_3^-, are discharged in the electron-transfer reaction. It is, however, counteracted by the contribution of MLf since in this case the reduced form, obtained immediately after the electron transfer, is a negative ion and better stabilized in water. From the trend of ΔG^0_{et} variation, it is readily explained that k_q increases for TH$^+$ and TP$^+$ when going from water to acetonitrile. For MLf the effect is less drastic since (i) the solvent dependence of ΔG^0_{et} is weaker and (ii) for this acceptor we are in the more negative ΔG^0_{et} region.

5. Discussion of the radical yields

Concerning k_q we noted that NO_2^- and N_3^- show the same trends with respect to variation of the acceptor and the solvent, the effects being qualitatively explicable by the ΔG^0_{et} dependence of an electron-transfer reaction rate constant. There appears, however, a characteristic difference between the two anions in the radical yield observed in the quenching reactions. For NO_2^- the radical yield Φ_r is close to unity for all three acceptor triplets in all solvents. For N_3^- the radical yield is generally in the order of 10–20% and still drops to smaller values when going from methanol to water. On the other hand there is no change in the radical yield between acetonitrile and methanol for MLf and TP$^+$, though in the latter case the quenching rate constant changes by two orders of magnitude between these solvents. Obviously a general correlation between k_q and Φ_r does not exist and additional factors have to be considered to explain the radical yields observed in the quenching reactions.

According to the scheme

$$
\begin{aligned}
{}^3A^z + D \xrightarrow{k_{et}} {}^3(A^{\cdot z-1}D^\cdot) &\xrightarrow{k_{fr}} A^{\cdot z-1} + D^\cdot, \\
&\xrightarrow{k_{ISC}} {}^1(A^zD^-)_0, \qquad \text{(I)}
\end{aligned}
$$

the radical yield is determined by the rate constant k_{fr} of dissociation of the primary electron-transfer product $[{}^3(A^{\cdot z-1}D^\cdot)]$ and the rate constant k_{ISC} of electron retransfer from the acceptor to the donor involving an intersystem crossing process since one ends up with the singlet ground states of the reacting molecules. Studying the influence of heavy-atom substituents, we could show that spin–orbit coupling is the main factor determining the latter processes [11,12]. In fact in the present case, too, the different spin–orbit coupling properties of $NO_2^\cdot$ and $N_3^\cdot$ radicals can provide an explanation for the effects observed.

Whereas normally the electronic orbital momentum is quenched in molecules with more than two atoms, this is not the case in $N_3^\cdot$ since this molecule is linear having doubly degenerate π orbitals [24] giving molecular orbitals with orbital angular momentum $l_z = \pm 1$ along the molecular axis.

The ground state of $N_3^\cdot$ in the gas phase is a $^2\Pi$ state with a spin–orbit splitting of 71.3 cm^{-1} [25], the electron spin being quantized along the molecular axis. Thus, if the molecular axis is turned slowly (in a time τ longer than 1 ps, since 71.3 cm^{-1} corresponds to $1/\tau \approx 2 \times 10^{12}$ s^{-1}) the electronic spin orientation follows the molecular axis, if the axis undergoes faster reorientation, spin flips will be induced with a maximum rate constant of 2 × 10^{12} s^{-1}. In solution the degeneracy of the π orbitals is lifted since the solvent shell is not rotationally symmetric. Fluctuations of the solvent shell, however, still give rise to transitions of the radical electron between the perpendicular π_g orbitals, whereby the spin–orbit coupling induces spin flips. By this mechanism the triplet spin correlation in the radical pair gets lost, i.e. the radical pair gains some singlet character allowing for electron retransfer from the acceptor radical to the $N_3^{\cdot}$ radical, thus providing a competitive channel to the radical dissociation.

On the other hand $NO_2^{\cdot}$, representing a 17-electron radical is non-linear. The degeneracy of the π orbitals in the linear case is destroyed and the orbital angular momentum strongly quenched. Thus a spin-coupling-induced spin flip as in the $N_3^{\cdot}$ case is not to be expected here.

In $NO_2^{\cdot}$ the radical electron possesses considerable s character leading to an appreciable hyperfine interaction with the nitrogen nucleus of 54.75 G [24]. It has been shown that the hyperfine interaction, too, can provide a mechanism for intersystem crossing in radical pairs [26]. For this mechanism to become effective, however, it is important that the diffusive separation of the radicals is not too fast, which can be achieved by Coulomb attraction in the radical ion pair [27] or by cage effects due to the environment [28]. In radical pairs, however, without Coulomb attraction and in low-viscosity solvents, as in our case, the hyperfine interaction does not lead to appreciable recombination to a state of multiplicity different from the pair's original one. Using the theory of Schulten and co-workers [27] we estimate the geminate recombination yield due to hyperfine-induced intersystem crossing in our systems with NO_2^- to be less than 3%. In fact this is a value smaller than the absolute accuracy of the radical yields detected.

The principal difference in the radical yields between NO_2^- and N_3^- being understandable from the different spin–orbit coupling properties of the corresponding radicals, it remains to be explained why the solvent dependence is much more pronounced in the case of N_3^-. In a recent investigation of the solvent influence on the radical yield in the quenching of thiopyronine triplet by halogen anilines [12], we demonstrated that the radical yield is sensitive to solvent influence only if $k_{ISC} \geqslant k_{fr}$. Furthermore with these systems, too, we observed that there was a substantial drop in the radical yield when going from acetonitrile and methanol to water. As an explanation of these effects we discussed a solvent polarity dependence of the energy gap between the solvent-relaxed charge-transfer state and the corresponding ground state with unrelaxed solvent orientation, whereby the rate constant of the electron retransfer should be sensitive to this energy gap according to the "energy gap law" of radiationless processes. The solvent effect described in the present paper is in qualitative accord with this explanation.

6. Conclusion

In this paper we wanted to demonstrate the importance of spin–orbit coupling considerations when trying to understand the radical yield in triplet quenching reactions. This argument does not only refer to heavy-atom effects. Strong spin–orbit coupling effects are also to be expected if the charge-transfer or radical-pair states primarily formed in the electron-transfer step are orbitally degenerate, the degenerate orbitals involving p orbitals on the same centre. This is the rule rather than the exception with inorganic anions as quenchers and may explain why in the case of mono- and di-atomic ions the intersystem crossing channel dominates over the dissociation into the free radicals.

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