Photoreduction of 3,7-Diaminophenoxazinylium Chloride ('Oxonine') by Iron(II). A Model System for Singlet-state Driven Photogalvanic Cells

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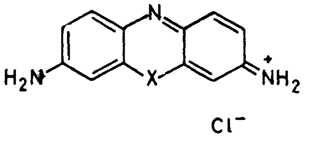
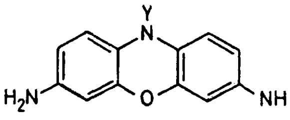
Summary Fluorescence of the title dye is quenched by iron(II) in water with concomitant photoreduction *via* a mechanism which does not involve significant induced intersystem crossing by the quencher.

IN a photogalvanic cell[1] the electroactive species are generated by a photochemical electron-transfer reaction in bulk solution. For maximum power output $\Delta E°$ for the reverse, dark reaction should be as large as possible. Most photogalvanic systems studied to date use a triplet state (T_1) driven photochemical electron-transfer reaction, but in principle a singlet state (S_1) driven reaction could afford higher voltages and greater power output by avoiding energy lost through intersystem crossing (I.S.C.). The title dye **(1)** is the oxygen analogue of thionine **(2)**, the most widely used dye in photogalvanic cells. The much longer singlet lifetime of **(1)** (τ_S 2·4 ns in air-saturated 10^{-2} N H_2SO_4) relative to that of **(2)** (τ_S 0·34 ns at pH 2·5 in 0·1 M K_2SO_4)[2] and its very small I.S.C. quantum yield ($\phi_{I.S.C.} < ca.$ 3×10^{-3} in water)[3] make it an excellent candidate for studies of dye singlet state photoreductions and model systems for singlet state driven photogalvanic cells. We report here that the mechanism of photoreduction of **(1)** by iron(II) in aqueous acid solution involves direct reaction of S_1 with Fe^{II} without the intermediacy of T_1.



(1); X = O
(2); X = S

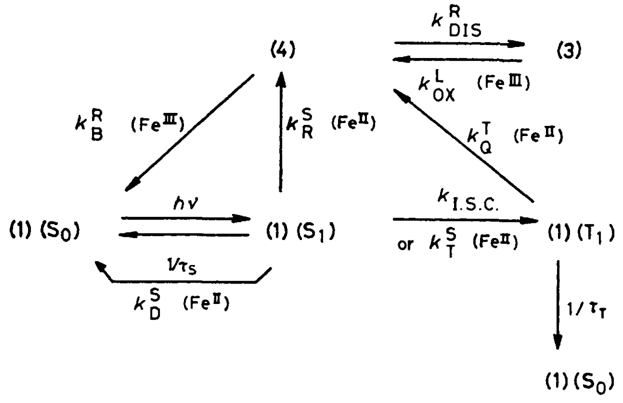


(3); Y = H
(4); Y = •

The dye **(1)** was synthesized by the method of Kehrmann and Saager[4] except that the reduction of 3,7-dinitrophenoxazine to the leuco dye **(3)** was more cleanly carried out by catalytic hydrogenation (H_2–Pd on C) rather than with zinc and hydrochloric acid. The colourless lecuo dye is oxidized immediately on exposure to oxygen to the brilliant red fluorescent free base of **(1)**, from which **(1)** can be obtained on treatment with HCl. A linear Stern–Volmer plot with slope 7·5 $dm^3 mol^{-1}$ was obtained for the quenching of the fluorescence of **(1)** by up to 0·2 M $FeSO_4$ in air-saturated 10^{-2} N H_2SO_4. The ionic strength was kept constant with $MgSO_4$ (to 0·2 M). From the known lifetime of **(1)** (S_1) an overall quenching rate constant $k_Q^S = 3{\cdot}1 \times 10^9$ $dm^3 mol^{-1} s^{-1}$ was obtained. No evidence for ground-state association of **(1)** and Fe^{II} could be obtained by visible absorption spectroscopy. Irradiation (Hg arc, interference filter, 578 nm) of **(1)** + Fe^{II} under the same conditions leads to completely dark-reversible photobleaching presumably due to the overall reaction (1).

$$(\mathbf{1}) + Fe^{II} + H^+ \underset{\text{dark}}{\overset{h\nu}{\rightleftharpoons}} (\mathbf{3}) + Fe^{III} \qquad (1)$$

We have investigated the reaction mechanism by both flash photolysis and steady-state methods. N_2-laser photolysis (337 nm, full-width at half maximum, F.W.H.M., 8 ns) of biacetyl in the presence of 10^{-4} M **(1)** in 10^{-2} N H_2SO_4 or dye-laser photolysis (560 nm, F.W.H.M. 200 ns) of $2{\cdot}5 \times 10^{-5}$ M **(1)** in the presence of 0·2 M KBr in 10^{-2} N H_2SO_4 led to observation of the protonated triplet state (T_1) of **(1)**, with a spectrum (λ_{max} 640 nm) similar to that previously reported,[5] and a lifetime (τ_T) of 13·5 μs. Quenching of **(1)** (T_1) with variable concentrations of Fe^{II} afforded a quenching rate constant $k_Q^T = 2{\cdot}1 \times 10^7$ $dm^3 mol^{-1} s^{-1}$ and resulted in the observation of the semireduced dye[5] **(4)** (λ_{max} 330, 380, and 750 nm) which disproportionates, presumably to **(1)** + **(3)** with $k_{DIS}^R = 7{\cdot}0 \times 10^9$ $dm^3 mol^{-1} s^{-1}$. The semireduced dye **(4)** reacts with Fe^{III} ($k_B^R = 1{\cdot}5 \times 10^5$ $dm^3 mol^{-1} s^{-1}$ as does the leuco dye **(3)** ($k_{OX}^L = 2{\cdot}1 \times 10^3$ $dm^3 mol^{-1} s^{-1}$). In direct laser-flash photolysis (Nd–YAG 532 nm, F.W.H.M. 9 ns) of **(1)** in the presence of 0·1 M Fe^{II} sufficient to quench *ca.* 40% of **(1)** (S_1), absorption due to **(4)** appears immediately after the flash. Our knowledge of k_Q^T enables us to calculate that if **(1)** (T_1) were a product of the reaction of **(1)** (S_1) with Fe^{II} then its (fast) decay (estimated τ_T *ca.* 0·5 μs) should have been superimposed on the slower decay of **(4)**. Such an observation was made[3] when **(1)** (S_1) was quenched by allylthiourea. In the present case photoreduction of **(1)** is apparently a direct singlet-state process although formation of **(1)** (T_1) which then does not escape from the encounter-complex with Fe^{II} cannot be ruled out. An overall mechanism is given in the Scheme. For greater clarity encounter-complexes and exciplexes are omitted.



Scheme

The singlet-quenching rate constant k_Q^S is a consequence of all the processes occurring when **(1)** (S_1) encounters Fe^{II}. The overall probability of net electron-transfer with formation of **(4)** (k_R^S/k_Q^S) in this type of singlet-quenching process is of considerable interest to the design of photogalvanic cells. Indeed, we find it possible to drive such a cell with Fe^{II}-quenched singlet in a reaction scheme like that outlined above. We have carried out a detailed steady-state photobleaching study of this system, analogous to that described by Wildes *et al.*[6] for the reaction of **(2)** (T_1) with Fe^{II}, but incorporating both singlet- and triplet-state processes in the steady-state kinetic analysis. Details of this work will be reported in a full paper. Our principal conclusion is that the probability of **(4)** escaping the encounter of **(1)** (S_1) with Fe^{II} is about 12%. A similar result was obtained by Bonneau[7] for the quenching of **(1)** (S_1) *vs.* **(1)** (T_1) by the organic electron-donor ethylenediaminetetra-acetic acid. Comparable low yields of semireduced dye have been observed[8] when Methylene Blue (S_1) is quenched by Fe^{II}. This relatively low efficiency may be a consequence of one or more factors. In the quenching of riboflavin (S_1) by Fe^{II}, energy transfer to the metal ion was proposed.[9] This is less likely for **(1)** since its singlet energy is *ca.* 0·5 V lower than that of riboflavin. Our experiments tend to rule out any mechanism (heavy-atom effect, catalysed spin-exchange) involving enhanced I.S.C. In any case this latter process would not tend to diminish the overall yield of **(3)**, since reaction of **(1)** (T_1) with Fe^{II} clearly gives rise to **(4)**. Since electron-transfer derived products are observed it is most economical to suggest that reverse electron-transfer from **(4)** to Fe^{III} occurs prior to escape of these products from the encounter complex. This effect will probably be the principal drawback to the development of singlet state-driven photogalvanic cells.

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