

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

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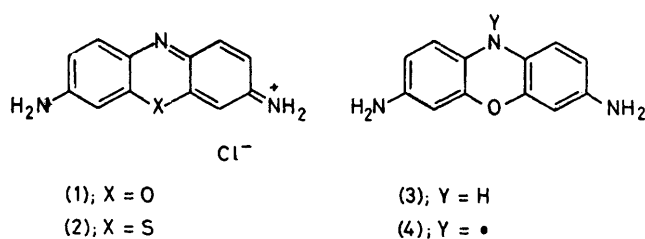
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**Summary** Fluorescence of the title dye is quenched by iron(II) in water with concomitant photoreduction *via* a mechanism which does not involve significant induced intersystem crossing by the quencher.

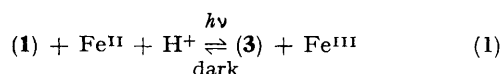
In a photogalvanic cell<sup>1</sup> the electroactive species are generated by a photochemical electron-transfer reaction

in bulk solution. For maximum power output  $\Delta E^\circ$  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) ( $\tau_S$  2.4 ns in air-saturated  $10^{-2}$  M  $H_2SO_4$ ) relative to that of (2) ( $\tau_S$  0.34 ns at pH 2.5 in 0.1 M  $K_2SO_4$ )<sup>2</sup> and its very small I.S.C. quantum yield ( $\phi_{I.S.C.} < ca. 3 \times 10^{-3}$  in water)<sup>3</sup> 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  $T_1$ .

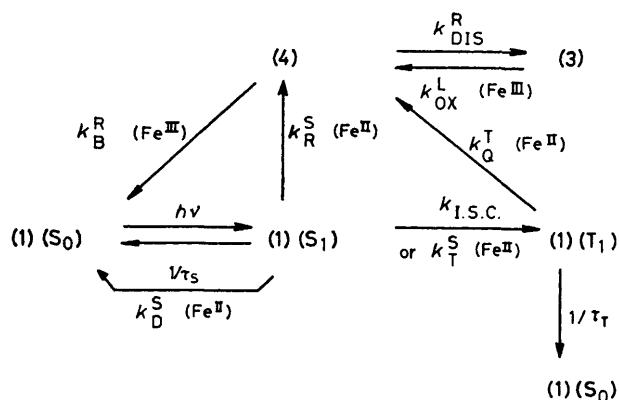


The dye (1) was synthesized by the method of Kehrman and Saager<sup>4</sup> except that the reduction of 3,7-dinitrophenoxazine to the leuco dye (3) was more cleanly carried out by catalytic hydrogenation ( $H_2$ -Pd on C) rather than with zinc and hydrochloric acid. The colourless leuco dye is oxidized 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  $7.5 \text{ dm}^3 \text{ mol}^{-1}$  was obtained for the quenching of the fluorescence of (1) by up to 0.2 M  $FeSO_4$  in air-saturated  $10^{-2}$  M  $H_2SO_4$ . 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  $k_q^S = 3.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  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).



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  $10^{-2}$  M  $H_2SO_4$  or dye-laser photolysis (560 nm, F.W.H.M. 200 ns) of  $2.5 \times 10^{-5}$  M (1) in the presence of 0.2 M KBr in  $10^{-2}$  M  $H_2SO_4$  led to observation of the protonated triplet state ( $T_1$ ) of (1), with a spectrum ( $\lambda_{max}$  640 nm) similar to that previously reported,<sup>5</sup> and a lifetime ( $\tau_T$ ) of 13.5  $\mu s$ . Quenching of (1) ( $T_1$ ) with variable concentrations of  $Fe^{II}$  afforded a quenching rate constant  $k_q^T = 2.1 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and resulted in the observation of the semireduced dye<sup>6</sup> (4) ( $\lambda_{max}$  330, 380, and 750 nm) which disproportionates, presumably to (1) + (3) with  $k_{dis}^R = 7.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The semireduced dye (4) reacts with  $Fe^{III}$  ( $k_B^R = 1.5 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) as does the leuco dye (3) ( $k_{ox}^L = 2.1 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ). 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  $\tau_T$  *ca.* 0.5  $\mu s$ ) should have been superimposed on the slower decay of (4). Such an observation was made<sup>3</sup> 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) ( $k_B^R/k_q^S$ ) 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.*<sup>6</sup> 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<sup>7</sup> 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<sup>8</sup> 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.<sup>9</sup> 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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