

## Photoreduction of the Paraquat Dication (1,1'-Dimethyl-4,4'-bipyridinium) by Visible Light *via* its Charge Transfer Complex with a Dithioanion

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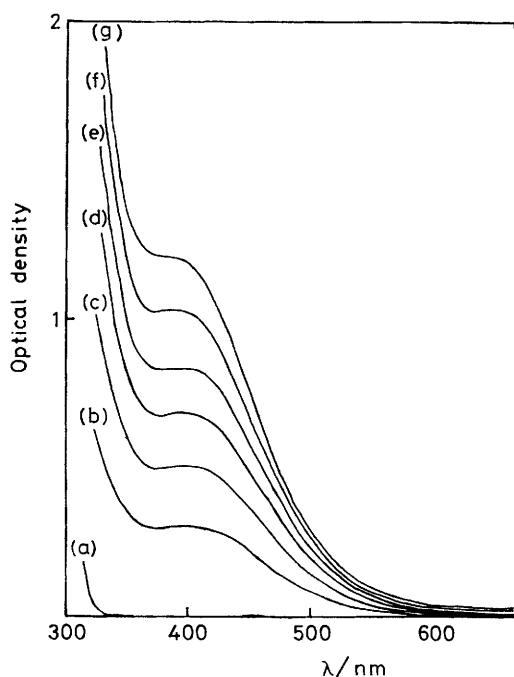
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Photoproduction by *visible* light of the mild reductant 1,1'-dimethyl-4,4'-bipyridinium ( $PQ^{\cdot+}$ ) occurs to an appreciable extent in acetonitrile *via* irradiation of the charge-transfer complex of  $PQ^{2+}$  with a dithioanion.

Photoreduction by visible light of 1,1'-dimethyl-4,4'-bipyridinium salts (paraquat,  $PQ^{2+}$ ) into the corresponding cation radical  $PQ^{\cdot+}$  which is a mild reducing agent, is currently achieved in the presence of a photosensitizer such as  $Ru(bpy)_3^{2+}$  or  $Zn(TPP)$  ( $bpy = 2,2'$ -bipyridine;  $TPP =$  tetraphenylporphyrin) and an irreversible electron donor. This system has been used extensively for photoredox catalysis, especially for the photoreduction of water.<sup>1</sup> We report here a new system where  $PQ^{\cdot+}$  is photoproduced by visible light in an organic medium *via* the irradiation of a charge-transfer complex between  $PQ^{2+}$  and a particular electron donor. It is well established that  $PQ^{2+}$  gives charge-

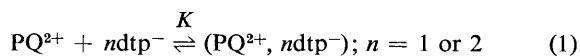
transfer complexes with various electron-donor species and that photolytic excitation in their charge-transfer band can result in electron transfer.<sup>2</sup> Generally, rapid back-electron-transfer prevents the effective build up of  $PQ^{\cdot+}$  by returning the system to the ground state.<sup>2</sup> In our system, the dark reaction is retarded by using a dithioanion as an irreversibly oxidizable electron donor. The only previously reported example where a net reaction occurred after excitation involved excitation in the u.v. region.<sup>3</sup>

An acetonitrile solution of  $PQ^{2+}[BF_4^-]_2$  in the presence of a large excess of the dithiophosphate anion  $dtp^-$  [ $dtp^- = (EtO)_2PS_2^-$  or  $(MeO)_2PS_2^-$  with  $Na^+$  as counter-ion; numeri-

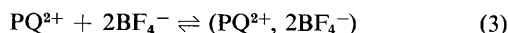
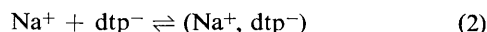


**Figure 1.** Spectral change accompanying the complexation of  $PQ^{2+}$  by  $dtp^-$  in MeCN:  $PQ^{2+} = 1.97 \times 10^{-3} M$ ; (a) no  $dtp^-$ ; (b)  $dtp^- = 4.2 \times 10^{-3} M$ ; (c)  $dtp^- = 10.6 \times 10^{-3} M$ ; (d)  $dtp^- = 20.4 \times 10^{-3} M$ ; (e)  $dtp^- = 37.6 \times 10^{-3} M$ ; (f)  $dtp^- = 70.2 \times 10^{-3} M$ ; (g)  $dtp^- = 12.2 \times 10^{-2} M$ .

cal results reported here are for the  $(MeO)_2PS_2^-$  system] exhibits an absorption band in the visible region centred around 400 nm (Figure 1). The origin of this band is attributed to a charge transfer transition between the two redox sites of the complex [equation (1)]. This new band is not

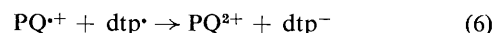
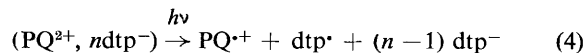


present with the isolated components. The equilibrium constant  $K$  of equation (1) cannot be determined easily by the usual spectrophotometric methods<sup>4</sup> because two other equilibria interfere with the equilibrium (1). First, as demonstrated previously by us,  $dtp^-$ , like other dithioanions,<sup>5</sup> is associated with its counter-ion to form an ion-pair [equation (2)].<sup>†</sup> Another complication arises from the possible association between  $PQ^{2+}$  and its counter-ion in acetonitrile [equation (3)].<sup>‡</sup>



Irradiation into the charge-transfer band of the  $(PQ^{2+}, ndtp^-)$  complex does not result in any emission in the 420–700 nm region at room temperature. Conventional flash photolysis with visible light ( $\lambda > 400$  nm) of an oxygen-free

solution of  $PQ^{2+}$  ( $5 \times 10^{-4} M$ ) and  $dtp^-$  ( $1.1 \times 10^{-2} M$ ) in acetonitrile shows that photoexcitation induces the electron transfer in equation (4).  $PQ^{+}$  remains in solution after the flash because the dimerization of two  $dtp^{\cdot}$  radicals into the corresponding disulphide  $(dtp)_2$  [equation (5)] is more rapid than the back-electron-transfer in equation (6) between  $dtp^{\cdot}$  and  $PQ^{+}$ . In an experiment using an excitation energy of



100 J,  $1.5 \times 10^{-6} M$  of  $PQ^{+}$  is produced after the flash, corresponding to a yield of 0.3% for the photoreduction of  $PQ^{2+}$ . With continuous irradiation, the amount of  $PQ^{+}$  builds up but its concentration reaches a maximum,  $[PQ^{+}]_{max}$ , which is relatively low in accordance with the low value of the yield observed by flash techniques:  $[PQ^{+}]_{max} = 0.25 \times 10^{-4} M$  after irradiation of  $PQ^{2+}$  ( $1.2 \times 10^{-3} M$ ) and  $dtp^-$  ( $10^{-2} M$ ) using filtered light ( $\lambda > 400$  nm) from a 250 W Hg lamp. When the illumination is stopped after  $[PQ^{+}]_{max}$  is reached,  $PQ^{+}$  disappears with first-order kinetics ( $k = 1.4 \pm 0.1 \times 10^{-3} s^{-1}$ ). This very slow reaction, which competes with the photoproduction of  $PQ^{+}$ , appears to be, at least in part, the reduction of  $(dtp)_2$  by  $PQ^{+}$  [equation (7)] into the starting material as demonstrated by the following electrochemical experiments.



As for some other dithioanions<sup>6</sup> electrochemical oxidation in acetonitrile containing 0.1 M  $Et_4NClO_4$  transforms  $dtp^-$  ( $E_p^a = 0.30$  V)<sup>§</sup> into the disulphide  $(dtp)_2$ . The latter in turn may be reduced back ( $E_p^c = -0.97$  V) to  $dtp^-$ . Although  $PQ^{2+}$  is reduced more easily ( $E_p^c = -0.74$  V) than  $(dtp)_2$ , exhaustive reduction at  $-0.80$  V of a solution of  $PQ^{2+}$  in the presence of 0.5 equiv. of  $(dtp)_2$  leads to quantitative formation of  $PQ^{+}$  and  $dtp^-$ . The total coulometry involves two electrons per mole of  $PQ^{2+}$ . At the beginning of the electrolysis the blue colour of  $PQ^{+}$  builds up very slowly. This behaviour is typical of that for the indirect reduction by an electrogenerated stable radical.<sup>7</sup> The homogeneous electron transfer between  $(dtp)_2$  and the electrochemically generated  $PQ^{+}$  is coupled with a fast chemical reaction, in our case the breaking of the S–S bond. Similar electrochemical indirect reductions of disulphides were reported recently.<sup>7</sup> This experiment shows clearly that  $PQ^{+}$  can reduce  $(dtp)_2$  although the  $\Delta G$  value estimated from the cyclic voltammetry results of reaction (7) seems to be positive.

Although the yield for  $PQ^{+}$  photoproduction is still low,<sup>¶</sup> our findings definitely indicate that this type of charge-transfer complex can be used to produce the mild reducing agent  $PQ^{+}$  in an exploitable amount by irradiation with visible light. By coupling this type of complex with an appropriate weak electron acceptor it should be possible to

<sup>§</sup> All potentials are determined at a Pt electrode by cyclic voltammetry with a sweep rate of 0.04 V s<sup>-1</sup>. Potentials are reported vs. Ag/Ag<sup>+</sup> ( $10^{-2} M$ ) as reference electrode.

<sup>¶</sup> This yield is calculated using the total concentration of  $PQ^{2+}$ , complexed and uncomplexed. If we assume a complexation constant  $K < 50$ , which is usually the case for  $PQ^{2+}$  charge-transfer complexes in organic solvents,<sup>8</sup> the yield is at least three times larger.

<sup>†</sup> Addition of  $NaClO_4$  causes a decrease of the charge-transfer band intensity because equilibrium (2) is displaced to the right.

<sup>‡</sup> Addition of a specific strong complexing agent of  $Na^+$  such as a crown ether does not result in an increase in the intensity of the charge-transfer band.

produce a photoredox cycle such as those described recently by us with the Ru(bpy)<sub>3</sub><sup>2+</sup>-dithioanion system<sup>9</sup> or to make a photoelectrochemical cell.<sup>10</sup> This is being investigated.

The author is grateful to Professor G. Cauquis for his interest in this work and for making his laboratory available for this study.

Received, 9th November 1981; Com. 1305

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