Tetrahedron Letters,Vol.25,No.27,pp 2867-2868,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

A PHOTO-INDUCED REDOX REACTION BY VISIBLE LIGHT VIA A CHARGE TRANSFER COMPLEX

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Summary : The reduction of tropylium cation (Tr^+) with the concomitant oxidation of O,O'-dialkyldithiophosphate anions (dtp^-) have been achieved by visible irradiation of their acetonitrile solution in presence of a bipyridinium dication ; the later via its charge transfer complex with dtp^- acts as a light-harvest and as an electron relay.

The photogeneration of the stable one electron reduced form of the mild reducing agents, bipyridinium dications such as diquat (6,7-dihydrodipyrido[1,2-a:2',1'-c] pyrazinedium dication, noted DQ^{2+}) or paraquat (1,1'-dimethyl-4,4'-bipyridinium dication, noted PQ^{2+}) can be achieved by the irradiation in the visible of their charge transfer complexes with a variety of organic electron donors [1-6]. In particular we have recently [2] reported the photoreduction of PQ^{2+} to its corresponding cation radical $PQ^{\cdot +}$ in acetonitrile via the irradiation of its charge transfer complex with a dithiophosphate anion dtp^- [dtp^- = $(C_2H_5O)_2PS_2^-$ or $(CH_3O)_2PS_2^-$ with Na^+ as counter-ion]. We report here the production of a photoredox cycle by coupling this system to an appropriate electron acceptor such as tropylium cation Tr^+ (with BF_4^- as counter-ion).

An acetonitrile solution of DQ^{2+} or PQ^{2+} (2×10^{-3}M) in the presence of a large excess of dtp^- (4×10^{-2}M) exhibits in the visible an absorption band centered around 430 nm and 400 nm respectively. This new band which is not present in the isolated components corresponds to a charge transfer transition between the electron acceptor DQ^{2+} or PQ^{2+} and the electron donor dtp^- (equation (1) with DQ^{2+} for example).

$$DQ^{2+} + ndtp^- \rightleftarrows (DQ^{2+}, ndtp^-) \quad n = 1 \text{ or } 2 \qquad (1)$$

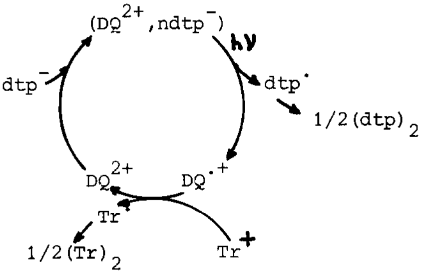
The addition to this solution of the second electron acceptor Tr^+ (6×10^{-3} M) causes a slight decrease of the charge transfer band intensity (< 10 %) because the weaker charge transfer complex (Tr^+, dtp^-) (equation (2)) is concurrently formed. However this complex does not absorb in the visible area.

$$Tr^+ + dtp^- \rightleftarrows (Tr^+, dtp^-) \qquad (2)$$

Selective irradiation (λ_{ex} > 410 mm) of this oxygen free solution (DQ^{2+} or PQ^{2+}, dtp^-, Tr^+) with filtered light of a 250 W Xe lamp induces the dtp^- oxidation into the corresponding disulphide $(dtp)_2$ [$(dtp)_2$ = $(C_2H_5O)_2\underset{\overset{\|}{S}}{P}\text{-S-S-}\underset{\overset{\|}{S}}{P}(OC_2H_5)_2$ or $(CH_3O)_2\underset{\overset{\|}{S}}{P}\text{-S-S-}\underset{\overset{\|}{S}}{P}\text{-}(OCH_3)_2$] and the Tr^+ reduction into the corresponding bitropyl $(Tr)_2$. The progress of the photocatalysed redox reaction (equation (3) was followed during the irradiation by quantitative HPLC analysis (on a Waters radial-pak µ Bondapak C_{18} cartridge, eluated with $MeOH/H_2O$; 70/30). After 6 hours of irradiation $(Tr)_2$ was obtained with a yield of 80 % in the

$$dtp^- + Tr^+ \longrightarrow 1/2(dtp)_2 + 1/2(Tr)_2 \qquad (3)$$

presence of DQ^{2+} and 50 % with PQ^{2+}, while a stoichiometric amount of $(dtp)_2$ was also formed. 90% of Tr^+ was consumed in both cases. The electronic absorption spectrum of the solution is unchanged at the end of the irradiation. This observation indicates that the bipyridium dications are not consumed during the irradiation. We have verified that the redox reaction (equation 3) does not occur in the dark or in the absence of DQ^{2+} or PQ^{2+}. The following scheme represents the mechanism of the photoinduced redox reaction :



As demonstrated previously[2] for the case of $(PQ^{2+}, ndtp^-)$ complex the light induces the charge separation of the complex leading to $PQ^{\cdot +}$ and $dtp^{\cdot}$. The $PQ^{\cdot +}$ (or $DQ^{\cdot +}$) species is built up because the dimerization of two $dtp^{\cdot}$ radicals is more rapid than the back-electron transfer between $PQ^{\cdot +}$ and $dtp^{\cdot}$. Then the photogenerated $PQ^{\cdot +}$ ($E_{1/2}$ = -0.45 V vs s.c.e.[7] in CH_3CN) or $DQ^{\cdot +}$ ($E_{1/2}$ = -0.35 V vs s.c.e.[5]) reduces easily Tr^+ (Ep_c = -0.22 V vs s.c.e.[8]) into the tropyl radical $Tr^{\cdot}$ which rapidly dimerizes into bitropyl $(Tr)_2$. The regenerated PQ^{2+} is complexed again by the excess of dtp^- and is ready for participation in another photoredox cycle.

Although the quantum yield is not yet measured, the long time needed to achieve the redox reaction indicates that it is still low. This is not surprising if we consider our previous photochemical study[2] on the $(PQ^{2+}, ndtp^-)$ complex. We observed that a yield of 0.3 % was obtained for the photoreduction at PQ^{2+} and that $PQ^{\cdot +}$ is built up very slowly. $[PQ^{\cdot +}]$ reached a relatively low maximum ($[PQ^{\cdot +}]_{max}$ = 0.25 x 10^{-4} M) after one hour of irradiation. The difference in the yield of reaction (3) where PQ^{2+} is used instead of DQ^{2+} is not actually well understood.

In conclusion it appears that the use of an in situ charge transfer complex as photosensitizer can be a suitable way to drive a redox reaction in the non-spontaneous direction by visible light. However from a practical point of view, it should be necessary in the future, to increase the yield of the primary photochemical process (charge separation) by an appropriate choice of complexes.

Acknowledgments : We are thankful to Professor G. Cauquis for his interest in this work.

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(Received in France 13 March 1984)