

Photophysical study of the decomposition of water using visible light and tungsten tris(dithiolenes) as photosensitizers-catalysts

R. Humphry-Baker^a, C.A. Mitsopoulou^{b,1}, D. Katakis^{b,*}, E. Vrachnou^c

^a *Institut de Chimie Physique, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland*

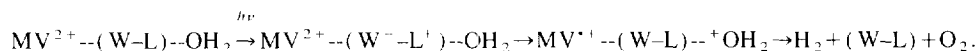
^b *Laboratory of Inorganic Chemistry, Department of Chemistry, University of Athens, Panepistimiopolis, 15 771 Zografou, Greece*

^c *N.C.S.R. 'Demokritos', POB 60 228, 153 10 Aghia Paraskevi, Attiki, Greece*

Received 24 March 1997; received in revised form 16 December 1997; accepted 19 December 1997

Abstract

Excitation of four unsymmetrically substituted tungsten tris(dithiolenes), in various solvents with 355 nm laser pulses produce weak but easily measurable transient absorptions. The four complexes used are characterized as photocatalyst–catalysts (PC–C) for the photodecomposition of water and their names are tris-[1-(4-dimethylaminophenyl)-2-phenyl-1,2-ethylenodithiolenic-*S,S'*]tungsten, tris-[1-(4-methoxyphenyl)-2-phenyl-1,2-ethylenodithiolenic-*S,S'*]tungsten, tris-[1-(4-methoxyphenyl)-1,2-ethylenodithiolenic-*S,S'*]tungsten and tris-[1-(phenyl)-1,2-ethylenodithiolenic-*S,S'*]tungsten. The lifetimes of the transient absorptions observed are long, persisting into the millisecond time domain. In acetone–water, and in the presence of MV^{2+} there are at least two transients, one corresponding closely to the known spectrum of MV^+ , assigned to the hydrogen precursor, the other living much longer and assigned to the O_2 precursor. The results indicate that the electron is quickly removed from the excited state of the photocatalyst–catalyst and is temporarily stored in the electron acceptor, in a way that is unfavorable to recombination. The first stages of the process can be schematically represented as:



The dotted lines connecting the reagents with the PC–C (W–L) were put in this scheme in order to emphasize the supramolecular nature of the interactions. The opposite charges created by light absorption are quickly transformed into repulsive positive charges due to the presence of the electron acceptor MV^{2+} and two centers are created, two molecular diameters apart, one the precursor of the H_2 , the other the precursor of O_2 . The combination of a small space separation charges and of the electrostatic factor (transformation of these charges into repulsive ones) are perhaps crucial factors in the separation of the reduction from the oxidation. However, there is also a kinetic factor. The reduction is quick, irreversibly leading to H_2 not to recombination. The splitting of water is time resolved. The reactions at the reduction end of the supramolecular complex (presumably because the involve fast proton and electron transfers) lead fast and irreversibly to H_2 formation.

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Keywords: Photophysical study; Visible light; Tungsten tris(dithiolenes)

1. Introduction

The photodecomposition of water (reaction 1):



is a combination of oxidation (to O_2) and reduction (to H_2). The kinetic stability of the resulting thermodynamically unstable system is achieved at the final stages of a complex reaction mechanism, namely after the formation of the bonds

of the diatomic products. Following the absorption of light, and until this state of kinetic stability–thermodynamic instability is reached, the system remains kinetically unstable too. Oxidation and reduction intermediates tend to react with each other and return the system back, with an associated dissipation of the absorbed energy in a degraded form.

The obvious strategy to avoid interaction between oxidized and reduced intermediates is of course to separate them. This is exactly what Nature is doing in photosynthesis by transporting and transferring electrons, protons, ions and molecules within the large multicomponent photosynthetic systems [1–3]. In photosystem II, the electrons end up in a quinone and do not return to react with the O_2 producing

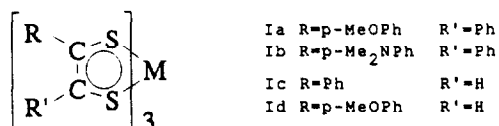
* Corresponding author. Fax: +30-1-7232094

¹ E-mail: cmitsop@atlas.uoa.gr.

intermediates. The reduced quinone is instead removed further and through a system known as cytochrome b_6/f , the electrons are transferred to the region of photosystem I, where they are used to reduce NADP^+ , and eventually carbon dioxide. The effective separation of charges is in fact completed at the early stages of this complex process, within 3 ps after photoexcitation (in bacterial photosynthesis).

In contrast to photosynthesis, the known non-biomimetic photocatalytic system [4,5] is homogenous and has only two components (apart from the acetone-water solvent) the photocatalyst-catalyst (PC-C) and the reversible electron acceptor (EA). There are no separate photosensitisers, antennas, catalysts, membranes, relays or other organized regions. How then can such a simple system overcome the period of kinetic instability? The photophysical experiments described in this paper provide some clues towards an answer to this vital question.

The complexes investigated as photocatalysts-catalysts (PC-C) are trigonal prismatic tungsten (tris)dithiolenes, of 'reduced' symmetry ($R \neq R'$ in formula I).



Complexes Ia and Ib are thermally and photochemically stable and efficient in driving reaction (1), as reported previously [4-6]. Complexes Ic and Id are unstable and inefficient; they were investigated for comparison purposes.

The reversible electron acceptor (EA) mostly used is methylviologen (MV^{2+}), but some experiments were also carried out with dibenzylpyridine (D^{2+}) (vide infra). The ability of MV^{2+} to form complexes (interact) with neutral species is known from the early literature [7-10]. Pre-complexation with Ia, in particular, has been documented [4].

2. Experimental

The synthesis of complexes I has been reported previously [11]. Experiments were done with and without MV^{2+} (1,1'-dimethyl-4,4'-bipyridinium dichloride) or DP^{2+} (1,1'-dibenzyl-4,4'-bipyridinium dichloride) added. In the mixed solvent acetone-water (70:30 or 80:20), both the photocatalyst-catalyst (PC-C) and the reversible electron acceptor (EA) have sufficient solubility. In the experiments with PC-C only, there is no need for a mixed solvent system and the experiments could also be done in dichloromethane and pure acetone. All solvents were of spectroscopic quality. Commercial MV^{2+} (Aldrich) was recrystallized from pure ethanol and dried for 5 h at 70°C. All solutions were prepared by dissolving the appropriate amount of complex in the desired solvent to give typically a 5×10^{-5} M solution. The solutions were degassed by bubbling with oxygen-free N_2 ,

which was passed through acetone, in order to saturate it in acetone vapor and prevent depletion of the mixed solvent in acetone. At higher water content, there is always the possibility for precipitation of the neutral PC-C. For complexes Ia and Ib, there is no evidence of decomposition. Complexes Ic and Id are thermally stable, but partly decompose during the illumination.

The pulsed laser photolysis experiments were carried out with an actively mode locked Nd YAG laser, using pulses of around 5 mJ, at 355 nm. Complex Ia was also studied with excitation at 440 nm with an OPO laser, with 3 mJ pulses. Up to 16 pulses were averaged for each point of the spectrum. The deaeration was done once at the beginning of this sequence. In some experiments however, it was done continuously throughout laser excitation. The excitation beam passed through 1 cm of solution; the analyzing light was focused through a pinhole approximately 1 mm from the front face of the cell. The path length of the analysing light was 0.5 mm for all the excitation wavelengths. The data acquisition and handling system included a Tektronix 2430A oscilloscope, monochromator (bandpass 38.4 nm), photomultiplier and optical cutoff filters (of 350 and 420 nm). Interference filters were used in order to avoid exposing the solution to UV light. The observation of the transients was always carried out perpendicular to the exciting pulse, using a 150 W Xe lamp source. Corrections for ground state bleaching effects were not made. The OPO laser, could be tuned from 420 to 450 nm. The reproducibility of the transient spectra was tested using fresh solutions.

Because of reaction (1), there is a spectacular gas evolution upon laser excitation, which introduces some additional noise, particularly at longer acquisition times.

3. Results

In the absence of MV^{2+} excitation of complexes I by the 355 nm pulses produces weak but easily measurable transient absorptions (Figs. 1 and 2). The base line is set in each case with the highly absorbing initial solution. Thus, even a small apparent transient OD means high absorptivity of the intermediates; it corresponds to absorbance above that of the PC-C. For the same reason, the positions of the observed maxima are expected to be somewhat shifted in relation to the real ones. The spectra of the complexes are given in Table 1.

The transient peaks for complex Ia are shown in Fig. 1. In dichloromethane (Fig. 1a), there is a broad nonsymmetric peak with a maximum at ca. 365 nm. In pure acetone the appearance is similar (Fig. 1b), except that now the whole absorption is shifted to longer wavelengths, as expected for a solvent of higher dielectric constant (acetone 20.7, dichloromethane 9.1). In acetone-water (Fig. 1c), there is a further bathochromic shift, a broadening because of the water and a decrease in intensity, by approximately a factor of two. With complex Ib in acetone:water (70:30), the maximum is at 475 nm (Fig. 2).

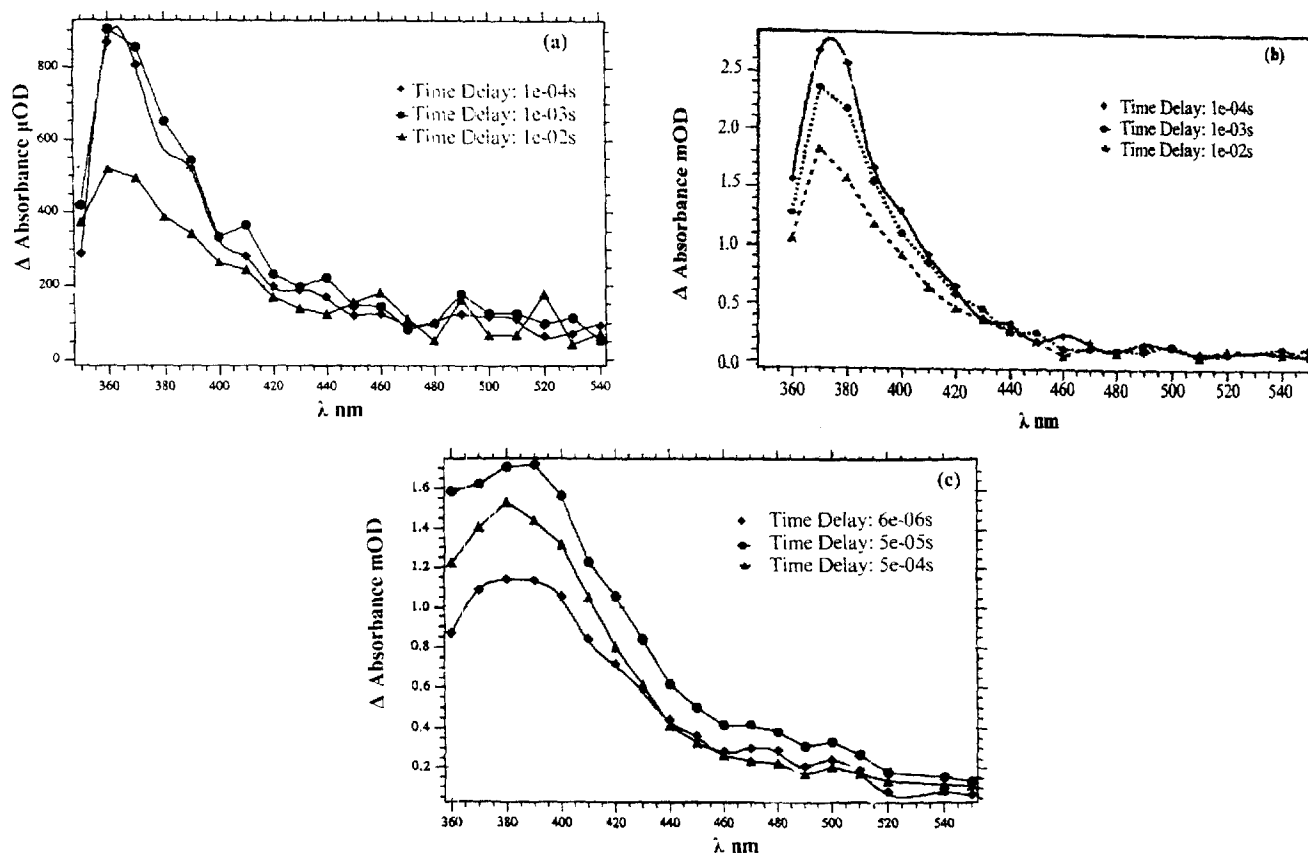


Fig. 1. Absorption resulting from the 355-nm laser flash photolysis of deaerated solutions containing 5×10^{-5} M of complex Ia (a) in pure CH_2Cl_2 , time delays: $\blacklozenge 1 \times 10^{-4}$ s, $\bullet 1 \times 10^{-3}$ s, $\blacktriangle 1 \times 10^{-2}$ s; (b) in pure acetone, time delays: $\blacklozenge 1 \times 10^{-4}$ s, $\bullet 1 \times 10^{-3}$ s, $\blacktriangle 1 \times 10^{-2}$ s; (c) in acetone:water (70:30), time delays: $\blacklozenge 6 \times 10^{-6}$ s, $\bullet 5 \times 10^{-5}$ s, $\blacktriangle 5 \times 10^{-4}$ s.

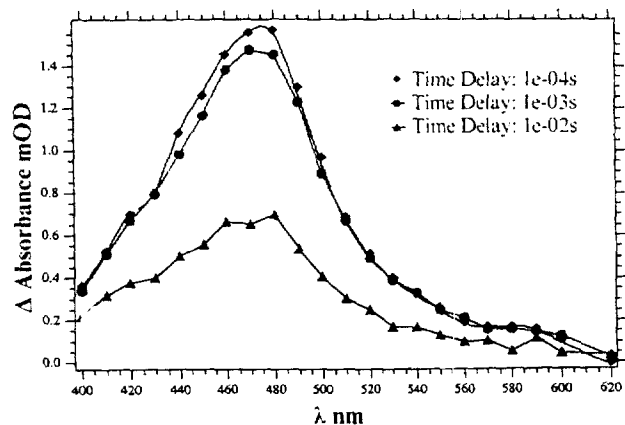


Fig. 2. Absorption resulting from the 355-nm laser flash photolysis of deaerated solutions containing 5×10^{-5} M of complex Ib, in acetone:water (80:20). Time delays: $\blacklozenge 1 \times 10^{-4}$ s, $\bullet 1 \times 10^{-3}$ s, $\blacktriangle 1 \times 10^{-2}$ s.

The kinetics in pure solvents, and as a matter of fact throughout this investigation, do not generally fit simple first or second order rate laws, but it is interesting to note that at short times (between 6×10^{-6} and 5×10^{-5} s in Fig. 1c), the transient still builds up and the decay dominates after times of the order of 20 ms. (Fig. 1a). It should also be noted that in acetone–water, the decay is faster by more than one order of magnitude compared to the other solvents.

In the presence of MV^{2+} , all experiments were done in acetone:water (70:30 or 80:20) except in the experiments presented in Fig. 5 where ethanol was also added. For complex Ia, there are two peaks now in the 350–420 nm range, sharper and more intense (Fig. 3a) compared to those in Fig. 1, and another one at ca. 510 nm. The two peaks at 350–420 nm do not belong to the same species because there is a marked difference in the rate of decay (Supplementary Figs. S1–S8). The short wavelength peak (360 nm) decays with rates comparable to those in the absence of MV^{2+} (Fig. 1c), but the corresponding intermediates are not the same; the peaks differ in width and in the position of the maxima. The peak at 510 nm seems to decay simultaneously with the peak at 390 nm and much faster than the peak at 360 nm, as shown by the spectra at different delay times (Fig. 3); they are both assigned to complexed MV^{+} .

In reduced viologen aggregates, MV^{+} is known to give enhanced absorptions in the ca. 450–500 nm range [12,13]. MV^{2+} alone without the photocatalyst–catalyst gives a small peak [14,15] when it is irradiated at 337 or 248 nm in aqueous or methanolic solutions, but this is only 1% of that obtained in the presence of the dithiolenic complex, and was disregarded.

Increase of the initial MV^{2+} concentration from 0.5 to 5 mM causes a small increase in the intensity of the maxima.

Table 1

The UV–Vis spectra of the dithiolenes complexes in acetone:water 70:30 mixed solvent. The active L → M absorptions for some complexes appear as shoulder and λ_{\max} was determined by taking the second derivative

Complex	L → M ^a	L → L	L → M
Ia	685 (18,500)		413 (10,250)
Ib	821 (22,600)		446 (15,100)
Ic	633 (14,100)		407 (8730)
Id	676 (18,800)		414 (11,700)
Ia	690 (8200)	585 (2600)	460 (5000)
Ib	720 (10,300)	574 (3000)	460 (10,000)
Ic	645 (7500)	560 (2500)	430 (6000)
Id	685 (9200)	580 (2700)	450 (6300)

^a λ_{\max} in nm (ϵ in $\text{dm}^3 \text{cm}^{-1} \text{mol}^{-1}$).

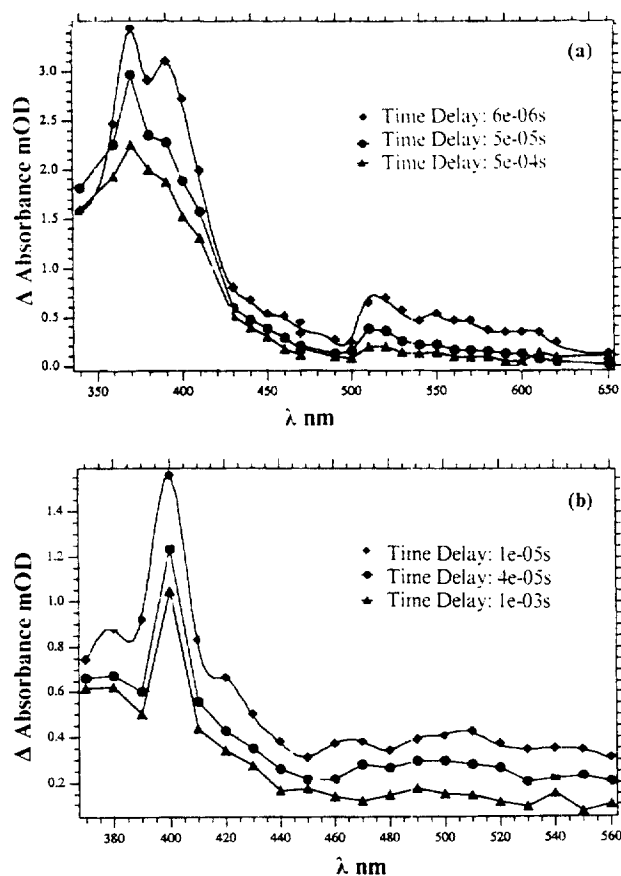


Fig. 3. Absorption resulting from the 355-nm laser flash photolysis of deaerated solutions containing 5×10^{-5} M of complex Ia in acetone:water (70:30) and (a) MV^{2+} 4.3×10^{-3} M, time delays: \blacklozenge 6×10^{-6} s, \bullet 5×10^{-5} s, \blacktriangle 5×10^{-4} s; (b) DP^{2+} 5×10^{-3} M, time delays: \blacklozenge 1×10^{-5} s, \bullet 4×10^{-5} s, \blacktriangle 1×10^{-3} s.

The absorptions observed here resemble those of the MV^{2+} in the mixed solvent reported in Ref. [16] (maxima at 395 and 605 nm), but they are not identical; they are shifted to shorter wavelengths (390 and 510 nm) presumably because of the presence of the photocatalyst–catalyst. There are other peaks too, in the visible, with intensities just above noise; they seem real but their assignment is not considered safe, at this stage. Thus, there seems to be at least two transients in the presence of MV^{2+} , neither of them identical to that

obtained without MV^{2+} ; the slower decay absorbing at 360 nm, the faster decay absorbing at 390 and 510 nm.

Excitation of complex Ia at 532 nm does not produce transients. Excitation at 420 nm still gives transients, but it was not investigated further. (See Section 4 for the corresponding electronic transitions).

Using DP^{2+} instead of MV^{2+} leads to analogous results. The peak at 400 nm and the associated smaller peak at 380 nm (Fig. 3b) corresponds to the 360 nm peak in Fig. 3a, and the peaks at 420 and 510 nm to the 390 and 510 nm peaks,

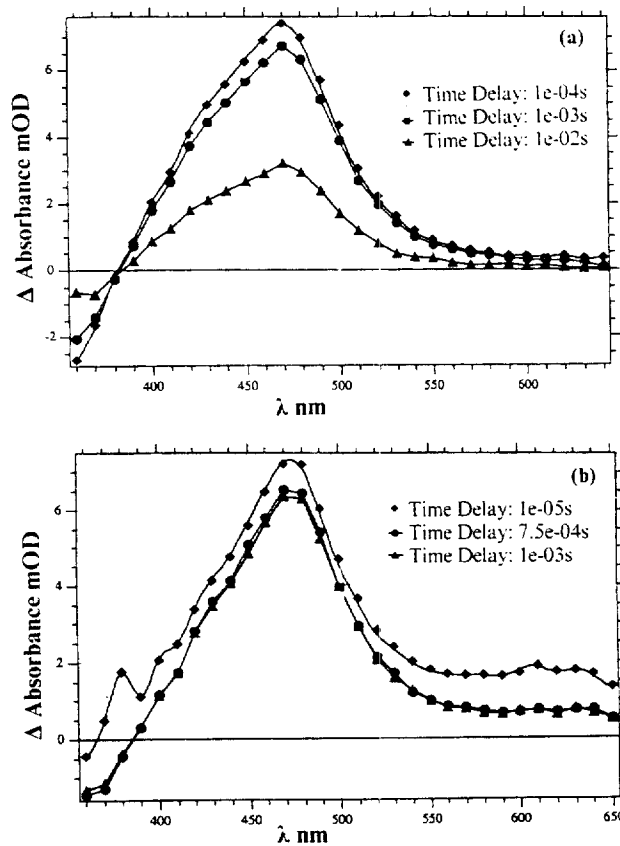


Fig. 4. Absorption resulting from the 355-nm laser flash photolysis of deaerated solutions containing 5×10^{-5} M of complex Ib in acetone:water (80:20) (a) MV^{2+} 0.5×10^{-3} M, time delays: \blacklozenge 1×10^{-4} s, \bullet 1×10^{-3} s, \blacktriangle 1×10^{-2} s; (b) MV^{2+} 1×10^{-3} M, time delays: \blacklozenge 1×10^{-5} s, \bullet 7.5×10^{-4} s, \blacktriangle 1×10^{-3} s.

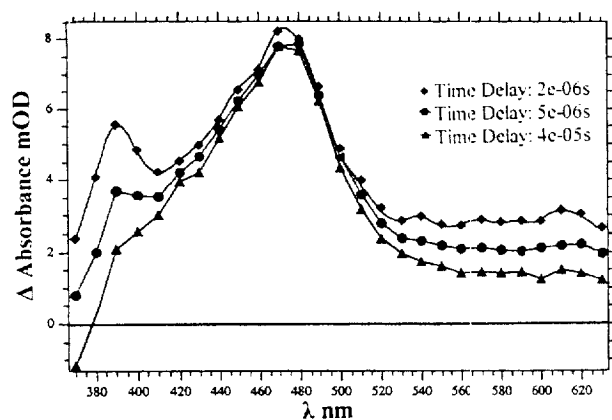


Fig. 5. Absorption resulting from the 355-nm laser flash photolysis of deaerated solutions containing 5×10^{-5} M of complex Ib in EtOH:acetone:water (10:70:20), time delays: $\blacklozenge 2 \times 10^{-6}$ s, $\bullet 5 \times 10^{-6}$ s, $\blacktriangle 4 \times 10^{-5}$ s.

respectively. There is again a number of smaller broad peaks in the 450–500 nm range [12,13].

The transient spectra of complex Ib in the presence of MV^{2+} in acetone:water 80:20 are given in Fig. 4. Again, there is a fast path involving interacting $MV^{\cdot-}$ free radical, at 390 nm, but its observation requires higher initial MV^{2+} concentrations. There is also a bleaching at short wavelengths. At short delays, the presence of the 390 nm peak

results in a decrease in the observed bleaching, which is maximized when this peak disappears. At longer times, the negative absorbance difference decreases and tends to zero; the time scale for this process is slow, of the order of 10 ms.

Excitation of Ib at 440 nm still shows transients, similar to those of Fig. 4, accompanied by bleaching at short wavelengths and the appearance of a longer lasting peak at 470 nm.

Previous experiments showed that addition of ethanol to the mixed solvent increases the yield, without destroying the PC-C [6]. In order to get more information about this effect, we repeated the flash photolysis experiments with complex Ib, in a three-component mixed solvent. The results are summarized in Fig. 5.

The results of the flash photolysis experiments for complexes Ic and Id in the presence of MV^{2+} are illustrated in Fig. 6. There seems to be no qualitative differences compared to the other complexes. Again, there is a faster decaying transient at ca. 400 nm for Ic (Fig. 6a) and 395 nm for Id (Fig. 6b), and a persistent broad (probably overlapping) absorption in the 420–540 nm range, and at 390 nm for complex Id.

In Fig. 6c, the initial solution of Id contained oxygen (partial deaeration), which is known to cause destruction of the complexes during illumination [4]. There seem again to be

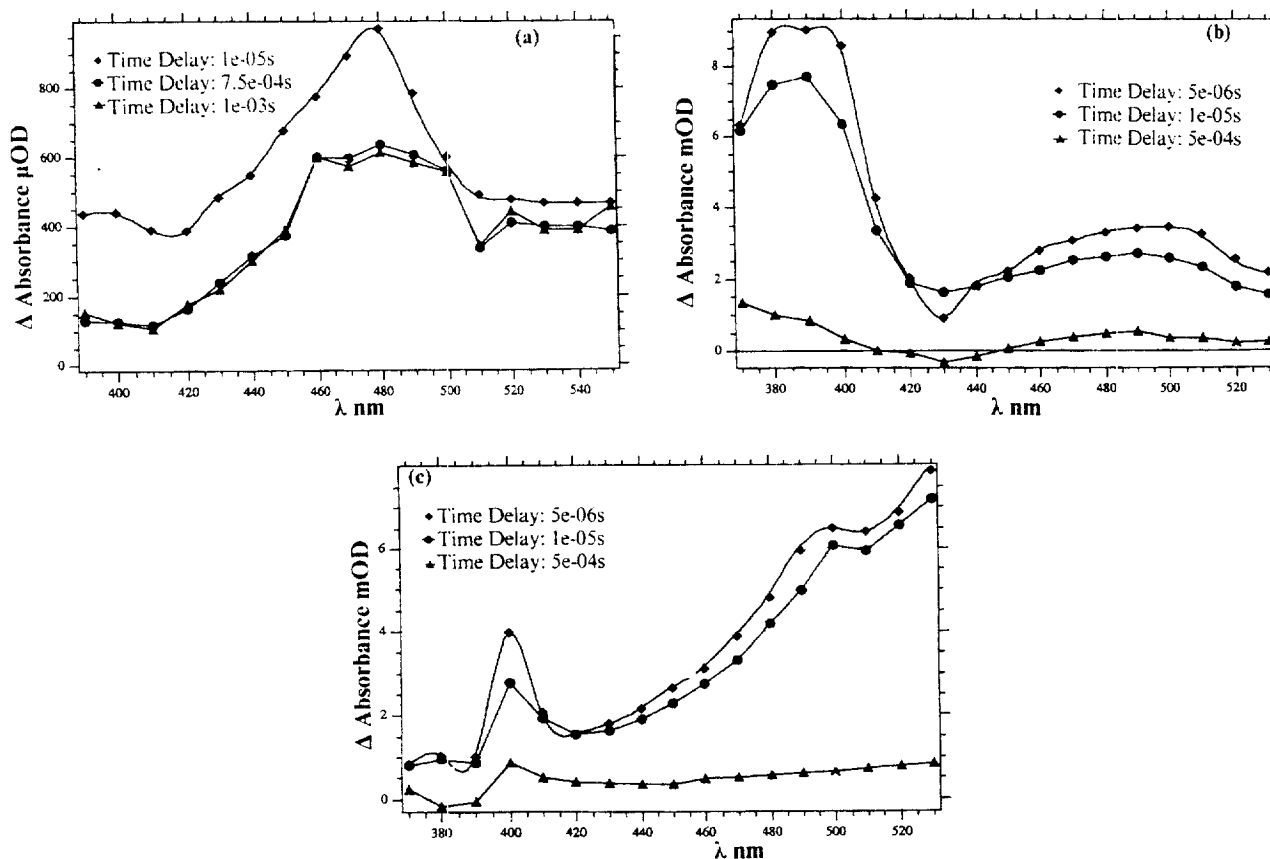


Fig. 6. Absorption resulting from the 355-nm laser flash photolysis of deaerated solutions containing MV^{2+} (5×10^{-3} M) in acetone:water (80:20) and (a) Ic 0.5×10^{-3} M, time delays: $\blacklozenge 1 \times 10^{-5}$ s, $\bullet 7.5 \times 10^{-4}$ s, $\blacktriangle 1 \times 10^{-3}$ s; (b) Id 1×10^{-3} M, time delays: $\blacklozenge 5 \times 10^{-6}$ s, $\bullet 1 \times 10^{-5}$ s, $\blacktriangle 5 \times 10^{-4}$ s; (c) Id 5×10^{-3} M not completely deaerated. Time delays: $\blacklozenge 5 \times 10^{-6}$ s, $\bullet 1 \times 10^{-5}$ s, $\blacktriangle 5 \times 10^{-4}$ s.

no significant qualitative differences, other than the small short wavelength bleaching at long times and the wavelength nonspecific steady increase at short times and long wavelengths.

4. Discussion

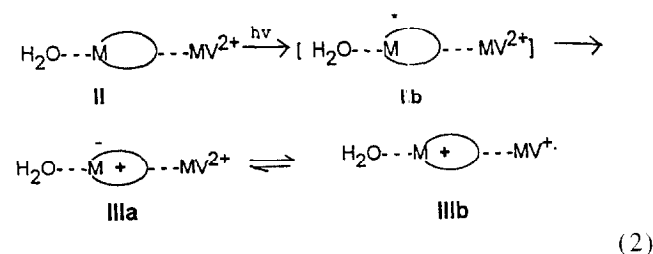
In view of the long build up and decay times, the transients observed in the presence or absence of MV^{2+} or DQ^{2+} cannot be assigned to a primary excited state of the dithiolene. It should also be recalled that there is no indication for a radiative excited state, since all attempts to detect light emission have failed [4,5].

In the continuous irradiation experiments [4], the formation of an intermediate complex was postulated, symbolised as $HO-C-MV^{2+}$ (C is the dithiolene), followed by the formation of an oxidized form, symbolised as $O-C$. The flash photolysis experiments seem to provide direct support for the formation of such species and clarify further their role.

In the presence of MV^{2+} , two transients are clearly observed, absorbing more than the highly absorbing original dithiolene. These transients can be distinguished from each other not only by their spectra but also by their decay times. Even though the kinetics are not simple first or second order, the delay times (Supplementary Figs. S1–S8) over which the peaks survive provide a semi-quantitative lifetime.

With complex Ib, there is also the bleaching at short wavelengths and short times, which can be attributed to ground state depletions. In this case, the short living transient absorbs less in the short wavelength range, but then when it is transformed into the second, longer living, intermediate the absorption tend to become more like that of the original PC–C. The time scale for this process is 10 ms, which is comparable to the lifetimes of the second transient.

It is proposed that the faster decaying transient, the spectrum of which resembles that of MV^{2+} , is the hydrogen generating species. At this stage, electron transfer from the excited PC–C to the acceptor has already occurred. Thus, the primary productive act can be formulated as follows:



where II represents a supramolecular complex formed in a pre-equilibrium between the photocatalyst–catalyst, water, and MV^{2+} . Evidence for this equilibrium has been reported previously [4,5]. The pre-equilibrium eliminates the need for diffusion-controlled or slower encounters, and can be

considered to involve formation of a special mini supramolecular system.

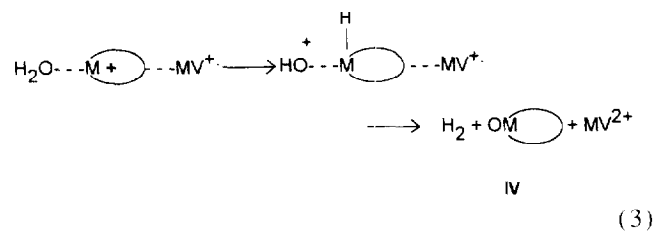
The effect of a mild donor like EtOH is to facilitate the accumulation of the bound to the PC–C, free radical $MV^{\bullet+}$ and consequently the reduction. Experimentally, we observe enhancement of the 390 peak (for the complex Ib), and bleaching at longer times.

Pairs of square planar anionic metal dithiolenes with MV^{2+} and other cationic bipyridines are strongly dissociated in DMSO and DMF solutions [17]. In the neutral-positive ion combination (II), the interaction and association of the partners is expected to be much weaker. Yet, it is sufficient for an effective electron transfer. The situation resembles that of the special pair (excited donor)–accessory bacteriochlorophyll (bridge), i.e., the interaction controlling the first event in bacterial photosynthesis [1–3]. It is also noted that the ion pair charge transfer peak in the dithiolene anion- MV^{2+} pairs appears at 773 nm in DMSO [17] and it is weak ($\epsilon = 40 \text{ M}^{-1} \text{ cm}^{-1}$). In our case, this peak is expected to be shifted to higher-energies, and be covered by the huge absorptions of the PC–C.

The excitation in Eq. (2) has been presented as a ligand-to-metal charge transfer. There seems to be no doubt about that anymore [18].

The separation of the positive charges in Eq. (2) is obviously more efficient than the usual inhibitive positive–negative ion-pair separation. The PC–C is neutral, the electron acceptor positively charged; after the transfer of the electron from the excited state to MV^{2+} , two single charged positive ions are formed. Hence, long range electrostatic attractions are not possible and there is no need to consider the electrostatic barrier due to the separation of opposite charges, as in organic photochemistry and in photosynthesis. The intrasupramolecular electron transfer from the donor excited state to the electron acceptor should probably take place within the nanosecond time scale or even faster. Such super fast electron transfer processes occur in photosynthesis between bulkier entities [1–3].

Fast proton transfer follows, leading to irreversible H_2 formation. The details of this step are not yet known. One possibility is the following intramolecular process:

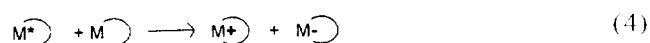


Intermediate IV has been postulated [4] to undergo further bimolecular reactions leading to O_2 formation and regeneration of the catalyst. On a shorter time scale, recombination of IV with reducing species does not seem to occur because of this fast irreversible formation of H_2 . The transient absorp-

tions at 360–380 nm (complex Ia), 475 nm (complex Ib), 480 nm (complex Ic) and at 500 nm (complex Id), as well as the bleaching in Figs. 4 and 5 seem to be related to species IV.

Several irreversible oxidations of dithiolenes and other sulphur compounds leading to oxygen-containing species have been reported [19–22], and there is a huge literature on molybdenum and tungsten oxotransferases and on the corresponding model systems [some recent reviews in Refs. [23–27]]. However, in view of the highly delocalized electron distribution of the complexes investigated here [18], one should be cautious in specifying the site of the oxygen atom attachment in intermediate IV.

Reaction (4) is probably also taking place:



both in the absence and in the presence of MV^{2+} . The long living transient (the positive hole) is also observed in the absence of MV^{2+} (Figs. 1 and 2), but also in the presence of MV^{2+} at short delay times, before the decomposition of the short living transient. Reaction (4) is essentially similar to reaction (2), with another acceptor molecule instead of MV^{2+} . In recently reported electrochemical data [11], evidence for positive ions was not included. However, more careful experiments show a positive ion at $E_{1/2} = 1.210$ V. So there is some direct evidence too for the postulated (Eq. (4)) positive ion formation here.

A mechanism consisting mainly of reactions (2)–(4) is not expected to give simple kinetics.

The broad peak in the absorption spectra of the ground state of the PC–C around 400 nm [16], believed to be the active one in water splitting, does not correspond to the HOMO–LUMO transition. In the neutral dithiolenes, it has been assigned [28] to two transitions $e' \rightarrow a_1$ and $a_2'' \rightarrow a_1$, both ending up in the metal-like LUMO a_1 , but originating in two ‘inside’ (below the HOMO) ligand centered orbitals. Within this context, it is interesting to note that certain transient spectra have unsymmetrical, non-Gaussian, peaks, (Figs. 1, 3 and 4). A possible explanation is that the holes staying behind, after the removal of the electron in the photochemical process, are of two kinds. It is not known if there is interconversion and/or differentiation in their chemical behavior, but it is noted that neutralization of the initially formed electron hole must necessarily take place by cascading or by jumping over the intervening energy levels.

The broadness of the peak at 400 (and elsewhere) is certainly partly also due to the fluxionality of the tris-dithiolenes and the presence of a mixture of *cis-trans* isomers [29]. The unsymmetrical nature of the ligands in the active PC–C is also expected to cause a further increase in the number of electronic levels involved in the transitions, by splitting the degenerate ones. Thus, we have a multiplicity of effective electronic transitions, and this must be related to the high observed yields [6].

5. Conclusions

The photochemical data reported in this paper show that the reduction and oxidation of water implied in reaction (1) are kinetically separated, and that there is no need for large space separation in space by membranes, vectorial or otherwise. The reduction, namely the transfer of the electron to water is much faster than the oxidation, that is the transfer to water of the hole. If this hole transfer is inhibited, the catalyst is subject to destruction, and the efficiency of water splitting is low.

The data are consistent with a mechanism involving transient formation of $MV^{\bullet+}$, and differentiates between ‘free’ (bulk) and ‘complexed’ $MV^{\bullet+}$. The former is associated with low yields and instability (especially in the presence of O_2), the latter to high yields.

The time scale of the events monitored here is much longer than the lifetime of an ordinary excited state. There is plenty of time for back reaction and deexcitation. Yet, these processes do not seem to compete effectively with electron transfer leading to water splitting. One reason may be that after the transfer, both the oxidized donor and the reduced acceptor are positively charged, and there is no coulombic barrier for their separation.

Finally, there is evidence that there are more than one effective excitations.

Acknowledgements

Authors would like to thank the graduate students D. Argyropoulos and E. Lyris for synthesizing some of the complexes.

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