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ELECTRON TRANSFER REACTIONS BETWEEN METHYL VIOLOGEN AND PORPHYRINS, BIS-PORPHYRINS, PHTHALOCYANINES, AND THEIR METAL DERIVATIVES *

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Summary

Anaerobic irradiation of several tetraphenylporphyrins, bis(tetraphenylporphyrins), phthalocyanines and their metal derivatives with visible light ($\lambda > 420$ nm) gave an electron transfer to the methyl-viologen cation. The reaction was studied in acetonitrile/2,6-lutidine (7/3) and in dimethyl sulfoxide.

The study of photoinduced electron-transfer reactions of porphyrins, phthalocyanines and their metallic derivatives is of interest for two main reasons. Firstly they can be regarded as models for the coordination centre of several metallobiomolecules [1,2] and secondly their optical spectra have strong bands between 400—700 nm, so that the molecules are easily excited by visible light and here can be used as photosensitizers in reactions leading to the storage of visible light energy [3—6].

We noticed during our previous study [7,8] that the compounds which do not sensitize the formation of $^1O_2$ do not cause any formation of $O_2^{\cdot-}$; and that the Zn and Pt phthalocyanines (ZnPc), (PtPc), and the Cu^{II}-tetraphenylporphyrin (Cu^{II}TPP), which were all able to induce the formation of $^1O_2$, did not cause any formation of $O_2^{\cdot-}$. We have shown that these compounds quench the $O_2^{\cdot-}$ formed by the photoinduced electron transfer of ZnTPP with O_2, and also the $O_2^{\cdot-}$ formed by a ground state chemical reaction, such as the decomposition of KO_2 in DMSO solution, which gives K^+ and $O_2^{\cdot-}$ only by a charge separation process. Thus we postulate that these compounds (ZnPc, PtPc and Cu^{II}TPP) react by transforming $O_2^{\cdot-}$ into O_2, as the superoxide dismutase (SOD) does

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[10—14] and not by quenching the electron transfer process:

$$P \xrightarrow{h\nu} {}^1P^* \rightarrow {}^3P^* \xrightarrow{O_2} P^+ + O_2^{\bar{\cdot}} \xrightarrow{SOD} O_2 + SOD^- \ldots$$

We have extended the study of these photochemical transfers by using other electron acceptors such as methyl viologen (MV^{2+}) [15,16] which in its reduced from ($MV^{+\cdot}$) reduces water to molecular hydrogen [17,19].

Our study was done in two different solvents: (i) a 7/3 acetonitrile/2,6-lutidine mixture, in which the lutidine provides the electron and is therefore able to reduce the oxidised photosensitizer P^+, and (ii) DMSO.

Reactions in 7/3 acetonitrile/2,6-lutidine

The photoinduced electron transfer reaction in a deoxygenated 7/3 mixture of acetonitrile/lutidine using the compounds (1—24) shown in Table 1, as donor and MV^{2+} as acceptor, is analogous to that observed with molecular oxygen [7] when the corresponding aerated solvent is used. This demonstrates that com-

TABLE 1

RELATIVE INTENSITY ($TPPH_2$ = 1) OF ESR SPECTRUM OF THE RADICAL CATION $MV^{+\cdot}$ IN IRRADIATED ANAEROBIC SOLUTIONS CONTAINING PORPHYRINS, BIS-PORPHYRINS, AND PHTHALOCYANINES 10^{-4} M/l AND MV^{2+} = 10^{-3} M/l (the irradiation time is 15 min with the same lamp)

Compounds	Relative intensity in acetonitrile/ 2,6-lutidine (7/3)	Relative intensity in DMSO
1 $TPPH_2$	1.0 (strong)	1.0 (strong)
2 H_2Pc	3.0 (very strong) [a]	1.0 (strong)
3 H_2TPP-*o*-C_3-*o*-$TPPH_2$	1.3 (strong)	2.0 (very strong)
4 H_2TPP-*p*-C_3-*p*-$TPPH_2$	0.8 (moderate)	2.0 (very strong)
5 CoTPP	0.0	0.0
6 CoPc4Tc	0.0	0.0
7 CoPc4T-t-Bu	0.0	0.0
8 CoTPP-*p*-C_3-*o*-$TPPH_2$	0.0	1.0 (strong)
9 ZnTPP	0.4 (weak)	1.5 (strong)
10 ZnTPP-*o*-C_3-*o*-TPPZn	0.2 (very weak)	0.0
11 ZnTPP-*p*-C_4-*p*-TPPZn	0.3 (weak)	3.4 (very strong) [b]
12 ZnPc4Tc	0.0	0.0
13 ZnPc4T-Aza	0.01 (trace)	0.0
14 CuTPP	0.0	3.0 (very strong)
15 CuTPP-*o*-C_3-*o*-TPPCu	0.4 (weak)	1.0 (strong)
16 CuTPP-*p*-C_4-*p*-TPPCu	0.01 (trace)	2.4 (very strong)
17 CuPc4T-t-Bu	0.01 (trace)	0.0
18 PtTPP	1.2 (strong)	1.5 (strong)
19 PtTPP-*o*-C_3-*o*-TPPPt	1.5 (strong)	0.0
20 PtPc4Tc	0.0	0.0
21 NiTPP	0.0	0.0
22 NiPc4T-Aza	0.0	0.0
23 MgTPP	0.0	0.0
24 MgPc4T-t-Bu	0.0	0.0

[a, b] Results obtained with a suspension, for a irradiation time 3 h.

pounds (1—4, 9, 10, 15—19) can induce the formation of $^1O_2$ and $O_2^{\cdot-}$ and can also reduce the MV^{2+} to $MV^{+\cdot}$, but compounds **12**, **14** or **20**, which cause decomposition of $O_2^{\cdot-}$, cannot reduced MV^{2+} to $MV^{+\cdot}$. In a study involving samples containing $MV^{+\cdot}$ freshly prepared in the tube, when one of the compounds (**12**, **14** or **20**) was added, either as a solid or dissolved in a suitable solvent, the ESR spectrum of $MV^{+\cdot}$ disappeared. (This was not due to the presence of oxygen in the tube since the solutions and the solid were carefully deoxygenated.) When Cu^{II}TPP (**14**) was added we observed a very small ESR spectrum of Cu^{II} accompanying the oxidation of $MV^{+\cdot}$ to MV^{2+}; this signal was due to a small proportion of Cu^{II} which had not been reduced.

$$Cu^{II}TPP\ MV^{+\cdot} \rightarrow Cu^{I}TPP + MV^{2+}$$

Cobalt (**5—8**), nickel (**21**, **22**), magnesium (**23**, **24**) complexes and ZnPc4Tc (**12**), CuTPP (**14**) and PtPc4Tc (**20**) undergo no electron transfer reaction with MV^{2+}; while zinc and copper derivatives (**9—11**, **15—17**) give the reactions to a very small extent but the free base tetraphenylporphyrin (**1**), the dimers (**3**, **4**), the phthalocyanine (**2**) and the platinum derivatives (**18**, **19**) give a strong or very strong ESR signal from $MV^{+\cdot}$.

Study in DMSO

The use of a basic solvent such as DMSO, which can coordinate to the metal can considerably modify the behaviour of the photosensitizer. Indeed, the anaerobic irradiation by visible light of copper porphyrins (**14**, **15**, **16**) in DMSO in the presence of MV^{2+} gave strong ESR signal of $MV^{+\cdot}$. Likewise, CoTPP-*p*-$(CH_2)_3$-*o*-TPPH$_2$ (**8**) which cannot form $^1O_2$ in toluene or $O_2^{\cdot-}$ and $MV^{+\cdot}$ in the acetonitrile/lutidine mixture, can reduce MV^{2+} photochemically in DMSO solution to $MV^{+\cdot}$ with approximately the same activity of TPPH$_2$ (**1**). However Zn and Pt porphyrins (**10**, **19**), which are very much more reactive for the formation of $^1O_2$ in toluene solution and the formation of $O_2^{\cdot-}$ and $MV^{+\cdot}$ in acetonitrile/lutidine, do not undergo an electron transfer with MV^{2+} in DMSO. In contrast, the corresponding monoporphyrin (**9**, **18**) does undergo such transfer. As in acetonitrile/2,6-lutidine, compounds **1—4** give a strong to very strong ESR signal for $MV^{+\cdot}$, while in DMSO **5—7**, **12**, **13**, **17** and **19—24** give no electron transfer reactions with MV^{2+}.

Discussion

On the basis of the results in the acetonitrile/2,6-lutidine mixture we can envisage the following possibilities:

1. There is an association between one excited molecule of the photosentizer and one molecule of MV^{2+} in the ground state to form an excimer:

$$P^0 \xrightarrow{h\nu} P^*$$

$$P^* + MV^{2+} \rightarrow [P^* \cdots MV^{2+}] \rightarrow [PMV^{2+}]^* \rightarrow P^0 + MV^{2+} + \Delta E$$

2. The excited state of the compounds studied (**12**, **14**, **20**) takes part in an

electron transfer to MV^{2+}, forming $MV^{+\cdot}$, which is decomposed by the photosensitizer in its ground state.

$$Cu^{II}TPP \xrightarrow{h\nu} [Cu^{II}TPP]^* \xrightarrow{MV^{2+}} [Cu^{II}TPP, MV^{2+}]^* \rightarrow Cu^{II}TPP^+ + MV^{+\cdot}$$

$$Cu^{II}TPP \text{ (ground state)} + MV^{+\cdot} \rightarrow Cu^{I}TPP + MV^{2+}$$

In this case the continuous irradiation of a mixture of $Cu^{II}TPP$ and MV^{2+} would lead to a decrease in the ESR signal of the $Cu^{II}TPP$, but in fact the ESR signal of the $Cu^{II}TPP$ remains constant through the irradiation. Since $Cu^{II}TPP$ is able to decompose $MV^{+\cdot}$ this reaction scheme can thus be discarded.

3. Either the excited state energy of the sensitizers **12**, **14**, **20** is to low to reduce MV^{2+} or their lifetimes are too short.

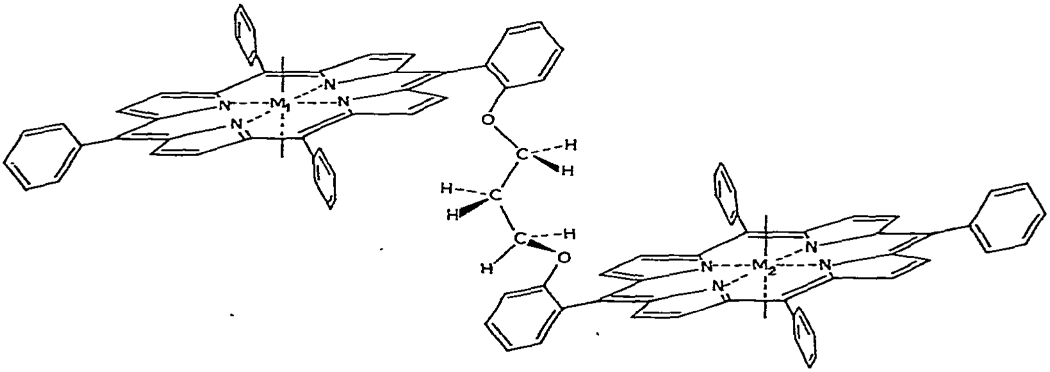
From the available results it is impossible to choose between hypothesis 1 or 3.

While the Zn and Pt phthalocyanines and their oxidation products cannot be detected by ESR, it is reasonable to assume that either the excited state of these compounds has an energy level or a lifetime too small to reduce the MV^{2+} or that the excimer formed after the irradiation dissociates again to MV^{2+} and the original photosensitizer (which returns to its ground state).

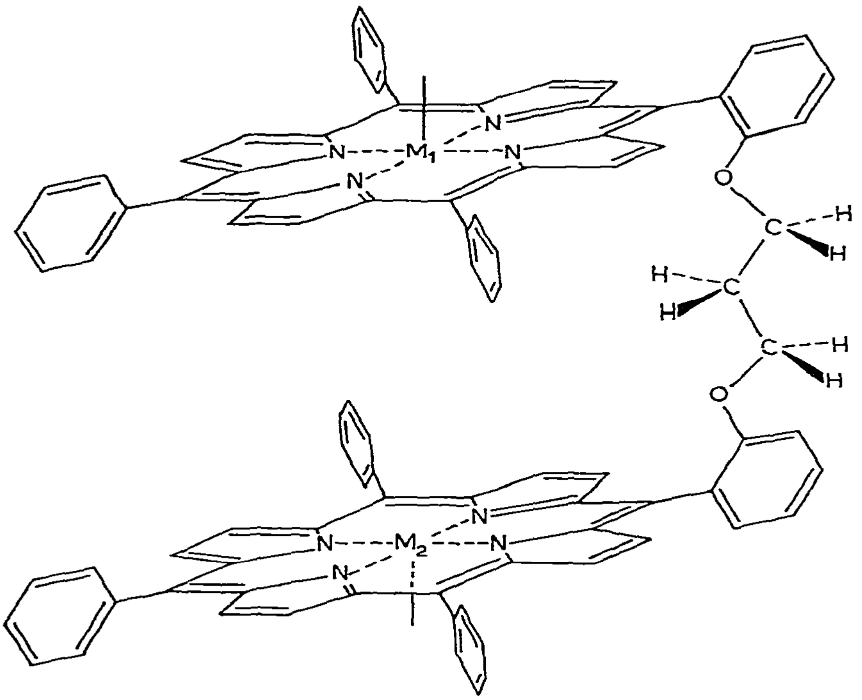
When the reaction is performed in DMSO, the porphyrin ring of **8** containing the cobalt atom is complexed, whereas the $TPPH_2$ unit of the same molecule is left unchanged. Thus **8** exhibits identical activity to the free base monoporphyrin (**1**).

In the case of zinc and platinum bis-porphyrins **10** and **19** the DMSO complexes on each outer face of the molecule, and being a σ donor [20], augments the electron density at the central metal atom and thereby increases the metal—metal interactions. This prevents any electron transfer. In contrast, ZnTPP-*p*-C_4-*p*-ZnTPP (**11**) and ZnTPP (**9**) act as expected because **11** and **9** can be solvated on each porphyrin moiety.

Two conformations are possible for the bis-porphyrins **10**, **19**: conformation A (twisted) and conformation B (eclipsed). The distance between the two macrocycles in configuration B measured on the SASM [21] molecular model is between 6 and 7 Å. The DMSO molecule has a diameter of 6.5 Å. Thus in the case of the eclipsed conformation B it is impossible for the DMSO to complex with both metal atoms inside the cavity between the two macrocycles.



CONFORMATION A (TWISTED)



CONFORMATION B (ECLIPSED)

In the case of the twisted conformation (A), the complexation of the metallic atoms by two molecules of DMSO will cause the bis-porphyrins to have the same reactivity in respect of complexation and photochemical activity as two isolated metalloporphyrins (MTPP). Therefore we conclude by comparison with the behaviour of the analogous monoporphyrins, that the photochemical behaviour of the bis-porphyrins can be explained only by the complexation of one molecule of DMSO at each outer face of the molecules in conformation B.

In the acetonotrile/lutidine mixture, the excited state of Cu^{II}TPP-*o*-C$_3$-*o*-TPPCu^{II} (15) can reduce MV^{2+} but, surprisingly the excited state of Cu^{II}TPP (14) cannot. The energy level of the excited state of 15 (which is solvated only on each outer face in the eclipsed form B) is high enough to reduce MN^{2+} ($E_{1/2}$ -0.44 V), but too low to reduce the oxygen molecule ($E_{1/2}$ -0.75 V) [17], while the Cu^{II}TPP (14) (solvated on one side of the porphyrin plane) has an excited state energy level too low to reduce either MV^{2+} or O$_2$.

In conclusion, we have shown that the photoinduced reduction of MV^{2+} by porphyrins and phthalocyanines depends strongly on the nature of the solvent in which the reaction is conducted. Changing the solvent can in certain cases completely invert the photochemical reactivity of the photosensitisers. This can be correlated to the recent observations made by Tanno and colleagues [22], who have demonstrated the marked effect of the presence of a little water on the photoreduction of MV^{2+} by phthalocyanines.

Experimental

The porphyrins, phthalocyanines, bis-porphyrins and their metal derivatives 1—24 were prepared as previously described [7,8,20]. Spectrograde acetonitrile was distilled in a closed system over anhydrous P_2O_5 before use; DMSO spectrograde (Merck) was used as received. The 2,6 lutidine was purified by distillation from potassium hydroxide pellets. The methyl viologen (Sigma) was used as the PF_6 salt, which made by reaction with NH_4PF_6 and crystallisation from water.

The solutions (at room temperature, 20°C) containing porphyrins, bis-porphyrins and phtalocyanines or their metallic derivatives, 10^{-4} *M*, and MV^{2+}, 10^{-3} *M*, were placed in a test tube in diffuse room light and degassed by bubbling with argon for 10—15 min. The solutions were then transferred to a 0.1 mm quartz ESR flat microcell B-ER 400X-F2T and again deoxygenated with a stream of argon introduced through a microcapillary tube for 5—10 mn. The cell was then inplaced in the ESR cavity ER 4102 of a Bruker ER 100D spectrometer. The samples were irradiated in the cavity with a Hanovia 977B0090-1000W mercury-Xenon arc lamp in a Model LH151H Schoeffel lamp housing. The light was focused through quartz lenses and filtered through a 15 cm flowing water filter and a Corning 3-73 glass filter.

The samples were irradiated for 15 min inside the ESR cavity. The ESR spectra were recorded after 5, 10 and 15 min irradiation. The intensity measurements were made after the 15 min irradiation. For H_2Pc 2, which is not very soluble in the acetonitrile/2,6 lutidine mixture, the irradiation time was three hours. All the experiments were carried out under the same conditions: microwave power 6dB, modulation field 0.125G, time constant 0.5s field range 100G. Scaning time 500s, radiofreqeuncy 9445 MHz.

The intensities of the ESR spectra of MV^+ radical cation obtained with the various compounds were compared with that of the strongest line of the $MV^{+\cdot}$ radical cation obtained for $TPPH_2$ 1, which is linearly related to the area of the spectrum and directly proportional to the $MV^{+\cdot}$ concentration.

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