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Oxidation of Metal Tetraphenylporphyrins

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Absorption spectra are reported for a series of metalloporphyrin π-radical cations produced by chemical oxidation in CH_2Cl_2. Where the parent metalloporphyrin is diamagnetic, the absorption spectral features of the π-radical cations are similar and there is a good correlation between the energies of the first spin-allowed transitions for the π-radical cation and for the parent porphyrin. In general, this is not the case for π-radical cations derived from paramagnetic metalloporphyrins where the lowest energy spin-allowed transition occurs at higher wavelength than anticipated from the studies with diamagnetic metalloporphyrins.

Introduction

Metalloporphyrins figure prominently in natural processes, such as photosynthesis, where they occupy key roles in electron transfer pathways and, currently, there is intense interest in the use of metalloporphyrins in simple model systems aimed at mimicking the more complex natural processes. One of the major reasons why metalloporphyrins are so popular in electron transfer schemes concerns their ability to undergo well-defined reduction and oxidation steps and the redox potentials for these couples are markedly dependent upon the type of porphyrin used and upon the nature of the central metal ion [1, 2]. Since there is an extremely wide range of available metalloporphyrins, it follows that it should be possible to select a compound that possesses the exact redox potential required for a particular purpose and, within certain limits, this situation can be realised in practice.

As regards oxidation of a metalloporphyrin, the removal of one electron can result in formation of a positive hole centred either on the porphyrin ring or on the metal ion [3]. The former case leads to formation of a π-radical cation whilst the latter case results in an increase in the formal oxidation state of the central metal ion. Both types of process have been investigated in detail and the literature contains a wealth of information about the properties of oxidised metalloporphyrins. However, most studies have been restricted to electrochemical oxidation techniques [1, 2], little is known about chemical oxidations [4], and the range of metalloporphyrins studied is not large. In this paper, we report on the oxidation of a series of metal tetraphenylporphyrins using chemical oxidants and, in particular, we have attempted to characterise the absorption spectra of the one electron oxidation products. It is hoped that such a study will assist the development of theories capable of accounting for the absorption spectral features of the π-radical cations which, hitherto, have not been well explained.

Experimental

Materials

The metalloporphyrins were prepared and purified as described in previous papers [5, 6] and all compounds gave satisfactory elemental analyses. Dichloromethane (BDH) was spectroscopic grade, refluxed over P_2O_5 and stored over molecular sieves. Iron(III) perchlorate (BDH) and bromine (BDH) were used as received whilst phenoxathiin hexachloroantimonate was prepared by the method of Reed *et al.* [7].

Methods

Absorption spectra were recorded with a Perkin Elmer 454 spectrophotometer and epr spectra were recorded with a Decca X3. Magnetic moments were measured by the Evans method [8] using concentric tubes and with benzene as reference material. All kinetic measurements were made with an Applied Photophysics Ltd. stopped-flow instrument (dead time 2 ms) and were recorded under pseudofirst order conditions. Electrochemical oxidations were made by conventional methods [1, 2] using a saturated calomel electrode as standard.

For the chemical oxidation studies, a small aliquot (~10 μl) of a standard solution of the oxidant in

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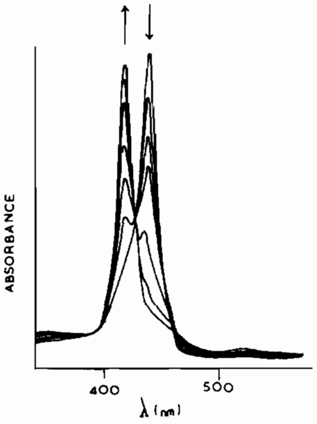

Fig. 1. Absorption spectral profile showing the one-electron oxidation of CdTPP with phenoxathiin hexachloroantimonate in CH_2Cl_2.

TABLE I. Oxidation of Metalloporphyrins in CH_2Cl_2 Solution.

Compound	E^0 (V *vs.* SCE)	μ_{eff} (BM)	k (M^{-1} s^{-1})
H_2TPP	0.95	–	1200
MgTPP	0.54	–	9000
ZnTPP	0.77	–	9800
CdTPP	0.63	–	1850
HgTPP	~0.55	–	1450
PdTPP	1.02	–	310
RuTPP	0.82	–	1000
Co^{III}TPP	1.06	–	910
CuTPP	0.90	2.9	610
Fe^{III}TPP	1.13	5.1	800
Mn^{III}TPP	1.10	3.9	1300
Cr^{III}TPP	0.79	2.8	31

CH_2Cl_2 was added, via a microsyringe, to a solution of the metalloporphyrin in CH_2Cl_2 contained within a spectrophotometric cell. The course of reaction was followed by absorption spectroscopy. For kinetic measurements, the stopped-flow was used to follow the absorption changes at the main B band (~420 nm) caused by rapid mixing of the metalloporphyrin solution with a dilute solution of Br_2 in CH_2Cl_2. Several different concentrations of Br_2 were employed so that the pseudofirst order rate constants obtained from the oscilloscope traces could be used to derive the bimolecular rate constants for oxidation of the metalloporphyrins with Br_2.

Results and Discussion

Phenoxathiin hexachloroantimonate dissolves fairly readily in CH_2Cl_2 at room temperature and the resultant solution of the free radical is stable over several hours standing in the dark. The solution is blue and the radical cation is a powerful one-electron oxidant, being reduced readily to the colourless phenoxathiin. These properties make the radical cation a useful oxidant for use with the metalloporphyrins, especially since the reduced form does not contribute to the final absorption spectrum in the visible region so that absorption spectroscopy can be used to follow the course of reaction.

Addition of phenoxathiin hexachloroantimonate to a CH_2Cl_2 solution of the metalloporphyrins caused changes in the absorption spectrum and, in most cases, a clear set of isosbestic points were observed. This is exemplified in Fig. 1 where the oxidation of cadmium tetraphenylporphine (CdTPP) is shown. Similar oxidations with H_2TPP, ZnTPP and MgTPP did not give clear isosbestic points. With the clean reactions, only one oxidation product of the metalloporphyrin was found at low concentrations of oxidant (~3 fold excess) and, from stoichiometry studies, the reaction corresponded to a one-electron process. Thus, the oxidation product may be either a porphyrin π-radical cation or a metalloporphyrin with the metal ion in a higher formal oxidation state. Identical absorption spectral changes were observed when iron(III) perchlorate or Br_2 were used as oxidant and, with the exception of Mn^{III}TPP and Fe^{III}TPP, addition of a large excess of oxidant caused further oxidation.

For H_2TPP, ZnTPP and MgTPP, oxidation with phenoxathiin hexachloroantimonate, iron (III) or Br_2 was not clean and clear isosbestic points were observed only for relatively low percentage conversions. In all cases, above about 30% conversion further oxidation became important and porphyrin dications [9] and isoporphyrins [10] were formed. The metal-free porphyrin was particularly difficult to keep at the one-electron step and, by chemical oxidation methods, we were unable to characterise the absorption spectrum of the one-electron oxidation product.

There have been many studies concerned with the electrochemical oxidation of metalloporphyrins in CH_2Cl_2 solution and the redox potentials (E^0) of most metal TPP's are well documented (Table I). Using controlled potential electrolysis, it was possible to generate identical absorption spectral changes to those produced by chemical oxidation of the metalloporphyrin and for ZnTPP and MgTPP it was possible to characterise the absorption spectrum of the one-electron oxidation product. However, even by careful electrolysis we were unable to prevent further oxidation occurring with H_2TPP.

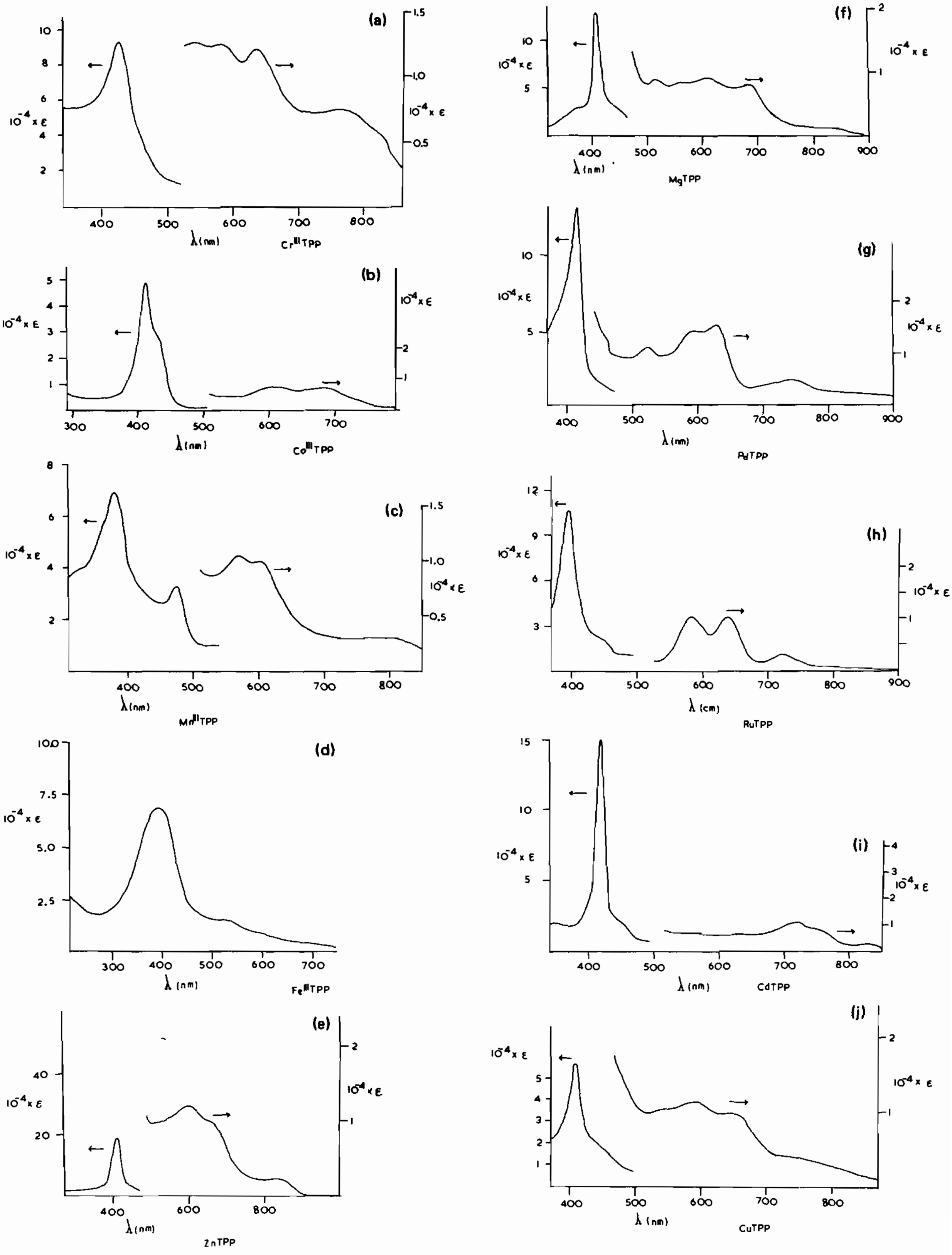

Fig. 2. Absorption spectra of the metalloporphyrin π-radical cations formed by oxidation with phenoxathiin hexachloroantimonate in CH_2Cl_2 (all extinction coefficients are in $l\ mol^{-1}\ cm^{-1}$); (a) $Cr^{III}TPP$; (b) $Co^{III}TPP$; (c) $Mn^{III}TPP$; (d) $Fe^{III}TPP$; (e) ZnTPP; (f) MgTPP; (g) PdTPP; (h) RuTPP; (i) CdTPP; (j) CuTPP.

The observed absorption spectra for the one-electron oxidation products are given in Fig. 2. By comparison with the literature [11–15], it was possible to assign the oxidation products for ZnTPP, MgTPP and CuTPP as metalloporphyrin π-radical cations and, for ZnTPP and MgTPP, epr measurements confirmed this assignment [16]. The absorption spectra of these three π-radical cations are very similar and consist of a strong band at about 410 nm, slightly to the blue of the main B band in the parent metalloporphyrin, and a series of at least three transitions in the near IR region, to the red of the Q bands in the metalloporphyrin. The molar extinction coefficients (ϵ) found for the major bands are also quite similar and, on this basis, it seems likely that the first oxidation product observed for CdTPP, PdTPP, HgTPP, RuTPP and $\mathrm{Co^{III}TPP}$ can be assigned as π-radical cations. Certainly, the observed epr spectra support this assignment.

Reed *et al.* [7] have carried out a detailed investigation of the reaction between $\mathrm{Fe^{III}TPP}$ and phenoxathiin hexachloroantimonate and all available evidence supports assignment of the reaction product as $\mathrm{Fe^{III}TPP^{+\cdot}}$. Our results are also in agreement with this assignment. The reactions of $\mathrm{Fe^{III}}$ and $\mathrm{Mn^{III}}$ porphyrins have much in common, suggesting that the one-electron oxidation of $\mathrm{Mn^{III}TPP}$ in CH_2Cl_2 solution should result in formation of $\mathrm{Mn^{III}TPP^{+\cdot}}$ [17]. Although no epr signal could be detected for either $\mathrm{Mn^{III}TPP}$ or $\mathrm{Fe^{III}TPP}$ oxidation products, the measured magnetic moments (Table I) are consistent with the products being π-radical cations.

Oxidation of $\mathrm{Cr^{III}TPP}$ with chemical oxidants results in formation of a species whose absorption spectrum shows a broad band centred at 424 nm, slightly to the blue of the B band in the parent $\mathrm{Cr^{III}}$-TPP, and weak, poorly-defined bands stretching across the visible and into the near IR region. The spectrum is similar to that found for $\mathrm{Fe^{III}TPP^{+\cdot}}$ but the measured magnetic moment is consistent with the product being either $\mathrm{Cr^{III}TPP^{+\cdot}}$ or $\mathrm{Cr^{IV}TPP}$. No epr signal was detected for the product and, overall, we favour assignment as $\mathrm{Cr^{III}TPP^{+\cdot}}$ although this is by no means conclusive.

The absorption and epr [16] spectra of the π-radical cations formed from diamagnetic metalloporphyrins are remarkably similar and the absorption spectra, in particular, are highly characteristic. These spectra consist of three important regions; a very intense B band at about 400–420 nm (log $\epsilon \sim 5$), a series of quite strong Q bands stretching across the visible region (log $\epsilon \sim 4$) and a weak, structureless band in the near IR (log $\epsilon \sim 3$). The weak near IR band is most probably a spin-forbidden transition whilst the energy of the first spin-allowed transition appears to correlate with the energy of the Q(0,0) transition in the parent metalloporphyrin, as shown in Fig. 3. This finding is useful in that it facilitates prediction of the spectral features of π-radical cations formed from diamagnetic metalloporphyrins and it may be used to clarify a tentative assignment where epr data are unavailable.

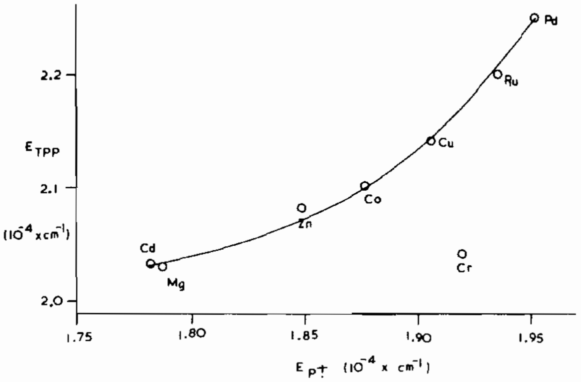

Fig. 3. Relationship between the energies of the first spin-allowed transition for the metal TPP (E_{TPP}) and for the π-radical cation (E_{P^+}).

The π-radical cations formed from paramagnetic metalloporphyrins ($\mathrm{Cu^{II}}$, $\mathrm{Mn^{III}}$, $\mathrm{Fe^{III}}$ and $\mathrm{Cr^{III}}$) do not exhibit epr spectra, presumably due to coupling interactions between the two paramagnetic centres. However, the absorption spectra of these π-radical cations are similar to those characterised for the π-radical cations derived from diamagnetic metalloporphyrins except that the bands, especially the main B band, seem to be somewhat broader and less intense. Interestingly, the B band observed for $\mathrm{Mn^{III}TPP^{+\cdot}}$ is split, just as it is in the parent $\mathrm{Mn^{III}}$-TPP [18]. With the exception of $\mathrm{CuTPP^{+\cdot}}$, the π-radical cations of these paramagnetic metalloporphyrins ($\mathrm{Mn^{III}}$, $\mathrm{Fe^{III}}$ and $\mathrm{Cr^{III}}$) do not form part of the smooth curve found in Fig. 3 and, instead, the lowest energy spin-allowed transitions appear at much higher energy than anticipated from the Figure. This must be a consequence of coupling between the two centres and it makes characterisation of such π-radical cations considerably more difficult than for the corresponding species derived from diamagnetic metalloporphyrins.

Some attempts were made to measure the rate of oxidation of the metalloporphyrins in CH_2Cl_2 solution using Br_2 as oxidant but the results were not very encouraging. When recorded under pseudo-first order conditions, the observed rate constant for bleaching of the porphyrin B band (~420 nm) followed first order kinetics for about two half-lifes, after which the kinetics became complex. The reproducibility of these observed rate constants was no better than ±30% and when more than a modest excess (~5 fold) of oxidant was used, the one-electron oxidation product was oxidised rapidly by the excess oxidant. Since it was necessary to use such an excess of oxidant in order to obtain pseudofirst order conditions, further oxidation steps must be taken into account so that the overall reaction scheme should be written;

$$\begin{aligned}
&\mathrm{MTPP} + \mathrm{Br_2} && \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{MTPP}^{+\bullet} + \mathrm{Br}^- + \mathrm{Br}^\bullet \\
&\mathrm{MTPP} + \mathrm{Br}^\bullet && \xrightarrow{k_2} \mathrm{MTPP}^{+\bullet} + \mathrm{Br}^- \\
&\mathrm{MTPP}^{+\bullet} + \mathrm{Br_2} && \xrightarrow{k_3} \mathrm{MTPP}^{2+} + \mathrm{Br}^- + \mathrm{Br}^\bullet \\
&\mathrm{MTPP}^{+\bullet} + \mathrm{Br}^\bullet && \xrightarrow{k_4} \mathrm{MTPP}^{2+} + \mathrm{Br}^- \\
&2\mathrm{Br}^\bullet && \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \mathrm{Br_2} \\
&2\mathrm{MTPP}^{+\bullet} && \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} \mathrm{MTPP} + \mathrm{MTPP}^{2+}
\end{aligned}$$

and, if steps 5 and 6 can be neglected, the observed rate constant (k) can be expressed in the form:

$$k = \left(\frac{k_1k_4}{k_{-1} + k_4}\right)\left[1 + \left(\frac{k_2k_3}{k_1k_6}\right)^{1/2}\left[1 + \frac{k_{-1}}{k_4}\right]^{1/2}\right]$$

The rate constants (k) observed under the above conditions are collected in Table I and it can be seen that, overall, the oxidation of a metal tetraphenylporphyrin by $\mathrm{Br_2}$ occurs rapidly. However, since the importance of further oxidation processes varies for the different metalloporphyrins (note, $\mathrm{Mn^{III}}$TPP and $\mathrm{Fe^{III}}$TPP do not undergo the second oxidation steps), it is difficult to correlate these rate constants with thermodynamic properties.

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