

The Oxidation of Oxomolybdenum Phthalocyanine

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Abstract

Chemical oxidation of the dichloromethane solutions of oxomolybdenum phthalocyanine (Mo(IV)OPc), using dilute solutions of bromine in dichloromethane or using ferric chloride results in the oxidation at the central metal ion, giving a Mo(V)OPc complex. Chemical oxidation is reversible in both the bromine and ferric chloride oxidized species. Oxidation of MoOPc is coupled to a reversible coordination of axial ligands to the oxidized species, with the possible formation of a six coordinate complex. Spectral data also reveal that the oxygen atom remains coordinated to the oxidized complex.

Introduction

The detailed nature of oxygen binding to transition metal complexes has been a subject of increasing interest because it represents a basic step in the understanding of the function of oxygen carrying metalloproteins in biological systems [1–3]. These studies have concentrated on the metalloporphyrins because of their presence in a variety of biological systems. Phthalocyanines have a similar structure to the porphyrins and provide a good model for the processes that occur in biological systems, but very few oxometallophthalocyanine complexes have been characterized [4–6].

An understanding of the nature of the redox processes occurring in phthalocyanines is essential for the use of these complexes as models in biological systems. The redox processes in phthalocyanines may occur at either the central metal atom or at the phthalocyanine ligand. Studies on the nature of the oxidation products of the phthalocyanine complexes in solution are limited to a few first row transition metal complexes [7–12], ruthenium phthalocyanine [13, 14] and magnesium phthalocyanine [15]; there is a need to extend this study to a wider range of phthalocyanine complexes.

The oxidation products of molybdenum phthalocyanine complexes have not yet been characterized. In particular, it would be of interest to determine

the effects of oxidation on the molybdenum–oxygen bond in oxomolybdenum phthalocyanine (Mo(IV)OPc) complexes. The purpose of this work is to identify the oxidation products obtained when solutions of MoOPc in dichloromethane are oxidized by bromine or ferric chloride. The oxidation products are characterized by electronic and infrared spectroscopies.

Experimental

Materials and Methods

Oxomolybdenum phthalocyanine was prepared, in air, using published methods [5].

Dichloromethane was purified, prior to each use, according to published procedures [7, 16]. Ferric chloride (BDH) and sodium borohydride (E. Merck) were used without further purification.

Spectroscopic Measurements

Absorption spectra of the solutions were recorded on the Shimadzu UV 210 double beam spectrophotometer. The infrared spectra (600 to 4000 cm^{-1}) of the neutral and oxidized oxomolybdenum phthalocyanine were recorded as Nujol mulls using the PYE UNICAM SP3-300 Infrared spectrophotometer and KBr disks. The oxidized species used for recording the infrared spectra, were prepared by exposing a finely ground sample of the Mo(IV)OPc complex to bromine fumes. The completeness of oxidation was tested by measuring electronic spectra of the oxidized species in dichloromethane.

Results and Discussions

Phthalocyanines have low solubilities in solvents that are suitable for the redox studies of these complexes. It has however been shown that axial ligand coordination to the central metal atom of metallophthalocyanine complexes increases the solubilities considerably [14, 15]. MoOPc was found to be slightly soluble in dichloromethane. It has also been reported that the MoOPc complex is slightly soluble in acetone [5], a solvent in which most phthalocyanine complexes are insoluble. This slight

increase in solubility of MoOPc is attributed to axial ligation of the oxygen atom. Attempts to recrystallize Mo(IV)OPc from dichloromethane resulted in the demetallation of the complex. It has been observed before [17] that Mo(IV) complexes are air sensitive; the blue solutions of MoOPc complexes were reported to be easily decolorized in air [4].

Electronic Spectral Data

The absorption spectra of Mo(IV)OPc dissolved in freshly distilled dichloromethane, Fig. 1, show the Q band at 700 nm, the Soret band at 350 nm and a shoulder at 630 nm. It has been noted before [5] that absorption spectra of solutions of Mo(IV)OPc complexes in pyridine changed with time. It was also observed in this study that long exposures of the oxomolybdenum phthalocyanine solutions to air or failure to use freshly distilled dichloromethane resulted in slight shifts of the spectral bands. These shifts are attributed to the air sensitivity of the MoOPc species.

When deoxygenated solutions of MoOPc in dichloromethane were oxidized with dilute solutions of bromine in dichloromethane, spectral changes shown in Fig. 1 were obtained. The 700 nm peak is reduced in intensity and a new peak is formed at 782 nm. The Soret peak shifts from 350 to 374 nm. Typical spectral behaviour following the ring oxidation of phthalocyanines is the general loss of intensity in the visible region, and the formation of a broad band around 500 nm [7, 11, 13, 14, 16, 18]. Metal oxidation on the other hand results in the shift of the bands, without much change in intensity [12, 18–20].

The absorption changes observed when solutions of Mo(IV)OPc are oxidized with bromine, are quite different from those observed when the π cation radical species are formed. The intensity of the

new band at 782 nm, Fig. 1, is comparable to that of the original Q band, suggesting, therefore, that the electron has not been removed from the phthalocyanine ring. These changes are similar to those observed upon oxidation of ferrous phthalocyanine complexes [18, 19] and are typical of a metal centred reaction. It has also been observed [2] that in oxomolybdenum porphyrins, redox processes occur at the molybdenum metal rather than at the phthalocyanine ligand, and because of the similarities in the structures of porphyrins and phthalocyanines, it is not surprising that the latter also undergoes redox activity at the metal. Oxidation–reduction processes in oxomolybdenum porphyrins involve addition or removal of one electron, resulting in the Mo(V) \rightleftharpoons Mo(IV) system [2]. It is thus suggested that, metal oxidation in Mo(IV)OPc is also a one electron process, giving a Mo(V)OPc complex. Preliminary electrochemical studies on Mo(IV)OPc also reveal a one electron oxidation process [21]. Aggregation in MPc(–2) complexes results in very broad Q bands [12]. No aggregation effects are evident in the spectra of both the neutral and oxidized oxomolybdenum phthalocyanine complexes.

Coordination of oxygen atoms to the axial position in metallophthalocyanine complexes cause a decrease in the energy of the Q band [6]. Known oxomolybdenum phthalocyanine compounds have Q bands at wavelengths equal to or greater than 700 nm [4–6]. The decrease in the energy of the Q band when Mo(IV)OPc is oxidized, is an indication that the oxygen atom is still coordinated to the oxidized complex.

Figure 2 compares the spectra due to the ferric chloride oxidized oxomolybdenum phthalocyanine with that of the original unoxidized MoOPc. The intensity of the new band at 760 nm implies that the oxidation of Mo(IV)OPc by ferric chloride also results in the removal of an electron from the central

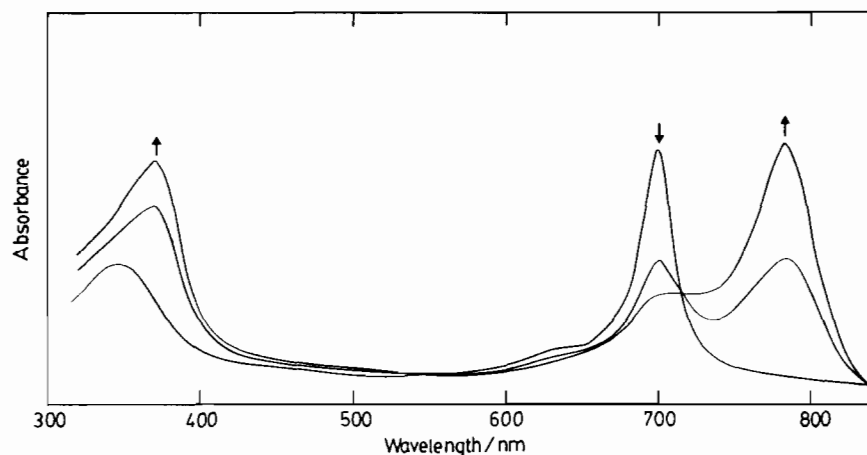


Fig. 1. Absorption spectral changes observed during the chemical oxidation (using bromine) of MoOPc dissolved in dichloromethane.

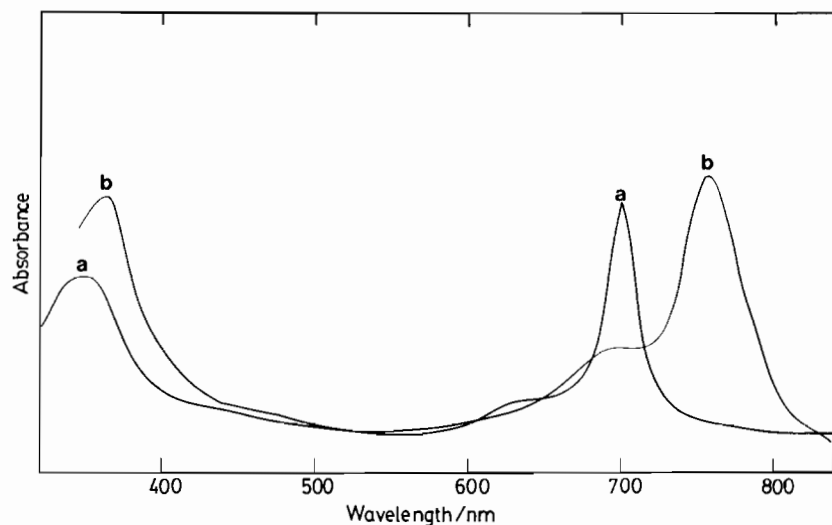


Fig. 2. The absorption spectra, in dichloromethane, of (a) neutral MoOPc; (b) ferric chloride oxidized MoOPc.

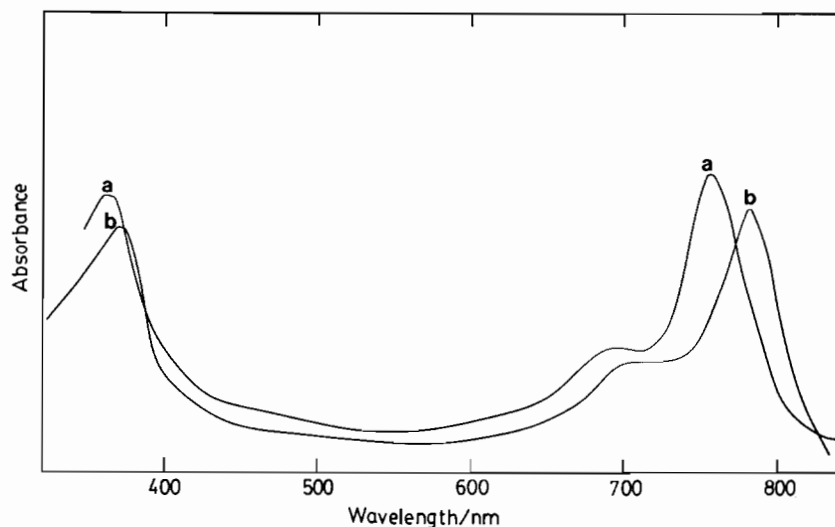


Fig. 3. The absorption spectra, in dichloromethane, of (a) ferric chloride oxidized MoOPc; (b) bromine oxidized MoOPc.

molybdenum atom. Figure 3 compares the spectra of Mo(IV)OPc oxidized by ferric chloride (a) with the spectra of the bromine oxidized complex (b). The peak observed at 782 nm in the spectra of the bromine oxidized MoOPc complex is located at 760 nm in the spectra of the ferric chloride oxidized species, the 374 nm peak of the bromine oxidized complex is observed at 366 nm. This variation of the peak position with the oxidizing agent suggests an involvement of axial ligands during the oxidation of MoOPc. Axial ligands are known to cause considerable shifts in the spectra of metallophthalocyanine [13, 14] and spectral data on Mo(V) porphyrin complexes show considerable sensitivity to changes in the axial ligand [2], as compared to the Mo(IV) complexes. It is thus, suggested that

metal oxidation in Mo(IV)OPc is coupled to an axial ligand coordination forming a six coordinate complex. The ferric chloride oxidized complex may be formulated as ClMo(V)OPc and the bromine oxidized complex as BrMo(V)OPc. More work in the far IR is needed for a more conclusive identification of these complexes.

The reduction, with sodium borohydride (Fig. 4), of the bromine oxidized MoOPc complex results in the regeneration of the spectra due to the original unoxidized species. However, the 782 nm peak shifts to 778 nm (c) as its intensity decreases, and as the original band at 700 nm is regenerated. The reduction also results in the initial shifting of the Soret band from 374 to 356 nm and finally to the position of the original band due to the unoxidized

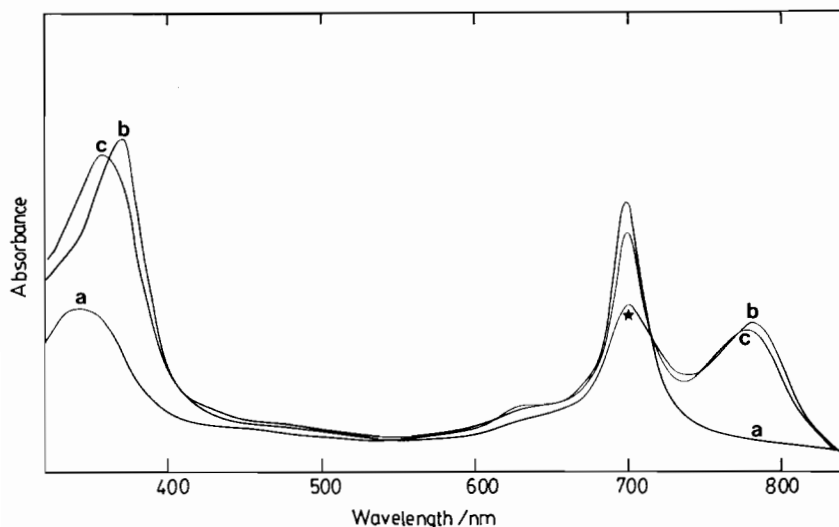


Fig. 4. The absorption spectra, in dichloromethane, of (a) neutral MoOPc; (b) bromine oxidized MoOPc; (c) intermediate formed during the reduction (with sodium borohydride) of the bromine oxidized MoOPc; * represents the remaining oxidized species.

species at 350 nm. This shifts suggest that an intermediate species is formed prior to the regeneration of the original unoxidized complex. The spectra of the original neutral species are regenerated with only 5% loss in intensity in the Q band, hence showing that the chemical oxidation of MoOPc and the axial ligand binding to the oxidized complex are reversible.

Reduction of the ferric chloride oxidized complex also shows that the oxidation and the axial ligand binding are reversible in MoOPc. The reduction goes through the same intermediate as for the reduction of the bromine oxidized species, as evidenced by the shifting of the bands due to the oxidized species from 760 and 366 nm to 778 and 356 nm, respectively, prior to the regeneration of the original complex. The nature of this intermediate has not been determined, but it seems quite likely that the axial ligands are lost during the reduction of the oxidized oxomolybdenum phthalocyanine complex, with the formation of a transient $[\text{Mo}(\text{V})\text{OPc}]^+$ complex.

Infrared Spectroscopy

The infrared spectra of the oxidized oxomolybdenum phthalocyanine complex, Fig. 5b, show bands that are quite similar to those observed for the unoxidized species, Fig. 5a. This is not surprising since the infrared spectra of metallophthalocyanines are almost insensitive to the central metal as has been noted before [22], and are thus not expected to vary much with the change in the oxidation state of the central metal ion.

The generation of the phthalocyanine π cation radical is normally identified by infrared spectra

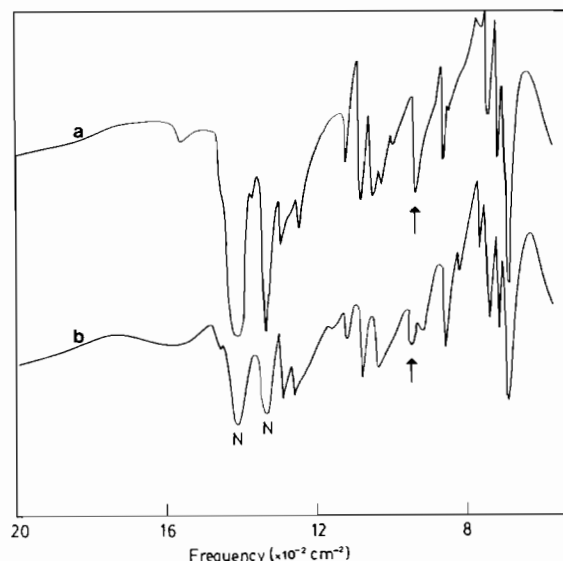


Fig. 5. The infrared spectra of (a) neutral and (b) bromine oxidized MoOPc. The arrow shows the Mo=O vibration. N = Nujol peaks.

that are markedly different from that of the $\text{MPc}(-2)$ complexes [10, 22]. The formation of new strong bands at 1050 cm^{-1} [22], and at 1350 and 1450 cm^{-1} [10], has been associated with the formation of the phthalocyanine π cation radical species. These bands are not observed in the infrared spectra of the oxidized MoOPc species; this goes further to confirm that a π cation radical species is not formed when MoOPc is chemically oxidized. The Mo=O vibration at about 970 cm^{-1} is still

observed, though broader, in the infrared spectra of the oxidized species, hence the coordinated oxygen atom is not lost during the chemical oxidation of the MoOPc species.

Conclusions

It has been shown in this work that in Mo(IV)-OPc, oxidation occurs at the metal, giving a Mo(V)-OPc complex, without loss of the oxygen atom. This oxidation is coupled with axial ligand coordination with the possible formation of a six coordinate complex. The study of the redox properties of the MoOPc complexes is essential for the understanding of the involvement of oxomolybdenum compounds in enzymes.

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