

Photochemically-induced ligand exchange reactions of ethoxy-oxo-molybdenum(V) tetraphenylporphyrin in chlorinated solvents

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Abstract

Photochemically-induced ligand exchange reactions of ethoxy-oxo-molybdenum(V) 5,10,15,20-tetraphenylporphyrin, Mo(V)O(TPP)-OEt, under irradiation at the Soret band region, were investigated. The reactions were performed in chlorinated solvents and followed with ultraviolet–visible (UV–vis) spectroscopy, whereas the products were analyzed with Fourier transformed infrared (FTIR) spectroscopy, electron spin resonance (ESR) spectroscopy and gas chromatography (GC). The chloro-oxo(TPP)Mo(V) complex was obtained as the final product, where the chlorine came from the solvent. Nevertheless, these reactions were not photocatalytic, due to the photochemical inertness of the formed chloro-oxo complex, and an excess of ethanol could not initiate a new photocatalytic cycle unless water was added as well, resulting in the formation of a biphasic system. On the other hand, addition of ethanol, water and NaOH to the reaction medium led to the formation of the corresponding oxo Mo(IV) complex. The studied photoassisted reactions of oxo Mo(V) porphyrins appear attractive for possible applications in the detection of chlorinated pollutants in sensing devices, but also for the dechlorination of pollutants upon suitable optimization of processing conditions.

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1. Introduction

The capability of porphyrins to mediate electron and energy transfer in a variety of systems, their electrocatalytic and photocatalytic properties, and their significant role in biological processes have attracted great attention and have motivated research efforts towards a broad range of applications [1,2]. The possible technological applications of these compounds in the past were referred mainly in

catalysis [3] but recently have expanded in areas such as artificial photosynthesis [4,5], molecular electronics [6] and chemical sensors [7–10]. Solid-state studies have been also conducted, where supramolecular systems [4,5,11,12] have been prepared and many film preparation methods [13–16] have been proposed.

In the case of analytical applications of porphyrins, their sensing function is usually based on either mass variation or variation in their electronic spectra caused by weak Van der Waals interactions, hydrogen bond interactions or coordination of the central ion of the porphyrin with the analyte [7a]. In this context, the coordination of their axial ligands has been found to be very sensitive to

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environmental changes, which could be easily followed, for instance by optical spectroscopy [7b].

Oxomolybdenum(V) complexes were among the porphyrins studied in the past for both catalytic and analytical purposes [1–3,17–27]. One point of interest in these compounds is that they present ligand exchange behaviour similar to that encountered in the biochemical function of iron porphyrins. The main difference between the iron and molybdenum porphyrins is that in the molybdenum case the oxo ligand is placed in one of the two axial positions and that ligand exchange reactions are based on the ease of removal of the ligand placed at the *trans* position to this oxo ligand [1,28–31]. These reactions are usually redox ones, accompanied by oxidation or reduction of the metal, and sometimes can be photoassisted. In the last case the oxomolybdenum(V) porphyrins function as photoreducing agents [32,33].

In this context, we are interested in investigating the photoassisted ligand exchange reactions of oxomolybdenum(V) porphyrins, mainly in view of possible sensing applications, but also for the dechlorination of chlorinated pollutants. Herein, we study the photochemical behaviour of oxomolybdenum(V) porphyrins in different chemical environments and under different conditions. More specifically, we report on the photochemically-induced ligand exchange reactions of the ethoxy-oxo(TPP)Mo(V) complex mainly in chlorinated solvents and secondarily in non-chlorinated solvents.

2. Experimental

2.1. Materials

The starting chemicals were reagent grade and were used without further purification, except as noted. The basic type I alumina column was activated at 150 °C for a minimum of 24 h. H₂(TPP) and Mo(CO)₆ were the starting materials used for the synthesis of the dimer μ -oxo(TPP)Mo(V) according to a slightly modified (dichloromethane was used instead of chloroform as eluant) Srivastava method [34,35]. The synthesis was performed under an argon stream atmosphere using Schlenk-tube techniques. The dimer was identified with FTIR and UV–visible spectroscopy and the spectra obtained were compared with the corresponding ones in the literature [28] (Fig. S1). Elution of the reaction mixture from the basic activated alumina column with dichloromethane, containing a small quantity of ethanol for stabilization, resulted in the formation of the ethoxy-oxo(TPP)Mo(V) complex, as was identified by UV–visible spectroscopy.

2.2. Instrumentation and physicochemical measurements

Absorption spectra were collected on a Perkin–Elmer Lambda 6 grating spectrophotometer and ϵ (M⁻¹ cm⁻¹) measurements were performed in CHCl₃ solutions of 0.05 × 10⁻³ M. FTIR spectra were recorded on a Perkin–

Elmer FT series 1760 spectrophotometer in KBr pellets. ESR spectra were obtained with a X-band Buker 220 SE spectrometer. GC analyses were conducted with a DANI 8521 gas chromatograph equipped with a flame ionization detector, using columns packed with Carbowax, 20 M, 5% on Chromosorb W-AW.

Solutions of the ethoxy-oxo complex with concentration 2.4 × 10⁻⁴ M in various solvents were initially prepared. More concentrated solutions of ~10⁻³ M of this complex were prepared only for detection reasons and it is explicitly stated when used. The solutions of the ethoxy-oxo complex were irradiated with a 500 W high-pressure Hg lamp (usually operated at 300 W) and the desired wavelength range (450–455 nm) has been selected with an ORIEL monochromator.

For the measurement of the quantum yield, e.g. of the photochemical conversion of the ethoxy-oxo complex to the chloro-oxo complex during the exposure at ~450 nm, the number of moles of photons absorbed was measured with radiometry at this wavelength and the number of moles of the ethoxy-oxo complex reacted was calculated from the corresponding UV spectra: initially (absorbance A_0 at 450 nm) and after the irradiation (absorbance A at 450 nm), where A_0 and A differ less than 10%. Repeated experiments indicated that this method for the determination of the quantum yield had an error of up to 20%.

3. Results and discussion

3.1. Photochemically-induced ligand exchange reactions

The first experimental evidence of photochemically-induced ligand exchange reactions of ethoxy-oxo(TPP)Mo(V) porphyrin has been obtained during its elution with dichloromethane in a chromatographic column. The green solution of this porphyrin was unstable under laboratory light and it was converted to a brown species, which was identified with UV–visible spectroscopy as the chloro-oxo derivative. More specifically, it was noticed that the characteristic 452 nm peak of the ethoxy-oxo complex was significantly reduced under laboratory light and the characteristic 497 nm peak of the chloro-oxo complex was formed, along with all the other peaks of that complex mentioned in the literature [1,28] (see Fig. 1 and Table 1).

This photochemical reaction was further investigated under controlled conditions. It was found that photoexcitation of a dichloromethane solution of the ethoxy-oxo complex (concentration 2.4 × 10⁻⁴ M) in the Soret band region (450–455 nm) induced a ligand exchange reaction: the ethoxy ligand was replaced by the chloride one. UV–visible spectroscopy indicated that the ethoxy-oxo complex was completely (100%) converted to the chloro-oxo complex (after 340 s of illumination under the experimental conditions used), as shown in Fig. 1. The quantum yield of this photochemical reaction at 450 nm was ~38 × 10⁻⁴ (Table 1). The reaction progress shown in this figure is similar to the one obtained through chloride anion addition to a

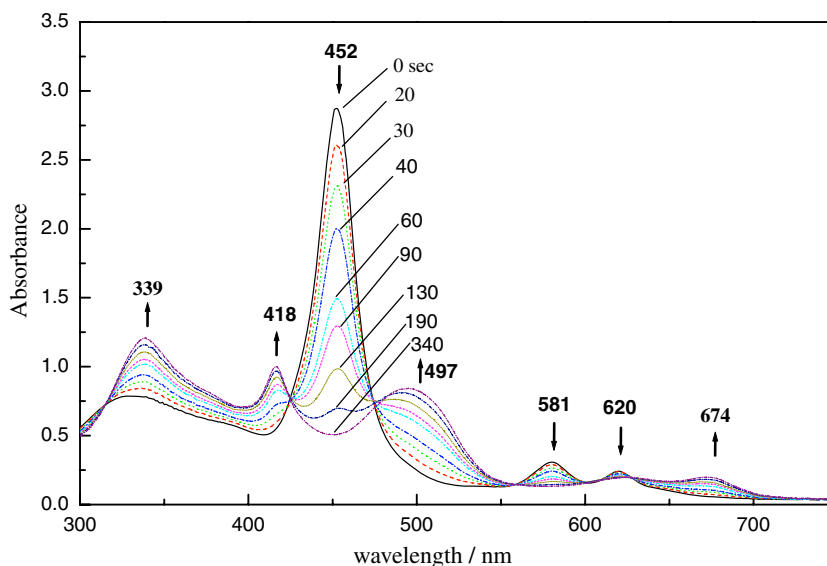


Fig. 1. UV-vis spectra evolution during Soret band irradiation of the ethoxy-oxo complex in dichloromethane. The ethoxy-oxo complex is completely converted to the chloro-oxo complex. (The exposure time is written on each spectrum.)

Table 1

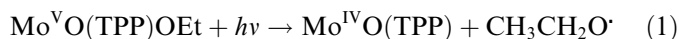
(a) UV-vis absorption data and (b) quantum yields of photochemical reactions of molybdenum porphyrins^a

(a)				
Complex	Solvent	Wavelength (nm) ($\epsilon \times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$)		Ref.
Ethoxy-oxo Mo(V)	dichloromethane	453(182), 540(3.5), 581(15.9), 620(10.9)		[1,28]
Chloro-oxo Mo(V)	dichloromethane	343(60), 417(3.3), 498(43), 628(8.6), 674(9.3)		[1,28]
Hydroxy-oxo Mo(V)	dichloromethane	464(90), 593(10.8), 635(8.4)		[1,28]
μ -Oxo Mo(V)	benzene	410(36), 444(59), 583(3.5), 617(4.2), 667(3.3)		[1,28]
Oxo Mo(IV)	dichloromethane	429(295), 480(2.43), 511(3.79), 553(17.2), 590(3.4), 640(1.2)		[1,23]
(b)				
Initial complex	Solvent	Additive-concentration (%v/v)	Photochemically formed complex	Quantum yield ($\Phi \times 10^4$)
Ethoxy-oxo Mo(V)	dichloromethane		chloro-oxo Mo(V)	38 ± 8
Ethoxy-oxo Mo(V)	acetone		oxo Mo(IV)	13 ± 3
Ethoxy-oxo Mo(V)	tetrachloroethylene		chloro-oxo Mo(V)	2.5 ± 0.5
Ethoxy-oxo Mo(V)	acetone	CH_2Cl_2 (2.5%)	chloro-oxo Mo(V)	2.5 ± 0.5

^a The concentration of the initial ethoxy-oxo complex was $2.4 \times 10^{-4} \text{ M}$.

methoxy-oxo(TPP)Mo(V) solution, as has been reported before [23].

The observed photoassisted ligand exchange process may be explained on the basis of reactions (1)–(4). According to the literature [32,33], photolysis of the ethoxy-oxo(TPP)Mo(V) porphyrin is expected to induce primarily the reduction of the metalloporphyrin and the formation of ethoxy radicals according to the following equation:



In agreement with this statement, irradiation of an acetone solution of the ethoxy-oxo complex (concentration $2.4 \times 10^{-4} \text{ M}$) in the Soret band provided evidence that some amounts of the oxo(TPP)Mo(IV) complex are accumulated. In fact, Fig. 2 shows a decrease of the ethoxy-oxo complex absorption at 450 nm and the growth of a new band at 420 nm, which can be ascribed to the forma-

tion of the oxo-complex [1,23,28]. The quantum yield of this photochemical reaction at 450 nm was $\sim 13 \times 10^{-4}$ (Table 1).

Evidence for the formation of ethoxy radicals was obtained by irradiating ethoxy-oxo porphyrin solutions containing phenyl-*tert*-butylnitron (PBN) as a spin trap [36a] in the cavity of an ESR spectrometer. This experiment was carried out in the presence of an excess of ethanol (2.5% v/v). The obtained spectrum reported in Fig. 3 consists of a triplet of doublets with the following values of the hyperfine splitting constants: $a_{\text{N}} = 14.2$ and $a_{\text{H}} = 2.5 \text{ G}$. This spectrum is consistent with the formation of a paramagnetic adduct between PBN and the photogenerated ethoxy radical [36b].

Ethoxy radicals are powerful reducing agents [37] and they are expected to react with dichloromethane resulting in the ejection of Cl^- , in accordance with Eq. (2) [38–41]:

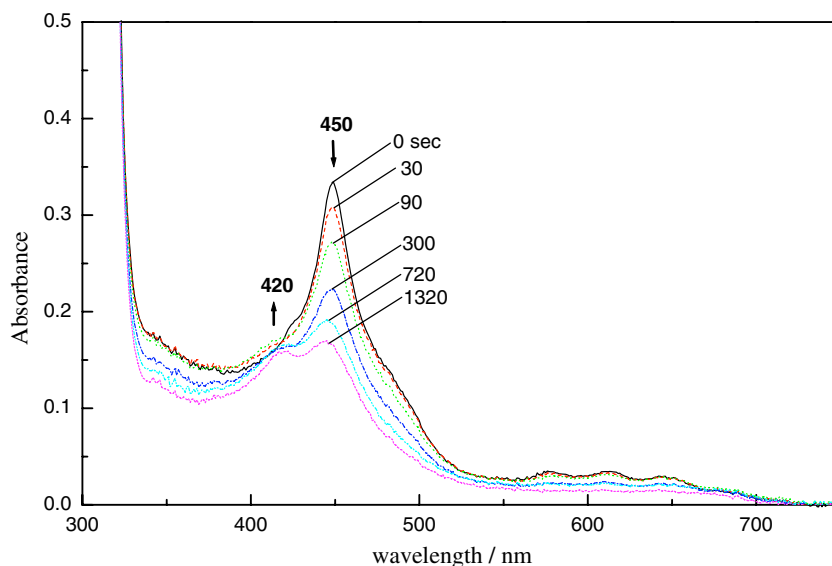


Fig. 2. UV-vis spectra progression during Soret band irradiation of the ethoxy-oxo complex in acetone. The ethoxy-oxo complex is converted to the oxo Mo(IV) complex. (The exposure times are shown.)

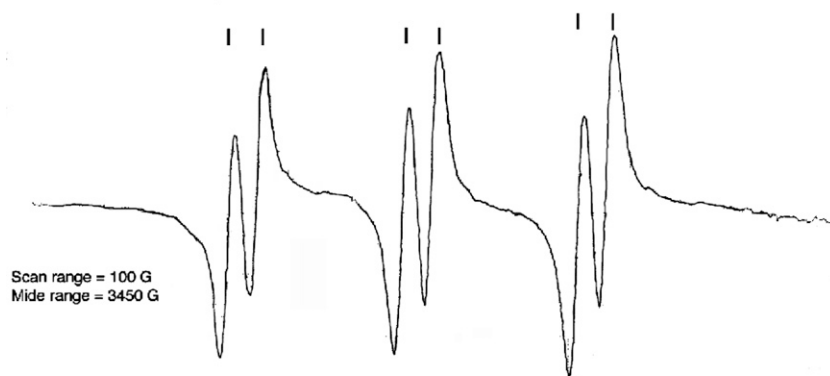
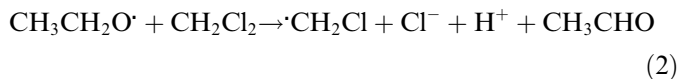
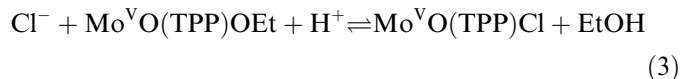


Fig. 3. ESR spectrum of the ethoxy-oxo complex ($\sim 10^{-3}$ M) in dichloromethane containing ethanol (2.5% v/v) and PBN that indicates the formation of a paramagnetic adduct between PBN and the photogenerated ethoxy radical.



The formation of acetaldehyde through Eq. (2) was demonstrated by gas chromatographic analysis of irradiated dichloromethane solutions of the ethoxy-oxo complex (2.4×10^{-4} M) containing ethanol and water (2.5% v/v each). In fact, we were able to detect with GC analysis the acetal derivative of acetaldehyde, formed through its reaction with EtOH under acidic conditions. Chain propagation reactions that lead to further dechlorination of the $\cdot\text{CH}_2\text{Cl}$ radical are also possible, as has been reported with other dechlorination photocatalysts [42]. The formation of chloride ions through Eq. 2 was verified indirectly by the formation of the chloro-oxo complex during reaction (3).

Thus, the dechlorination reaction (2) is likely to be followed by the equilibrium reaction (3), where Cl^- ions replace the ethoxy ligand of the porphyrin:



Reaction (3) has already been reported [23,43] but we also verified it: addition of HCl to the solution of the ethoxy-oxo complex resulted in ligand exchange and the formation of the chloro-oxo complex with the characteristic optical spectrum. We also noticed that the photochemically formed chloro-oxo complex was stable in the absence of light and it did not reconvert to the initial ethoxy-oxo complex, as observed from its optical spectrum.

The reduced complex formed by Eq. (1) is also able to react with dichloromethane, leading to the dechlorination of this solvent and to the formation of the chloro-oxo(TPP)Mo(V) complex according to the following equation:



A similar behaviour has been previously reported for iron *meso*-tetraarylporphyrins and other iron porphyrins dissolved in CCl_4 or CHCl_3 [38–40,44].

In an alternative route, it is possible that the photoreduced complex is oxidized by oxygen forming the superoxide ion, O_2^- , which, in turn, has been reported to lead to dechlorination reactions [25,45–48]. This dechlorination pathway is expected to occur with lower efficiency, because the opposite redox reaction, the reduction of oxo(TPP)-molybdenum(V) porphyrins by the superoxide ion, has been reported to take place in similar systems [20].

As it has been already reported [1,33] for analogous compounds, the chloro-oxo complex did not undergo photochemically-induced ligand exchange reactions, a behaviour attributed to the high polarity of the axial coordination bond. It is generally known that the more ionic the axial coordination bond of an oxomolybdenum(V) complex the less readily the complex is photoreduced, because this bond is cleaved homolitically upon photoirradiation [1,33].

3.2. Effects of the reaction medium on the photoproduct formation

3.2.1. Homogeneous systems

The photoassisted ligand exchange reaction of the ethoxy-oxo metalloporphyrin was also investigated in tetrachloroethylene, in the presence of oxygen. Thus, a tetrachloroethylene solution of the ethoxy-oxo complex (concentration 2.4×10^{-4} M) was irradiated at the Soret band. The ethoxy-oxo complex was completely (100%) converted to the chloro-oxo complex after ~ 72 min exposure via the same photochemical ligand exchange reaction, as shown in Fig. 4. In this figure, two isosbestic points appear again, but these points are red shifted (at 384 and

467 nm) in comparison with the spectra obtained before in dichloromethane. On the other hand, the disappearance of the characteristic 450 nm peak of the ethoxy-oxo complex and the appearance of the characteristic 492 nm peak of the chloro-oxo complex shows an almost identical behaviour with the one observed in dichloromethane. Additionally, the photochemical reaction in tetrachloroethylene is significantly slower than in dichloromethane, since the quantum yield of the ligand exchange reaction in tetrachloroethylene ($\sim 2.5 \times 10^{-4}$) is almost one order of magnitude smaller than the one in dichloromethane (Table 1). Similar photochemical behaviour of the ethoxy-oxo complex was also observed in experiments with other chlorinated solvents, such as 1,2-dichloroethane and 1,2,4-trichlorobenzene.

The photoinduced ligand exchange process was also investigated in acetone containing a low percentage of a chlorinated solvent, to be compared with results obtained in pure acetone. Thus, an acetone solution of the ethoxy-oxo complex (2.4×10^{-4} M) containing dichloromethane (2.5% v/v) was irradiated at the Soret band. The ethoxy-oxo complex was converted to the chloro-oxo complex, but with lower efficiency than in pure dichloromethane. Indeed, the quantum yield was $\sim 2.5 \times 10^{-4}$, which is almost one order of magnitude smaller than the one in dichloromethane only (Table 1).

Spectral evidence indicates that the described photoassisted formation of the chloro-oxo metalloporphyrin occurs also when irradiation is carried out in the presence of a large excess of ethanol (molar ratio EtOH/complex $\sim 220:1$) in dichloromethane solution. This is a clear indication that equilibrium (3) remains shifted to the right despite the high concentration of the ethanol added. The high stability of the chloro-oxo complex in the presence of ethanol was confirmed by the finding that addition of ethanol

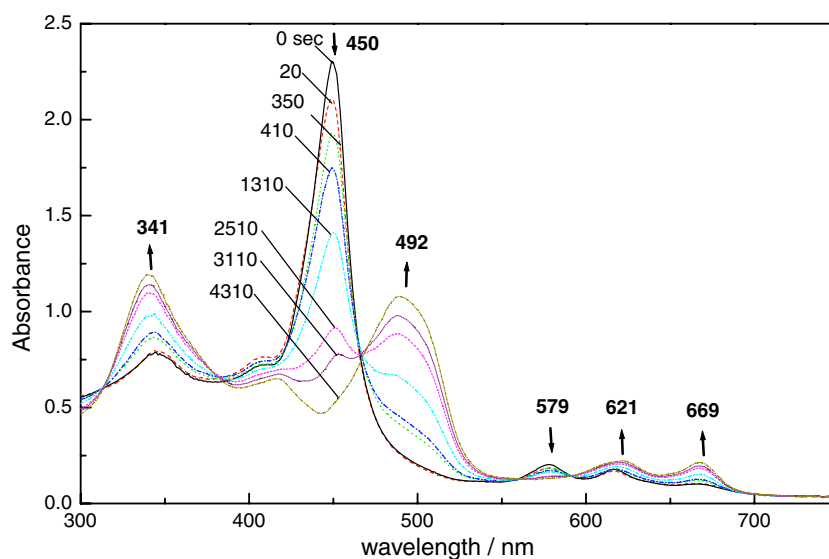


Fig. 4. UV-vis spectra evolution during Soret band exposure of the ethoxy-oxo complex in tetrachloroethylene. The ethoxy-oxo complex is completely converted to the chloro-oxo complex. (The exposure times are given; compare with data of Fig. 2.)

(0.5% v/v) to a dichloromethane solution of the photochemically obtained chloro-oxo complex (2.4×10^{-4} M) did not induce any spectral changes. An undesired consequence of these results is that the restoration of the initial ethoxy-oxo complex for initiating a new photocatalytic cycle is not possible by simple addition of ethanol in excess.

3.2.2. Biphasic systems

The results discussed so far indicate that the photochemical conversion of the ethoxy-oxo complex to its chloro-oxo derivative puts an end to the desired photoassisted ligand exchange process, due to the high stability of the chloro complex, also in the presence of an excess of ethanol. In the following, we demonstrate that the use of biphasic sys-

tems enables us to regenerate the starting ethoxy-oxo porphyrin, so inducing the photoassisted ligand exchange process in a cyclic manner.

Addition of ethanol and water (2.5% v/v each) to a dichloromethane solution of the photogenerated chloro-oxo complex (2.4×10^{-4} M) resulted in its quantitative conversion to the ethoxy-oxo derivative, as was observed with UV–visible spectroscopy (Fig. 5a). Under these conditions, water removes high amounts of Cl^- ions from the organic phase, where the metalloporphyrin complex is dissolved, favouring in this way the detachment of Cl^- from its axial position and the coordination of ethanol. Subsequently, Soret band irradiation for 170 min of the last solution resulted in the complete formation of the chloro-oxo

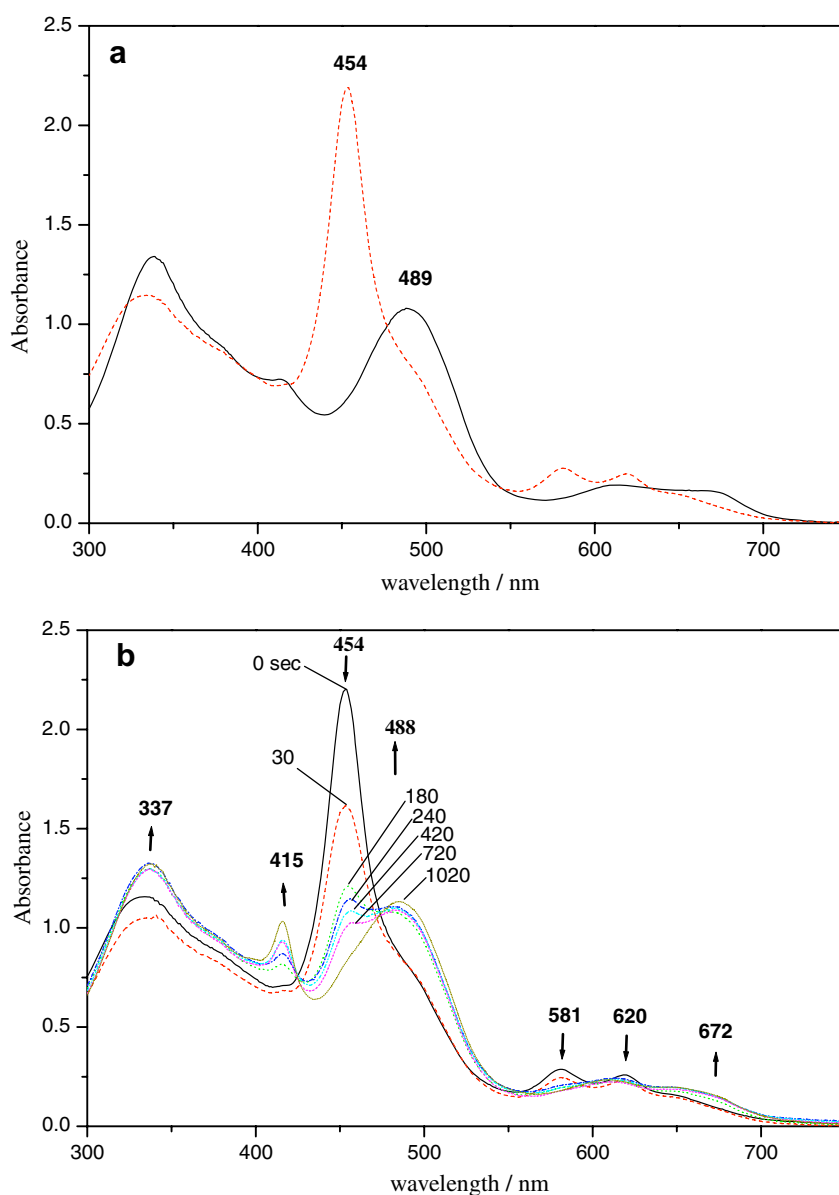


Fig. 5. UV–vis spectra progression during: (a) addition of ethanol and water (2.5% v/v each) to the photochemically converted chloro-oxo complex (2.4×10^{-4} M in dichloromethane), which resulted in the formation of the initial ethoxy-oxo complex; (b) Soret band irradiation (for 170 min) of the ethoxy-oxo complex formed in case (a), which resulted in the formation of the chloro-oxo complex.

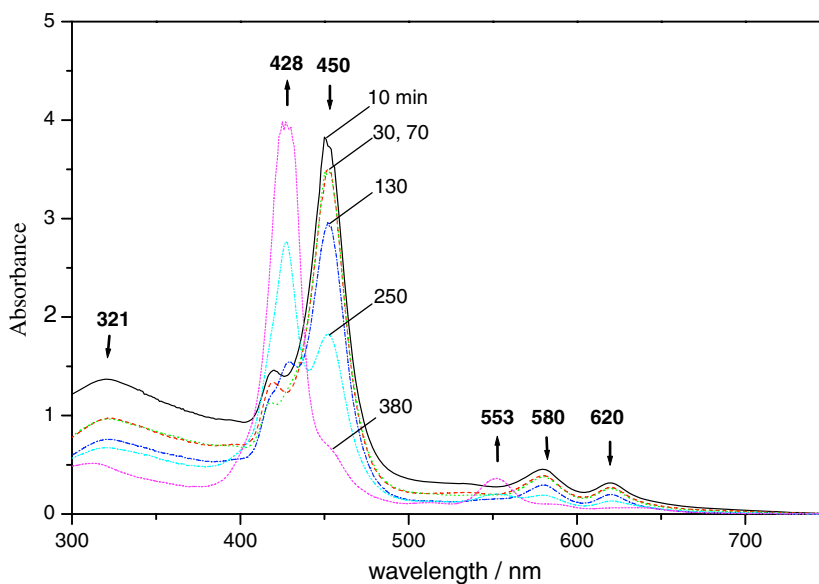


Fig. 6. UV-vis spectra evolution during Soret band exposure of a dichloromethane solution of the ethoxy-oxo complex (2.4×10^{-4} M) containing EtOH, H₂O and aqueous NaOH solution 1 M (2.5% v/v each). The ethoxy-oxo complex is completely converted to the oxo(TPP)Mo(IV) complex.

complex through the same photochemical ligand exchange route (Fig. 5b). In this case, the whole heterogeneous solution was irradiated, but in fact the organic phase was exposed and the UV-visible spectrum of this phase was obtained, as the small quantity of the added water occupied the bottom of the cell. In Fig. 5b, the complete disappearance of the characteristic 454 nm peak of the ethoxy-oxo complex and the appearance of the characteristic 488 nm peak of the chloro-oxo complex are presented.

Consequently, the formation of the biphasic system (dichloromethane/water with a major concentration of ethanol) of the ethoxy-oxo complex favours the photocatalytic inducement of the previous ligand exchange route. The photocatalytic cycles are terminated as soon as the whole quantity of ethanol in the organic phase is photooxidised. New catalytic cycles can be achieved by the biphasic system with addition of a further quantity of ethanol. Thus, the studied photoassisted ligand exchange process could be used for the dechlorination of pollutants upon addition of ethanol and water forming a biphasic system.

In order to increase the photocatalytic cycles of the photoassisted ligand exchange process, ethanol, water and NaOH were added to a dichloromethane solution of the ethoxy-oxo porphyrin. More specifically, ethanol, water and aqueous NaOH solution 1 M (2.5% v/v each) were added to a dichloromethane solution of the ethoxy-oxo complex (2.4×10^{-4} M). Subsequently, Soret band irradiation of the solution for 380 min led to the complete formation of the oxoMo(IV) complex, as was observed by UV-vis spectroscopy (Fig. 6). The formation of the hydroxy-oxo(TPP)Mo(V) complex, which could be expected in this case, was not observed (i.e. the major 464 nm peak of the hydroxy-oxo complex along with the other peaks of that complex were not observed, see Fig. 6

and Table 1). On the other hand, both the characteristic peaks at 428 and 553 nm of the oxoMo(IV) complex were obtained. Furthermore, detection of the acetal derivative in this irradiated biphasic system with GC analysis was not feasible, due to the predominant basic conditions. Therefore, in this last, quite complicated biphasic system, the photoassisted ligand exchange route was changed, as no chloro-oxo complex was observed. A possible explanation is that NaOH removes more effectively the Cl⁻ ions from the organic phase than water does. Nevertheless, further investigation on this system is necessary in order to clarify the picture.

4. Conclusions

In this contribution, the photoassisted ligand exchange reactions of ethoxy-oxo(TPP)Mo(V) porphyrin were studied. In this first investigation specific attention has been given to the formation of the photochemically inert chloro-oxo complex, which results in a net overall photoassisted ligand exchange reaction. This reaction is easily followed due to the characteristic UV-visible spectra evolution in different chlorinated solvents. Regeneration of the starting ethoxy-oxo complex and, thus, photocatalytic inducement of the ligand exchange route was not possible by simple addition of ethanol in excess, but only with the addition of water and ethanol in the reaction medium, where a biphasic system is formed. Further addition of NaOH changed the photoassisted ligand exchange route, and led to the formation of the oxoMo(IV) complex, instead of the chloro-oxo complex. The mechanistic details and the possible practical value of the described chemistry in bonded chlorine detection and dechlorination of pollutants appear worthy of further investigation.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.poly.2006.06.027](https://doi.org/10.1016/j.poly.2006.06.027).

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