

# Synthesis, photophysical properties and photocatalytic activity of tungsten porphyrin (TPPWCI<sub>4</sub>)

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Dedicated to Professor Özer Bekaroğlu on the occasion of his 80th birthday

Received 3 January 2013 Accepted 6 March 2013

**ABSTRACT:** Although tungsten porphyrins are known as mimicking models in biology, only a few papers about its chemical properties have been reported, the rarity of studies being attributed to the difficulties encountered in their synthesis due to their low stability. In this paper 5,10,15,20-tetra-p-phenyl-porphyrin tungsten(VI) chlorine (TPPWCl<sub>4</sub>) was studied, this metallo-porphyrin characterized by different analytical techniques: UV-vis, FTIR, ESR, mass spectrometry, including photophysical determination of its singlet oxygen quantum yield, too. Its photodegradation reaction with the mechanism and species involved into this destruction reaction processes is discussed, too. Also, in order to maintain its photostability, TPPWCl<sub>4</sub> has been incorporated into solid substrates, such as ZnO and TiO<sub>2</sub>, and these composites were subsequently tested in the photooxidation reaction of isoamylenes (2-methyl-2-butene and 2-methyl-1-butene mixture).

KEYWORDS: metalloporphyrins, tungsten porphyrin, photodegradation, isoamylenes, photooxidation.

## **INTRODUCTION**

With a large and polarizable  $\pi$ -systems, long conjugation lengths and small HOMO-LUMO energy band gaps, the porphyrins and metalloporphyrins are recognized as very versatile compounds with chemical and thermal stability, rigid planar geometry, intense UV-visible absorption, and fluorescence and phosphorescence emission [1]. They have a high and selective ability to coordinate metals, with rich substitution chemistry, and can perform metal-to-metal or metal-to-ligand electron transfer [2].

Porphyrins and metalloporphyrins have attractive properties for useful materials for charge transport [3], catalytic and photocatalytic processes [4–7] and photoelectronic conversion [8], solar energy conversion [9, 10], ultra-fast switching technology [11], non-linear optics [12],

organic light emitting diodes [13], diagnosis and photodynamic therapy [14, 15]. Currently, several porphyrinbased drugs are under various stages of development as phototherapeutic agents and X-ray radiation enhancers [16]. The current state of pharmaceutical development of metalloporphyrins in medicine is highlighted. With the development of bionics, chemists attempt to mimic the biological properties of natural enzymes using stable mimetic enzymes [17]. As the mimetic enzyme was not so good as the natural enzyme in catalytic selectivity, different sorts of peroxidase were mimicked only through synthesizing metalloporphyrins with different possible metals and different possible substitutents. On the other hand, myoglobin (Mb) and HRP substituted by molybdenum and tungsten were studied by Shiro et al. [18] to mimic the heme environmental structures of compounds I and II for hemoproteins with high valent iron porphyrin moieties.

Up to now, only a few papers have been reported on tungsten porphyrins [19], usually with large axial ligands strongly linked to the central metal, or in aggregated

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forms, like dimeric forms. Collman and co-workers studied the W–W quadruple bond in dimeric metalporphyrin complexes  $[W(TOEP)]_2$  [20–23]. Also, Kim *et al.* [24] studied the rotation of dimeric tungsten-TPP complexes  $[W(TPP)]_2$ , which involves a formal rotation about a tungsten-tungsten quadruple bond, and found it to be 11.3 kcal.mol<sup>-1</sup> by NMR line shape analysis.

The conventional method for the preparation of tungsten porphyrin involves refluxing of the corresponding hexacarbonyl and porphyrin in a high-boiling solvent [25, 26]. The rarity of studies in tungsten complexes may be attributed to the difficulties encountered in the synthesis of such complexes.

Kinetic study of porphyrin metalation is indispensable in order to understand *in vivo* metal incorporation processes leading to the formation of natural metaloporphyrins. Normally, metalloporphyrins are synthesized in two steps, where the free-base porphyrins are synthesized first, followed by the metalation reaction [27–31]. Metalloporphyrins are fairly stable to thermal and oxidative decomposition, and parameters of that process depend on the number, position, and on the presence of other substituents. However, the synthesis of tungsten porphyrin is difficult. In the W porphyrin system, the effect of peripheral functional groups or spacer ligands on the thermal stability has not been fully investigated [32, 33].

Also, the rarity of these metalloporphyrins is explained by their reduced photostability [34–37]. Despite significant advances from the past years, preparation of suitable porphyrin derivatives that are sufficiently stable towards oxidative degradation still remains a major challenge. It is known that the enhanced stability and the efficiency of the metalloporphyrins are due to their stereochemical features and to the electron-withdrawing halogen substituents. The metallo-porphyrins are very susceptible to photodegradation due to the instability of their excited states. Upon illumination, photoinduced electron transfers from the porphyrin ligand to the metal center (LMCT), followed by demetalation and cleavage of the porphyrin ring take place [38, 39]. To the best of our knowledge, there have been few reports describing effective strategies to protect metallo-porphyrins from photodegradation in aqueous solution [40]. Metal complexes derived from porphyrins are fairly stable to thermal and oxidative decomposition, and parameters of that process depend on the number, position, and on the presence of other substituents. The effect of peripheral functional groups or spacer ligands on the thermal stability has not been fully investigated [41] in the W porphyrin system. Several effective methods to maintain the photostability of metallo-porphyrins by incorporating them into solid substrates, since many photochemical or photophysical reactions occur in aqueous media [42-44].

This paper will show the photodegradation reaction pathway of a new metallo-porphyrin, TPPWCl<sub>4</sub>, and

its photostabilization, too, by supporting it on two metallic oxides:  $TiO_2$  and ZnO. The photodegradation mechanism will also be presented, taking into acount all the adjacent species able to be formed during such reaction.

Due to its singlet oxygen capacity,  $TPPWCl_4$  supported on two metallic oxides  $TiO_2$  and ZnO, will be tested as photosensitizers in the photooxidation reaction of isoamylene (a mixture of 2-methyl-2-butene and 2-methyl-1-butene).

## EXPERIMENTAL

#### **General instrumentation**

*Elementary analysis.* Determination of weight percent carbon, hydrogen, nitrogen, sulfur or oxygen is done using a "2400 CHN Elemental Analyzer" by Perkin Elmer Series II. After proper calibration, the result is expressed as a percentage by weight of nitrogen, carbon, hydrogen and sulfur or oxygen.

*UV-vis spectra* (*nm*). The absorption diffusereflectance spectra were recorded on a SPECORD M400 Carl Zeiss Jena spectrophotometer with double beam and microprocessor using MgO as reference solid powder.

*The FTIR spectra.* Were recorded using a Perkin Elmer Spectrum GX spectrometer, by using KBr pellets and DRIFT techniques. Scans in the range of 400–4000 were accumulated for each spectrum at a spectral resolution of 4 cm<sup>-1</sup>. It was possible to use the drift accesory with the powdered pure substance, thereby allowing for a better and easier analysis.

<sup>1</sup>*H NMR spectra.* Were obtained at 300 MHz on a Varian Gemini spectrometer or at 270 MHz on a Bruker SY270 spectrometer equipped with variable-temperature capabilities. Chemical shifts are reported in units of  $\delta$  (from tetramethylsilane), but were measured using the residual methyl resonance of toluene in toluene-d8 or benzene resonance in benzene-d<sub>6</sub> as internal references.

ESR spectroscopic measurements. were carried out by the method previously described [45] using a JES-MF-3X spectrometer operating in X-band frequency under the following conditions: frequency, 9 GHz; microwave power, 5.0 mW; modulation frequency, 100 kHz; modulation amplitude width, 0.63 mT; response, 0.03 s; scanning time, 4 min; magnetic field,  $340 \pm 100$  mT. The field was calibrated using crystalline diphenyilpicrylhydrazyl (g = 2.0036) as the internal standard. The spectrometer has a TE011 cylindrical resonant cavity and 100 kHz modulation frequency. Powder samples were placed into quartz tubes with a 2.4 mm inner diameter. The signals of all samples were recorded in the dark. For calibrating the magnetic field and to measure the magnetic field at the sample has been used a teslameter (or gaussmeter) with an intra-cavity probe which can be placed in the sample position and then compared that value with the field value that the Hall probe detects. All measurements were performed at room temperature and at liquid nitrogen temperature (77 K). For liquid nitrogen temperature measurements, each sample was frozen in a Dewar task inside the resonator. Samples were introduced in quartz tubes sealed under high vacuum ( $10^{-3}$  torr); some samples were prepared in a dry argon atmosphere.

**EI-MS (Electron Impact Mass Spectra).** They have been recorded with a mass-spectrometer Varian MAT (450 °C, Tor, 70 eV) type and with an ESI-MS (Electron Spray Ionization), Finnigan-Mat TSQ 700 type. The m/z values refer to the highest peak of the isotopic pattern ratio according to the natural abundance of the isotopes.

*The photodegradation reaction.* The photodegradation reaction mechanisms were studied in an immersion photoreactor equipped with magnetic stirring and surrounded by a temperature controlled support. The solution in a quartz cell (10 mm width) equipped with magnetic stirring placed 15 cm from the center of the lamp was irradiated with a Romlux 250 W mediumpressure mercury lamp and surrounded by a temperature controlled support. After photobleaching the porphyrin was extracted with chloroform. The chloroform extract was dried over sodium sulphate, filtered and analyzed by UV-vis, IR and chromatography-mass spectrometry.

**Determination of singlet oxygen quantum yield**  $[\phi({}^{I}O_{2})]$ . The singlet oxygen quantum yield has been detected with a phosphorescence instalation (excitation with a Xe-arc, detection at 1270 nm through a PTI S/N 1565 monochromator, emission monitored by a liquid nitrogen-cooled Ge-detector). The reference solution was TPP in CHCl<sub>3</sub> ( $\phi_{\Delta} = 0.55$ ) [46].

Photooxidation of olefins and product analysis. The sample in a Pyrex reactor was bubbled with oxygen during irradiation. A 375-W medium pressure Hanovia Hg lamp was employed as the light source, and a glass filter was used to cut off light with a wavelength below 400 nm. The filter is necessary to avoid the direct excitation of the olefin substrates. These conditions were chosen in order to minimize any possible allylic hydroperoxide decomposition which might mask the true reaction regioselectivity. Oxygen was bubbled into the solution in an impinger, while the substrate was cooling in an ice/water bath. The reaction was carried out for 6-13 h. After irradiation, the products were extracted with isopropanol, analyzed by iodometric methods and compared with authentic samples. Traditional iodometric titration methods with thiosulfate are the most accurate assay chemically [47]. It is stoichiometric, linear, and useful for high peroxide concentrations, being considered the only method providing absolute quantitation of hydroperoxides.

Reactants consisted of an isoamylene mixture of 2-methyl-1-butene (6 wt.%) and 2-methyl-2-butene (94 wt.%) (FLUKA, Buchs).

The values of quantum yield of the photochemical reactions were calculated from the following adopted formula [48]:

$$\varphi = (\Delta C) / i \times s \times t \tag{1}$$

where  $\Delta C$  = hydroperoxide concentration variation after t seconds of irradiation by comparison with the initial one; i = intensity of radiation impinging on the cell containing the solution (photons.cm<sup>-2</sup>.s<sup>-1</sup>);  $\varphi$  = quantum yield of the photochemical reaction (molecules.photons<sup>-1</sup>); s = cross section of absorption (cm<sup>2</sup>.molecule<sup>-1</sup>); s = 3.8 × 10<sup>-2</sup> ×  $\varepsilon$  ( $\varepsilon$  - molar coefficient of extinction at given wavelength).

#### Materials

Synthesis of TPPWCl<sub>4</sub>. 5,10,15,20-tetra-p-phenylporphyrin tungsten(VI) chlorine (TPPWCl<sub>4</sub>), was obtained by equimolar reaction of WCl6 and free tetraphenyl-porphyrin TPPH<sub>2</sub>, in CCl<sub>4</sub>, at refluxing temperature, for 24 h, using our own method (Fig. 1). WCl<sub>6</sub> purification was achieved by sublimation at a temperature of 200 °C, under Ar purge. After that, it is loaded into thin vials, purged with argon through a glass narrow tube. In a glovebox, a 100 mL roundbottom flask equipped with a Teflon vacuum valve and a ring side arm was charged with 10 mL of CCl<sub>4</sub>, TPPH<sub>2</sub> (250 mg, 0.468 mmol), WCl<sub>6</sub> (800 mg, 2.27 mmol) and a stirrer bar. The headspace was evacuated at  $10^{-2}$ Torr for 10-15 min to remove adventitious oxygen and water. The sealed flask was heated at 180 °C for 6 h, cooled to ambient temperature, and transferred to the glovebox and held at -20 °C overnight. The TPPWCl<sub>4</sub> was collected by filtration and washed with cold hexane. It was purified by dry column chromatography with Al<sub>2</sub>O<sub>3</sub>. Chromatographic purification was repeated twice. The purification method was suitably modified by introducing gradient elution which comprised of



Fig. 1. The reaction pathway for TPPWCl<sub>4</sub> synthesis (R = phenyl)

chloroform and petroleum ether 50:50% followed by evaporation of the solvent mixture. TPPWCl<sub>4</sub> purification process was repeated twice with the same mobile phase. The purity of above metalloporphyrins was checked on TLC using chloroform and petroleum ether 80:20% and found to be very satisfactory. The yield was 73 mg (9.8% based on porphyrin).

Anal. calcd. for  $C_{44}H_{28}N_4WCl_4$ : C, 68.97; H, 3.66; N, 7.29%. Found C, 68.27; H, 3.68; N, 7.01%. <sup>1</sup>H NMR (300 MHz;  $C_6D_6$ ):  $\delta_H$ , ppm 8.72 (s,  $\beta$ -pyrrole H), 7.80 (s, p-phenyl-H). FTIR (400–1700 cm<sup>-1</sup>, KBr): v, cm<sup>-1</sup> 708, 758 Y(C–H), 1075, 1180  $\delta$ (C–H), 1485, 1610 v(C=C), 805 Y(C–H), v(C–N),  $\delta$ (C–H), 1335 v(C–N), 1445 v(C=N), 1540 (skeletal vibrations of the pyrrole ring), 447 (W–N), 430–460 (W–Cl). UV-vis (CCl<sub>4</sub>):  $\lambda_{max}$ , nm (log  $\epsilon$ ) 447 (92.6); 609 (3.2); 660 (5.4). MS (FAB): *m/z* 936 (calcd. for [M + H]<sup>+</sup> 937.84).

Synthesis of [W(TPP)]<sub>2</sub>. TPPH<sub>2</sub> (0.3 g) and an excess amount of  $W(CO)_6(1 \text{ g})$  were suspended in decalin  $(10 \text{ cm}^3)$ . The solution was deoxygenated by bubbling with nitrogen for 15 min. Then, the mixture was refluxed for 24 h under nitrogen. The black product, [W(TPP)]<sub>2</sub>, was precipitated by cooling the reaction mixture (Fig. 2). The solid product was filtered under nitrogen. The yield was ca. 90% on the basis of the free ligand. Anal. calcd. for C<sub>88</sub>H<sub>56</sub>N<sub>8</sub>W<sub>2</sub>: C, 66.34; H, 3.51; N, 7.03%. Found C, 67.17; H, 3.618; N, 7.01%. <sup>1</sup>H NMR (300 MHz; benzene- $d_6$ : room temperature):  $\delta$ , ppm 9.18 (d, o'-Ph), 8.28 (s, β pyrrole), 8.18 (s, β pyrrole), 7.72 (m, m'-Ph), 7.50 (m, p-Ph), 7.22 (m, m-Ph). IR (Nujol): v, cm<sup>-1</sup> 1198(w), 1175(w), 1152(w), 1070(s), 1009(vs), 846(w), 790(m), 751(s), 719(m), 703(s), 663(w), 621(w). UV-vis (toluene):  $\lambda_{max}$ , nm (log  $\epsilon$ ) 436 (4.178), 523 (4.161), 657 (3.80). MS (FAB): m/z 1591.7 (calcd. for  $[M + H]^+$ 1592.5).

**Synthesis of [WO(TPP)]\_2O.**641 mg (1.2 mmole) TPP, 1.3 g (2.2 mmoles) WCl<sub>5</sub> were heated to boiling under agitation in 75 mL trichlorobenzene in a 100 mL two-neck flask at reflux and under nitrogen bubbling. The reaction has stopped after 4 h, when a dark brownish residue was separated in methylene chloride by filtration and chromatografed on an alumina column. 40 mL



**Fig. 2.** The structure of  $[W(TPP)]_2$ 



**Fig. 3.** The structure of  $[WO(TPP)]_2O$ 



Fig. 4. The structure of WO(TPP)Cl

of this solution was agitated with 2 g KOH in 20 mL water for 18 hours. After solvent removal, the precipitate was washed with water, 750 mg of redish powder being obtained (Fig. 3). Anal. calcd. for  $C_{88}H_{56}N_8O_3W_2$  (MW = 1639.7): C, 64.40; H, 3.41; N, 6.83%. Found C, 64.87; H, 3.41; N, 6.89%. <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>):  $\delta$ , ppm 9.1 (s, 8H, beta-pyrrole), 8.6 (d, 8H). 8.4 (d, 4H), 7.8 (m, 8H). IR (KBr): v, cm<sup>-1</sup> 670, 726 for W-O-W systems. UV-vis (CCl<sub>4</sub>):  $\lambda_{max}$ , nm (log  $\epsilon$ ) 366 (4.74), 430 (5.09), 558 (4.1), 660 (3.32). MS (FAB): *m/z* 1639.7 (calcd. for [M + H]<sup>+</sup> 1640.9).

Synthesis of WO(TPP)Cl. A solution of 246 mg (0.15 mmole) WO(TPP)<sub>2</sub>O in 30 mL CHCl<sub>3</sub> was agitated overnight with 4 mL 37% aqueous HCl. After the solvent had been evaporated, the residue was washed with neutral distilled water. Crystallization from toluene yielded 225 mg as dark green WO(TPP)Cl (Fig. 4). Anal. calcd. for C<sub>44</sub>H<sub>28</sub>N<sub>4</sub>OWCl: C, 62.32; H, 3.31; N, 6.6%. Found C, 64.27; H, 3.38; N, 6.82%. <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>):  $\delta$ , ppm 8.61 (s, pyrrolic H), 7.26 (s, phenyl H). IR (KBr):  $\epsilon$ , cm<sup>-1</sup> 950 (W=O), 436 (W-Cl). UV-vis (methanol):  $\lambda_{max}$ , nm (log  $\epsilon$ ) 466 (5.26), 604 (3.95), 632 (4). MS (FAB): *m/z* 847.34 (calcd. for [M + H]<sup>+</sup> 847).

Adsorption of TPPWCl<sub>4</sub> on metallic oxides (MeO). 6.3 mmol of metallic oxides (MeO=TiO<sub>2</sub>, ZnO) were suspended in 250 mL of 0.4 mM TPPWCl<sub>4</sub> solution in  $CCl_4$  for 1 h. The mixture was stirred overnight at 20 °C. Afterwards, the solid was filtered, washed with distilled water and dried at room temperature [49]. A sample of TPPWCl<sub>4</sub>/MeO was examined by UV-vis spectroscopy, for determination of the metalloporphyrin that leached out from the support after the reaction and the washing process. The obtained solids were oven-dried at 30 °C for 48 h.

### **RESULTS AND DISCUSSION**

Porphyrins have a distinctive electronic absorption spectrum, the absorption spectrum being characterised by an intense "B" band (known as Soret band) typically in the region 400–450 nm with a molar extinction coefficient of the order of  $10^5$  M<sup>-1</sup>.cm<sup>-1</sup>. In the red region of the spectrum, there are some absorption bands of weaker intensity known as the "Q" bands. Their intensity is around  $10^3$  M<sup>-1</sup>.cm<sup>-1</sup> and usually is registered between 500 and 650 cm. The absorption spectra of metalloporphyrins typically show only two Q-bands (the [alpha] and [beta] bands) in addition to the strong Soret band. The lower energy band is Q(0.0) ( $\alpha$  -band) and the higher energy band is labeled as Q (1.0) ( $\beta$ -band) which has been shown to from several vibronic states [50].

The porphyrin molecules have the ability to coordinate to metal ions, yielding stable compounds. The good stability of metalloporphyrins is due to four equivalent  $\sigma$ bonds  $N \rightarrow M$  inside these macrocycles and to the planar macrocycle structure with an 18  $\pi$ -electron system. Most metalloporphyrins exhibit square-planar coordination with the metal ion sitting in the plane of the four porphyrin-nitrogen atoms. However, the porphyrin can also function as a bis tri-or hexadentate ligand, and the metal ion may possess 2-, 3-, 4-, 5-, 6- or 8-coordination. Like other macrocyclic ligands, porphyrins have a central cavity, whose size can be altered by puckering of the macrocycle, but this phenomenon is limited and the range is generally observed to be between 1.93 and 2.05 Å. When the optimum Me-N (pyrrole) distance for a metal is at variance with optimum core size of the planar porphyrin macrocycle (2.05 Å), then the macrocycle distorts to accommodate the metal ion. In many complexes the metal ion is too large to fit inside the hole and will be forced to lie out of the plane of the macrocycle. The ruffling and saddling are necessary to accommodate small metals, doming is often observed for large metals. Axial ligand-metalloporphyrin interactions are known to induce non-planar distorsions of the porphyrins. Such out-of-plane complexes are of great interest, because the unusual geometry affects both the chemical reactivity, for example the site (metal or ring) of oxidation [51] and the electronic property of the porphyrins, influencing their lifetimes and other dynamic photophysical properties [52-54].

Electronic absorption spectra of a TPP-WCl<sub>4</sub>, is a rich source of information about coordination, indicating

a Soret (418 nm) and two visible bands, at 608 and 662 nm. The wavelength of the Q(0.0) ( $\alpha$ -band) appears to be related to the band I (646) and III (546) in the free TPPH<sub>2</sub> spectrum and the Q(0.0) ( $\beta$  band) appears to be related to the bands II (585) and IV (515). The spectral changes during the photolysis in methanol at 0, 1, 2, 3, 5, 7, 9, 11, 13, 15, 17 and 20 min reaction times (1 cm quartz cell, 298 K, aerobic conditions) show a strong decrease with splitting in three bands of the Soret band, and the Q-bands belonging to the free base TPP. More than that, a broad and not very well resolved band at longer wavelenght (around 760 nm) is observed, as a proof for the dioxetane form of this metalloporphyrin (Figs 5 and 6). Similar results could be found in our previous papers [38], and at other authors [57, 35].

The complex was characterised by FT-IR, too. The FT-IR spectrum of TPPWCl<sub>4</sub> shows two characteristic strong absorption bands at 939 (W=O) cm<sup>-1</sup> and 860 (O-O) cm<sup>-1</sup>, a weak shoulder at *ca*. 870 (O-O) cm<sup>-1</sup>. The <sup>1</sup>H NMR data of free base porphyrin in comparison with metalloporphyrin TPPWCl<sub>4</sub> showed that highly shielded peak at around -2.9 ppm is the N-H at the center of porphyrin ligand and this peak disappeared after complexation of porphyrins with metal because the two H atom are replaced by metal ion. This is a great movement to high field on the basis of strong shield effect of porphyrins ring. Magnetic resonance spectroscopy methods are sometimes also applied to the detection of compounds in high oxidation states. Obviously, this requires that the species in question is stable on the time scale of the magnetic resonance experiment, which in the NMR case excludes very short-lived species. The NMR chemical shift of the central atom may be relatively specific for a given oxidation state [55], but it depends on many other variables as well. Therefore no direct conclusions about oxidation states are possible, unless quantum-chemical calculations may provide additional information. The same holds for electronic g-tensors and hyperfine couplings measured in EPR spectroscopy. According to the literature reports, the signals of the pyrrolic protons are known to be sensitive to the electron density of the porphyrin which is in turn affected by the ruthenium oxidation state [56].

With metalloporphyrins, during the light irradiation, a reduction of the metal valence occurs at first, after which a porphyrin dianion is generated and a breakdown of the methine bond occurs; a linear chain with a hydroxyl and/or ketone groups is formed, responsible for the subsequent dioxetane species involved in the degradation reaction [57, 58]. TPPWCl<sub>4</sub> (ionic radius = 0.66 Å), where there are four Cl atoms to the W cation, contributes to a stronger stability of this compound [59]. When W was substituted in the porphyrin ring to form TPPWCl<sub>4</sub>, the geometry of the six coordinated compound is a square rombohedric with  $C_{6v}$  symmetry. In this case, the central W atom is not displaced from porphyrin plane. Due to



Fig. 5. The absorption spectrum of TPPWCl<sub>4</sub> variation during light irradiation; t = 1200 s



Fig. 6. The schematic diagram for TPP photodegradation

this reason the stability of the compound is expected to be less than other compounds.

Almost all metals form complexes in a ratio of 1:1 with different chelates, although Na, K, Li complexes are 2:1

in which the metal atoms are incorporated slightly below and above the porphyrin macrocycle plane. When divalent metal ions (*e.g.* Co(II), Ni(II), Cu(II)) are chelated, the resulting tetracoordinate chelate has no residual charge. While Cu(II) and Ni(II) in their porphyrin complexes have generally low affinity for additional ligands, the chelates with Mg(II), Cd(II) and Zn(II) readily combine with onsse more ligand to form pentacoordinated complexes with square-pyramidal structure. Some metalloporphyrins (Fe(II), Co(II), Mn(II)) are able to form distorted octahedral with two extra ligand molecules [60].

The metals in hypsocomplexes from Groups VIII or IB have filled pseudoshell  $t_{2g}$  ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$ ) and adopt an octahedral symmetry. In TPP-WCl<sub>4</sub>, the tungsten atom displaces two hydrogen ions from the porphyrin ligand and forms four coordinative donor-acceptor bonds with nitrogen atoms.

A mechanism proposed for the demetalation, is involving replacement of Cl by O<sub>2</sub> coordinated to TPP-WCl<sub>4</sub>, then subsequent reduction of W(VI) to W(V) within this O<sub>2</sub> complex and loss of the porphyrin ligands from W(VI). The main species generated during the photodegradation process are [WO(TPP)]<sub>2</sub>O (a), [W(TPP)]<sub>2</sub> (b), WO(TPP) Cl (c), and finally, TPP. They have been put into evidence by spectral deconvolution. At the same time, these deconvoluted spectra show absorption bands specific to unreacted TPPWCl<sub>4</sub> (444–446 nm) and unmetallated TPP (413–417 nm).

Based on these facts, a preliminary scheme for TPPWCl<sub>4</sub> photodegradation has been proposed (Fig. 8).

Typical IR spectra of TPPWCl<sub>4</sub> as presented in Fig. 9 indicated vibration W-Cl bond (415, 365, 350, 240 cm<sup>-1</sup>) and absence of a specific band of deformation for N-H bond at 3400-3600 cm<sup>-1</sup>. Following photodegradation, the compound shows v(NH) at 3122 cm<sup>-1</sup>. The deshielding influence of M-M triple bonds is well established for H atoms lying over the M-M bond [61]. In such context, Floriani recently reported on the preparation and characterization of some complexes containing W=W, W $\equiv$ W, and W $\equiv$ W bonds [62]. The tungsten-totungsten bond varies between single and quadruple bonds. The lower the valence state, the higher the degree of W–W bond. A quadruple bond is a type of chemical bond between two atoms involving eight electrons. This bond is extensions of the more familiar types *i.e.* double bonds and triple bonds. Stable quadruple bonds are most common among the transition metals in the middle of the d-block, such as rhenium, tungsten, molybdenum and chromium. Typically the ligands that support quadruple bonds are  $\pi$ -donors, not  $\pi$ -acceptors.

The  $[W(TPP)]_2$  reacts with  $H_2O_2$  in acetonitrile and methylene chloride mixed solvents to produce W(O) $(O_2)(TPP)$  in 20 min at room temperature [63]. The IR spectrum [v(O-O) at 930 cm<sup>-1</sup> and v(W=O) at 886 cm<sup>-1</sup>] of this compound was that obtained from the oxidation of W(O)(OH)(TPP). In the IR spectrum, two IR absorption bands between 1263 cm<sup>-1</sup> and 1211 cm<sup>-1</sup> have been recognized due to the reported [64] combination of the M–N and N–C stretching vibrations whereas absorptions due to W–Cl bonds were observed between 400 and 200 cm<sup>-1</sup>. Peaks around 727 and 800 cm<sup>-1</sup> are assigned to



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**Fig. 7.** The absorption spectra of different TPPWCl<sub>4</sub> species (with spectral deconvolution): (a) [WO(TPP)]<sub>2</sub>O; (b) [W(TPP)]<sub>2</sub>; (c) WO(TPP)Cl

W–O stretching vibration bonds [65–68]. The metal–N stretching vibration was found at 426 cm<sup>-1</sup>, The IR active stretching vibration  $v_{as}$  (N–N) is assigned to the prominent peak at 1932 cm<sup>-1</sup>.

ESR investigation carried out on the TPPWCl<sub>4</sub>, in frosen  $CH_2Cl_2$ , indicates that paramagnetic species are present. Three resonance lines are located at  $g = 2.0040 \pm 0.0005$ ,



Fig. 8. The schematic mechanism of TPPWCl<sub>4</sub> photodegradation



Fig. 9. The IR spectra of  $\text{TPPWCl}_4$  initial (----) and photodegraded (\_\_\_\_\_)

 $g = 1.9670 \pm 0.0005$  and  $g = 1.8815 \pm 0.0005$  respectively. The first two lines are ascribed to free radicals [69]. The strongest resonance located at g = 1.8815 with a line width of about 122 Gs, has been ascribed to W ions, with an electronic configuration analogous to W(V) [70]. Following photodegradation, TPPWCl<sub>4</sub> presents four resonance lines. The lines associated with free radicals are not significantly affected, the intensity of the resonance line located at g=1.8815 is significantly reduced and a resonance line located at g = 1.8010 with a peak to peak linewidth of about 60 G is noticed. This line has been tentatively assigned to the modification of ligands by substitution of W [W(IV)O(TPP)]<sub>2</sub>O. Here have to take into acount that the aggregation is occuring during the metalloporphyrin photobleaching [71].

After photodegradation, a second signal with a g-factor of  $1.680 \pm 0.04$ ,  $\Delta H = 110 \pm 10$  G, assigned to a W(III) species was detected. This species is very unstable and is very fast transformed in W(V), in good agreement with literature data [72–75]. In our case, the g values for W(V)O(TPP)Cl were:  $g_1 = 1.979 \pm 0.0005$ ,  $g_2 = 1.918 \pm 0.0005$ ,  $g_3 = 1.872 \pm 0.0005$ , most probably due to the complex surrounding of porphyrin (W(V) is a complex with g values in the range of 1.84 to 1.97 [76, 77]).

All the generated species during TPPWCl<sub>4</sub> photodegradation have been identified by mass-chromatography ESI-MS (Electron Spray Ionization, Fig. 10). Except the above mentioned species, in this figure could be identified mass-fragments with less chlorine ions linked to W resulted during the photodegradation process, as usually observed for metalloporphyrins [38]. After loosing all the chlorine ions, the metalloporphyrin TPPWCl<sub>4</sub> is loosing



Fig. 10. The ESI-MS diagram for the species generated during TPPWCl<sub>4</sub> photodegradation

the central metal (W), afterwards the photodegradation diagram of porphyrin free base is obeyed (Fig. 6).

#### Adsorption on metallic oxides

The porphyrin component enhances the visible light-sensitivity of the  $TiO_2$  matrix thus increasing its photocatalytic activity [78–83]. By adding diverse functional groups to the macrocycle the efficiency of  $TiO_2$ -TPPWCl<sub>4</sub> systems will be influenced, depending on highly electronegative atoms, *e.g.* O or Cl, combined.

 $TiO_2$  has Ti-sites, which are Lewis acids (due to the oxygen atoms from the surface forming oxide sites), and meanwhile are Brönsted bases (due to the titanium atoms from the surface). Water dissociates by the following

mechanism: Ti draws in lone pairs from oxygen to satisfy electron demand. After that, protons cause electron deficiency and migrate to other electron-rich sites, which are the oxygen ions. This is also an acid reaction: the protons play the role of a Brönsted acid (Fig. 11). 9

The importance of the hydroxyl groups from the point of view of adsorption comes from the fact that the higher the percentage of active Me-OH per surface area unit, the larger the efficiency of the adsorption process [84].

Otherwise, the rate of binding of TPPWCl<sub>4</sub> to the metal oxide surface is proportional to the lability of the auxiliary anionic ligands, Cl<sup>-</sup> being less labile than other ligands (HPO<sub>4</sub><sup>2-</sup> or OAc<sup>-</sup>). The metalloporphyrin is able to bind either through N(NH) groups from inside the macrocycle, or by electrostatic interactions between Cl<sup>-</sup> ligands and Me<sup>+n</sup> from the metal oxides. A deprotonation of hydroxyl

groups on the metal's oxides surface or the presence of the anionic ligands in the vicinity will occur. That's why the metalloporphyrin is not removed from the TiO<sub>2</sub> or ZnO by washing with different solvents. On ZnO the adsorption is lower than on TiO<sub>2</sub>, due to lower concentration of OH groups of the first by comparison with the second one [85]. By deposition on metallic oxides, for TPPWCl<sub>4</sub>, some distinct ESR signals were recorded: the first signal ( $g_1 = 1.911 \pm 0.005$ ) was assigned to a W(V) species, the second ( $g_2 = 1.720 \pm 0.03$ ) to a W(III) species and the third ( $g_3 = 1.982 \pm 0.0005$ ) to a radical species. The ESR spectrum obtained at the finas step of the photodegradation exhibited characteristic signals to the W(V) and W(III) species. The photodegradation reaction of TPPWCl<sub>4</sub> diminished



Fig. 11. The interaction between the Cl atoms and OH groups of titanium dioxide



Fig. 12. The photodegradation kinetics of TPPWCl<sub>4</sub> on TiO<sub>2</sub> and ZnO

significantly, most probably due to the coexisting of W(III) and W(V) species, the first one acting as an electrons pump [86]. On TiO<sub>2</sub> the metalloporphyrin becomes more stable than on ZnO (Fig. 12), most probably due to hydrogen bonds between OH groups of metallic oxide and the chlorine and/ or nitrogen atoms belonging to the metalloporphyrin [36].

#### **Photooxidation reaction**

Light induced oxidation of the hydrocarbons can occur in the absence or presence of photosensitizers *via* the ground state oxygen ( ${}^{3}O_{2}$ ) or excited singlet oxygen ( ${}^{1}O_{2}$ ) respectively [87].

The photosensitizer in its first singlet  $(S_1)$  and triplet  $(T_1)$  excited states can be obtained by absorption of UV-vis radiation from its ground state  $S_0$ .  $T_1$  is yielded by the relaxation of  $S_1$  through intersystem crossing. The type I-process involves hydrogen atom abstraction or electron transfer between the excited sensitizer and the substrate, yielding free radicals. These radicals can react with oxygen to form the superoxide anion. The type-II process involves energy transfer from  $T_1$  to molecular oxygen to produce singlet oxygen  $O_2$  (1 $\Sigma$ g). The type-I process can involve  $S_1$  or  $T_1$  [88]. However, due to the short lifetime of  $S_1$ , the sensitizer can only react in this state if it is intimately associated with a substrate. In a photooxidation process, porphyrins are known as the most efficient photosensitizers, due to their high quantum yield of singlet oxygen generation. When a metal-oxide semiconductor is present, electron-hole pairs are generated through photonic excitation of wide-band-gap, such as ZnO, titanium dioxide (TiO<sub>2</sub>), etc. and an electron transfer from their valence band to conduction band of porphyrin occur, creating a better photosensitizer system [89].

For TPPWCl<sub>4</sub>, the singlet oxygen quantum yield is 0.64, so is an optimum quantum yield for a selective photooxidation reaction [90, 91].

By supporting this metalloporphyrin on metal oxides, a longer stability is observed and a higher rate of photooxidation, too. In our case, the olefin supported to photooxidation is an isoamylene (2-methyl-1-butene and 2-methyl-2-butene), where the photosensitizers used were: TPPWCl<sub>4</sub>/TiO<sub>2</sub> and TPPWCl<sub>4</sub>/ZnO. In this case the same rule as previously applied is valid: the highest

singlet oxygen quantum yield led to the highest photooxidation yield. This rule is more accentuated for TiO<sub>2</sub> [ $\phi$ (<sup>1</sup>O<sub>2</sub>) = 0.55] [92] (Figs 13 and 14). ZnO is possible to generate singlet oxygen, superoxide anion, or even hydrogen peroxide [93], which could influence the experimental peroxide concentration.

The products formed are shown in Fig. 15. Quantum yield of the photooxidation reaction is 0.546 for TPPWCl<sub>4</sub>/TiO<sub>2</sub> and 0.436 for TPPWCl<sub>4</sub>/ZnO, the order being related to singlet oxygen quantum yield above mentioned.



Fig. 13. The photooxidation kinetics on TPPWCl<sub>4</sub>/ZnO



Fig. 14. The photooxidation kinetics on TPPWCl<sub>4</sub>/TiO<sub>2</sub>



Fig. 15. The main photooxidation products formed by isoamylenes photooxidation

## CONCLUSION

A mechanism for the photodegradation reaction of TPPWCl<sub>4</sub> is proposed in this paper, through the replacement of Cl by  $O_2$ , followed by a subsequent reduction of W(VI) to W(V) within this  $O_2$  complex and loss of the porphyrin ligands from W(VI). The main species generated during the photodegradation process are [WO(TPP)]<sub>2</sub>O, [W(TPP)]<sub>2</sub>, WO(TPP)Cl and finally, TPP. They have been evidenced by UV-vis spectral deconvolution, FTIR, ESR analysis, mass spectrometry and singlet oxygen generation, too. Also, in order to maintain its photostability, TPPWCl<sub>4</sub> has been supported on solid substrates, as ZnO and TiO<sub>2</sub>, and tested subsequently in the photooxidation reaction of isoamylenes (2-methyl-2-butene and 2-methyl-1-butene mixture).

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