PHOTOCATALYTIC PROCESSES WITH TUNGSTEN OXYGEN ANION CLUSTERS

Elias Papaconstantinou, Anastasia Hiskia and Aristidis Troupis

Institute of Physical Chemistry, NCSR Demokritos, 153-10 Athens, Greece

TABLE OF CONTENTS

1. ABSTRACT

Polyoxometalates (POM) have a rich and promising photochemical behavior. Upon illumination at the O→M CT band (i.e., in UV and near-visible area) become powerful oxidizing reagents able to oxidize various organic compounds. In the process POM undergo stepwise reduction accumulating electrons that can be subsequently delivered, via thermal reactions to a variety of oxidants. This way a great variety of organic compounds are oxidized and indeed mineralize to CO_2, H_2O and inorganic anions and several organic and inorganic compounds can be reduced via a photocatalytic process in which POM serve as electron relays. Thus, in principle, POM can serve as decontamination photocatalysts of aquatic media removing both organic pollutants and metal ions. Under special conditions controlled photocatalytic reactions have been reported. In addition the reduction precipitation of metal ions mediated by POM may lead to formation of metal nanoparticles in which POM serve as reducing reagents and stabilizers.

2. INTRODUCTION

The Chemistry of what is now known as polyoxometalates (POM) goes back to Berzelius in the early nineteenth century. The development, as everything else in those days, has been quite slow picking up momentum in the early twentieth century with Werner's coordination theory and the contribution of several pioneers in Inorganic Chemistry. Today, modern sophisticated instrumentation has open new ways to explore and study the rich diversified Chemistry of these compounds (1).

The first notice on the photochemical properties of POM was published in 1916 (2) followed by another one sometime later 1952 (3). It was also observed in the early sixties that POM precipitated out with dioxane and exposed to light turned blue, the characteristic color of the reduced POM (4). The oil embargo in the early seventies and the search for solar energy conversion and storage has been the starting point for systematic photochemical work on POM.
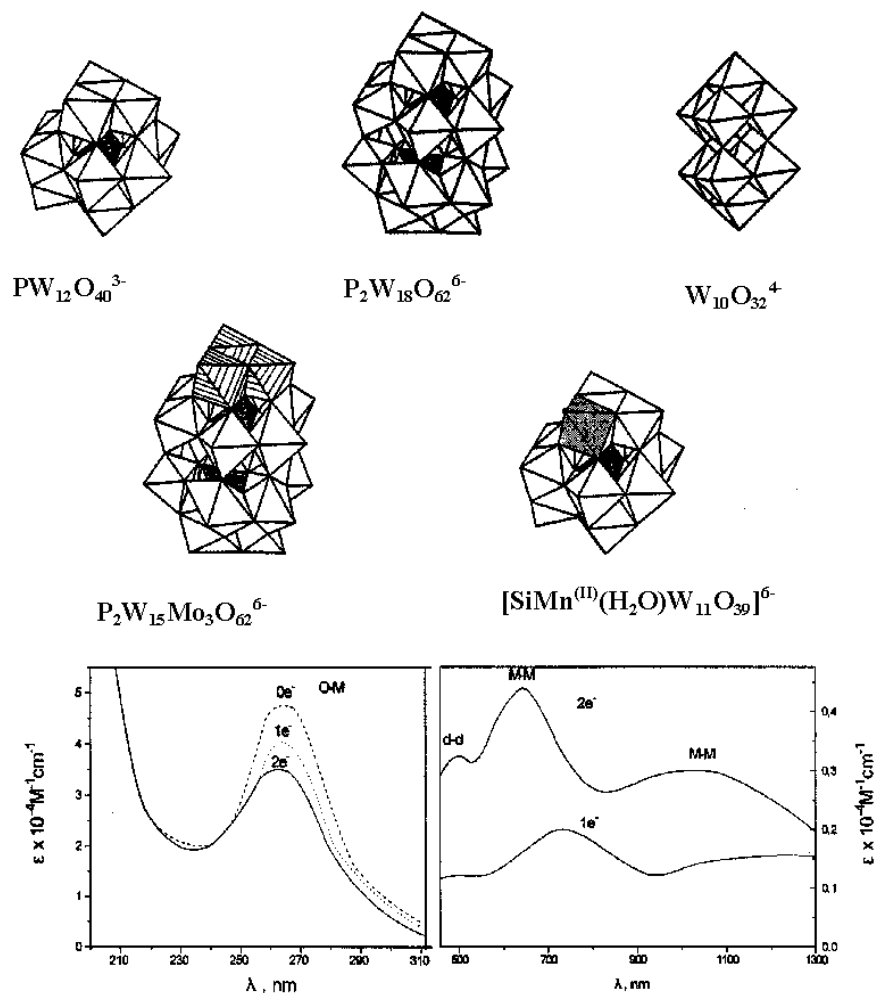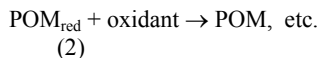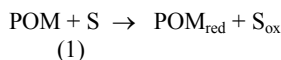
Figure 1.   The structures of several categories of POM. $PW_{12}O_{40}{}^{3-}$, Keggin structure; $P_2W_{18}O_{62}{}^{6-}$, Dawson-Wells structure. The stucture of isopoly $W_{10}O_{32}{}^{4-}$.   Mixed Dawson-Wells structure, for instance $P_2W_{15}Mo_3O_{62}{}^{6-}$ in which three W atoms have been replaced by Mo atoms.   Transition metal substituted polyoxometalate (TMSP) with Keggin structure, for instance, $(PW_{11}O_{39}Mn(H_2O))^{6-}$. Oxidized and reduced (by one and two electrons) spectra of $PW_{12}O_{40}{}^3$, showing the O→M CT band, d-d transitions and the intervalence electron transfer band   (M—M CT).
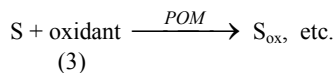
Some typical categories and structures are presented in figure 1.

One of the characteristic properties of POM is that they undergo stepwise multielectron redox reactions keeping their structure intact. Thus POM can serve as multielectron relays. POM can also serve as oxygen relays, replenishing the consumed oxygen with atmospheric oxygen (5).   The last two properties have made POM important catalysts in a variety of redox reactions.

The basic catalytic reactions involved in both cases are:

$$POM + S \;\rightarrow\; POM_{red} + S_{ox}$$
(1)

$$POM_{red} + oxidant \rightarrow POM, \; etc.$$
(2)

Overall

$$S + oxidant \;\xrightarrow{\;POM\;}\; S_{ox}, \; etc.$$
(3)

where S = substrate

The most effective and benign oxidant is dioxygen. However, a variety of other oxidants can serve in this purpose.

In photocatalytic processes the same overall reactions are involved. The basic difference is that reaction (1) is driven by light.

3. THE PHOTOCATALYTIC CYCLE

It is now well documented that illuminating POM with near-Visible and UV light, that is at the oxygen to
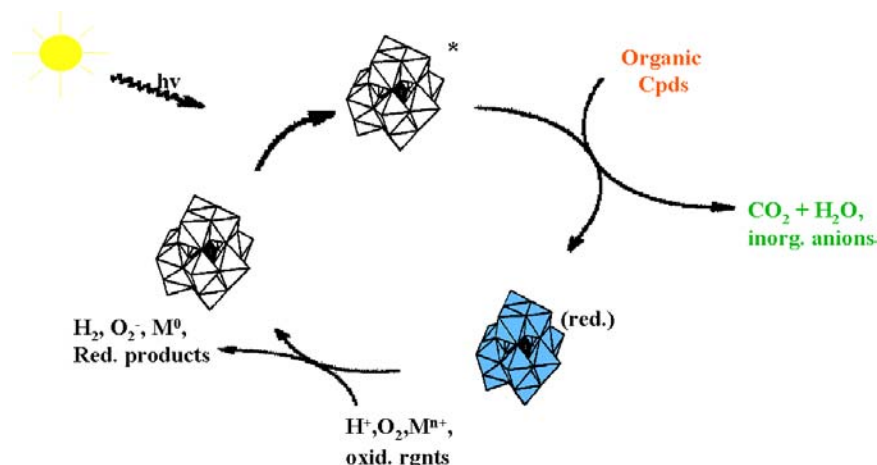
Figure 2. Schematic diagram of the photocatalytic cycle with the Keggin structure.

metal charge transfer (O $\rightarrow$ M CT) bands renders POM powerful oxidizing reagents able to oxidize a variety of organic compounds, whereas, at the same time POM are reduced to usually blue POM (6).

The overall photochemistry of POM can be described by the photacatalytic cycle of figure 2. The various stages involved in this cycle are as follows:

Firstly, there have been various data suggesting that upon mixing of POM with organic species a preassociated complex or preequilibria, not shown in figure 2, is established.
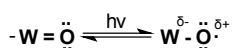
$$POM + S \rightarrow (POM\text{---}S) \tag{4}$$
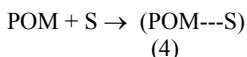
Where S = substrate

Excitation with UV near-Vis. light at the O $\rightarrow$ M charge transfer (CT) band, renders POM powerful oxidizing reagents
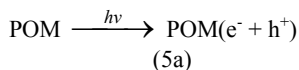
Avoiding for simplicity reasons the preassociated complex

$$POM \xrightarrow{hv} POM^* \tag{5}$$
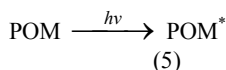
In analogy with metal oxide particulates, excitation of POM can be considered as electron (e^-), hole (h^+) separation represented as

$$-W = \overset{..}{\underset{..}{O}} \xrightleftharpoons{hv} W^{\delta-} - \overset{..}{\underset{..}{O}}{}^{\delta+}$$

Thus using semiconductor notation

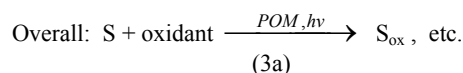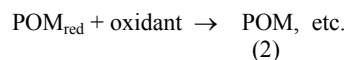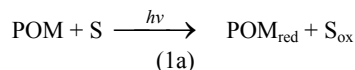$$POM \xrightarrow{hv} POM(e^- + h^+) \tag{5a}$$

The excited POM is able to oxidize and indeed mineralize, as we'll see below, a great variety of organic compounds and for that matter organic pollutants of diversified structure and properties.

In the absence of a strong oxidant continuous illumination accumulates electrons on POM driving the redox potentials to more negative values until an oxidant in the solution is able to act as electron acceptor and close the photocatalytic cycle. We have more to say on the subject later. Reduced POM can be obtained also by a variety of inorganic and organic reductants and electrolysis (6).

Electrons accumulated on POM can be withdrawn by various electron acceptors. In the absence of such oxidants, in deoxygenated solutions, the nice blue color of the reduced POM develops and the photoreaction is easily followed spectrophotometrically, figure 3.

Dioxygen, the most common and benign oxidant, restores the catalyst to the original oxidized form. In the process dioxygen undergoes reductive activation, O_2^-, initiating further oxidations.

The overall reactions involved in this cycle are analogous to those in thermal chemistry (6).

$$POM + S \xrightarrow{hv} POM_{red} + S_{ox} \tag{1a}$$

$$POM_{red} + oxidant \rightarrow POM, etc. \tag{2}$$

$$Overall: \ S + oxidant \xrightarrow{POM, hv} S_{ox}, etc. \tag{3a}$$

As a general rule, molybdates are better oxidants than tungstates, (eqn 1). Their reoxidation, however, requires strong oxidizing reagents. Tungstates, on the other hand, are poor oxidants. However excitation renders
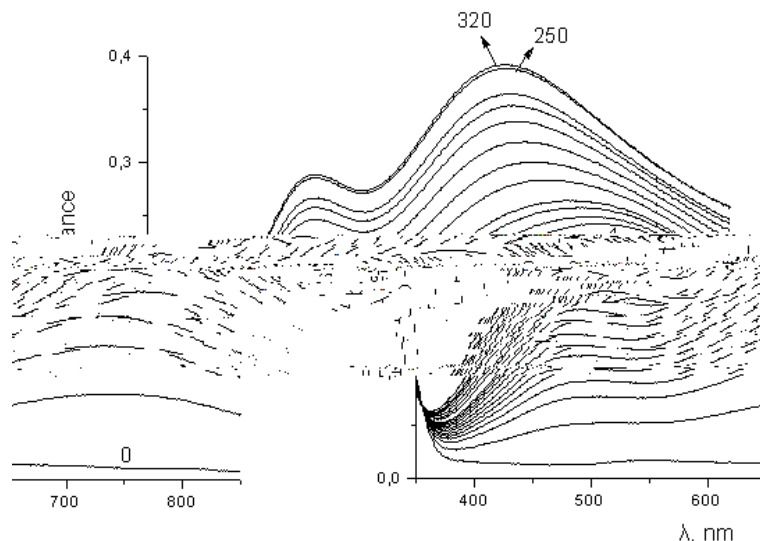
Figure 3. Gradual photoreduction of $PW_{12}O_{40}^{3-}$, showing the successive formation of one-electron (750 nm) and two-electron blue reduction products. $PW_{12}O_{40}^{3-}$, 0.1 mM; propan-2-ol, 2 M; in 0.1 M $HClO_4$, deaerated with Ar. Photolysis with $\lambda > 320$ nm; photolysis time is indicated on spectra.

tungstates powerful oxidizing reagents (eqn. 1a) and due to their fast reoxidation by dioxygen, effective photocatalysts.

The turn over number, i.e., the number of photocatalytic cycles is indeed great and, practically, goes on until the organic substrate has been consumed.

The above is an overall view of the variety of redox reactions that take place in the photocatalytic cycle.

3.1. Similarities with metal oxide particulates
The photochemistry of POM resembles very much the chemistry of semiconductors (7) as mentioned earlier. With respect to the above, it should be noted that, like POM, aggregates of various sizes can be formed by condensation of metal oxides such as TiO_2 or WO_3. Their size depends on the preparation method. Particles with diameter over roughly 15 nm behave, generally, as bulk semiconductors (SC), whereas, smaller particles, say less than 5 nm have, more or less, molecular characteristics and characterized as quantum size clusters or quantum dots. POM, then, in SC terminology, may be considered ideal quantum size clusters, or quantum dots. Impinging light $\lambda > E_g$ (E_g the band gap energy between valence band (VB) and conduction band (CB)) leads to electron (e^-) hole (h^+) separation in analogy to $O \rightarrow M$ CT band, mentioned earlier. It turns out that those two systems have an overall similar behaviour (7). Figure 4 depicts the parallel photocatalytic action of these two systems

3.2. Factors that influence the photocatalytic process
Several factors appear to influence the photocatalytic behavior of both systems: (a) The value of preassociated equilibrium constant (eqn. 4), figures 2, 4 (b)

the excited state life time, (c) the redox potential of POM, (d) the nature of organic substrate and (e) the pH of the solution which seems to exert an important influene at the reoxidation rate of reduced POM by dioxygen (8) and other oxidants.

The differences in the photochemical behavior that exists between tungstates and molybdates ought to be mentioned. Figure 5 shows plots of the quantum yields (QY) of the 1-electron reduced POM with concentration of S. (QY is the number of molecules of reactant consumed or product formed, per photon absorbed).

It can be seen that in order to reach saturation (i.e., zero-order kinetics) the required concentration of S (propan-2-ol) is $\cong 0.1$ M for tungstate and $\cong 10$ M for molybdate. The latter one coupled with the fact that reduced molybdates are very resistant to reoxidation, makes the photocatalytic behavior of polyoxomolybdates very poor.

An advantage, from theoretical point of view, of POM relative to metal oxide particulates is that POM have well defined structures and properties and their redox chemistry involves stepwise addition and removal of electrons easily followed spectrophotometrically (7). We provide some typical examples in every case.

4. PHOTOOXIDATION OF ORGANIC COMPOUNDS

Practically all organic compounds upon illumination in the UV near-visible area in the presence of POM undergo oxidation, reacting either directly with the excited state (eqn. 6)
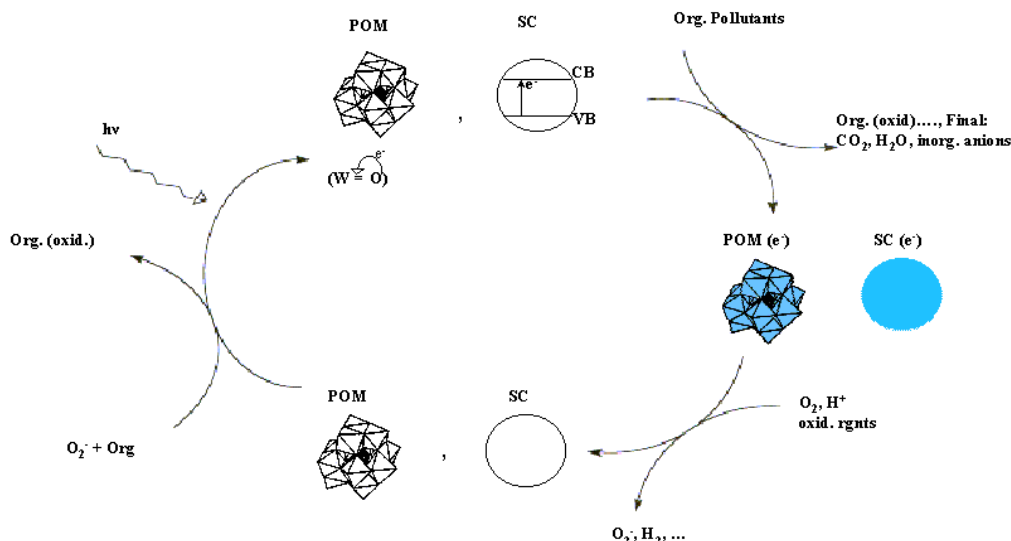
Figure 4. Schematic diagram showing the parallel photocatalytic action of POM and semiconducting particles.
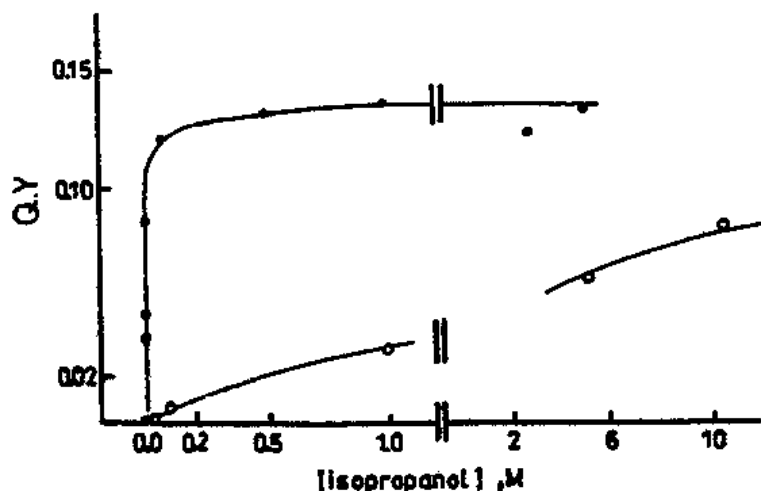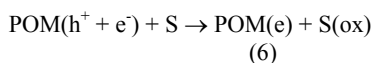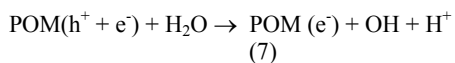

Figure 5. Variation of quantum yield (Q.Y) of the one-electron reduced POM with concentration of propan-2-ol at 252 nm, in 0.1 M $HClO_4$; (each point represents at least five measurements with different concentrations of POM that secure 100% absorption at 252 nm). Concentration range $(0.8 – 80) \times 10^{-4}$ M for $PW_{12}O_{40}^{3-}$ • • and $P_2Mo_{18}O_{62}^{6-}$ o o , respectively.

$$POM(h^+ + e^-) + S \rightarrow POM(e) + S(ox)$$
$$(6)$$

or, indirectly via OH radicals (eqn. 7)

$$POM(h^+ + e^-) + H_2O \rightarrow POM(e^-) + OH + H^+$$
$$(7)$$

(where $POM(e^- + h^+) = POM^*$)

Whether the excited POM reacts with organic substrates directly, i.e., via (h^+), or indirectly via OH radicals, the process results in oxidation of the organic compound and reduction of the catalyst POM.

There is ample evidence that the excited catalyst reacts also with H_2O (oxidative hole trapping) creating surface bound OH radicals (9), resulting in indirect reaction of excited POM with substrate: (a) ESR trapping experiments have detected OH radicals(10, 11). (b) OH adduct (hydroxylation products) have been detected in photolysis experiments involving a variety of organic compounds (pollutants) (12, 13); see below. It should be mentioned that an argument goes on as to whether the OH adduct is a product of OH addition in substrate R or it is a hole addition followed by hydrolysis, as shown below.

$$R + OH \rightarrow ROH$$
or
$$R + h^+ \rightarrow R^+$$
$$R^+ + H_2O \rightarrow ROH + H^+$$
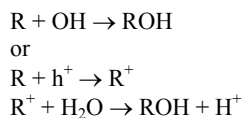
(This argument has been mainly raised with metal oxide particulates). (c) A H-abstraction mechanism, creating radical R, which has all characteristics of OH
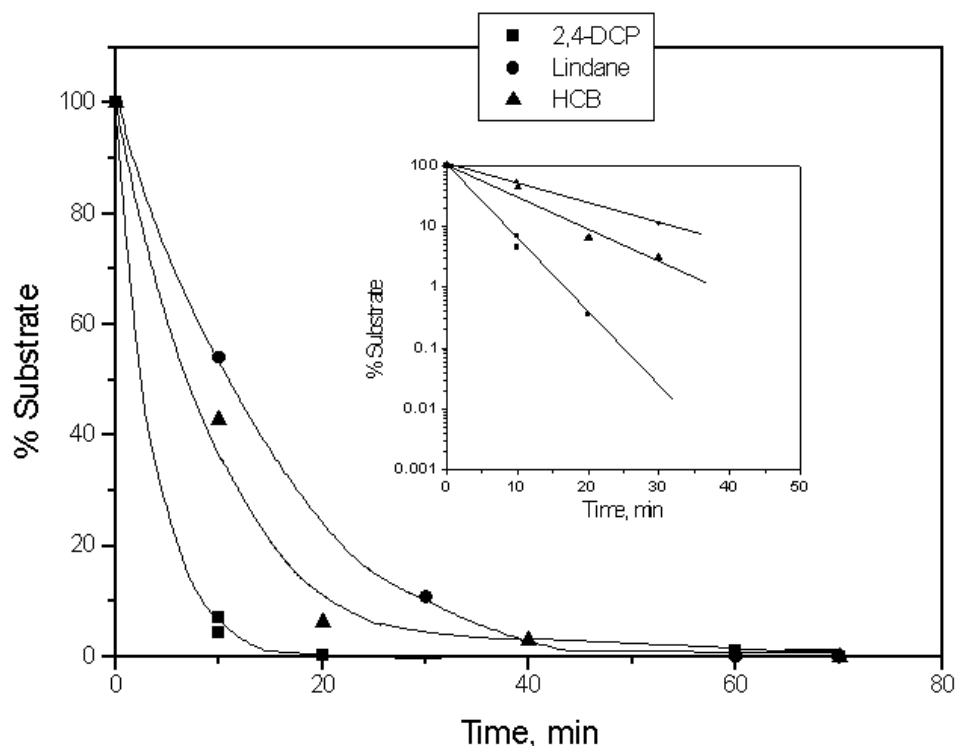
Figure 6. Photodegradation of 2,4DCP 4 10^{-4} M, lindane 3.7 10^{-5} M and partially dissolved, HCB 7.0 10^{-6} M ($\approx$2 ppm), upon photolysis of oxygenated aqueous solutions (0.1 M $HClO_4$) in presence of $PW_{12}O_{40}^{3-}$ 7 10^{-4} M. T $\cong$ 20 ^{0}C. Insert: Pseudo first-order diagrams for the decomposition of the substrates. The scattered results with HCB are in accordance with the partial dissolution of substrate.

radical attack on organic substrates RH seems to prevail (6, 9). (d) The generation of OH radicals is also suggested by the high oxidizing ability of the excited POM which like excited metal oxide particulates is able to oxidize H_2O

$$OH + H^+ + e^- \rightarrow H_2O \quad E = 1.90 \text{ V vs. NHE}$$

Direct reaction of the excited POM with S has been also shown to take place. Firstly, the photochemistry in inert organic solvents, as it will be discussed below, proceeds in the absence of water and, therefore, OH radicals. Experiments performed with POM dissolved in pure substrate have shown that photoreactions proceed, most of the time, considerably slower than the corresponding reactions through OH radicals. Generally, experiments have shown that the rate of photooxidation of an organic substrate decreases as the ratio substrate/water increases, following a peak performance (9).

However, the formation of OH radicals by POM cannot be generalized. Recent laser flash photolysis kinetics by Texier et al of excited $W_{10}O_{32}^{4-\,*}$ with a variety of organic compounds, rather exclude the possibility of taking place through OH radicals (14). Also photochemical experiments, in the presence of OH radical scavengers, suggest that the predominant oxidation of organic compounds is the direct reaction. The argument, however, has not been settled and it is not only of academic interest. Reactions through OH radicals, i.e., through a common

powerful oxidizing reagent, means lack of selectivity on the catalyst part, whereas, direct redox reactions ought to be regulated by the structure, redox potential etc., of the excited catalyst.

4.1. Mineralization of organic pollutants.

The reaction of the substrates either directly with the excited state, or indirectly via OH radicals, results in complete photodecomposition (i.e., mineralization to CO_2, H_2O and inorganic anions) of practically all organic compounds and for that matter organic pollutants. In other words, the organic substrates act as adsorbed traps for the photogenerated holes and/or "surface" OH radicals created on illuminated POM, as mentioned earlier.

The polyoxotungstates that have been mainly studied are $PW_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$ and the isopoly compound $W_{10}O_{32}^{4-}$. As a matter of information, the stability of these compounds in aqueous solution varies with pH. ($PW_{12}O_{40}^{3-}$ is stable at pH 1; $SiW_{12}O_{40}^{4-}$ up to pH 5,5 and $W_{10}O_{32}^{4-}$ is stable for a few hours at pH 2.5). These compounds effectively decompose a variety of organic pollutants. Pesticides, incecticides, pollutants of diversified structures and properties, all undergo mineralization upon illumination in the presence of POM (7). Figure 6 demonstrates the effectiveness of POM catalysts in the photodecomposition of diversified organic pollutants (15).
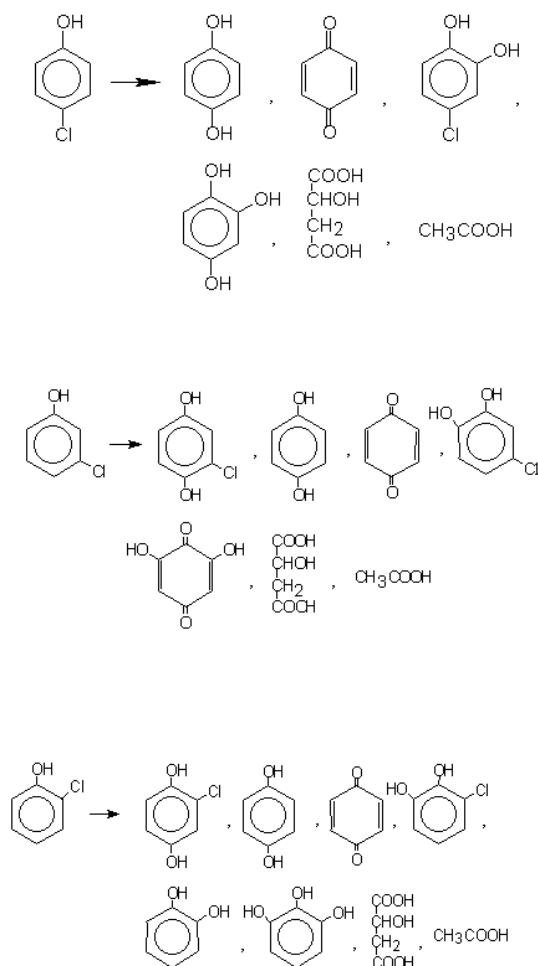
Scheme 1. Intermediates detected during the course of mineralization of chlorophenols by polyoxotungstates, that are in accordance with the electrophilicity of OH radicals. (Reprinted with permission from ref. 13).

The only exception so far is atrazine which photodecomposes to cyanuric acid that undergoes no further decomposition (16). Similar behavior is also experienced by TiO_2, see below.

The photodecomposition proceeds via the formation and decay of several intermediates formed by OH addition (hydroxylation), dehalogenation, deamination, decarboxylation, dealkylation, H-abstraction, breaking of C-C bond in aliphatic and aromatic compounds. Prior to CO_2 evolution, short chain aliphatic acids and acetic acid have been detected.

Notice that POM being at their highest oxidation state (all tungsten are W^{6+}) participate in the photoredox processes, at the beginning, exclusively as oxidants. However, the formation of CH_2 and CH_3 groups detected in the intermediates that result, from aromatic carbon (i.e. CH groups) implies that there is a reductive (hydrogenation) pathway besides the oxidative process. Some characteristic examples follow: Scheme 1 illustrates the intermediates and final degradation products formed by orho, meta and

para chlorophenols illuminated in the presence of POM. Figure 7 depicts the characteristic profile of the photodegradation of ortho-chlorophenol (o-ClPh), i.e., the formation and decay of some intermediates and the gradual development of the final degradation products CO_2 and Cl^- (13)

Another example shows the photodecomposition of 2,4,6-trichlorophenol (2,4,6-TCP) and the development of the final degradation products, i.e., CO_2 and Cl^-, (figure 8), whereas, scheme 2 registers some of the intermediates detected in the process (17).

The only case so far in which mineralization of the organic compound has not been observed is atrazine, as mentioned earlier. The pathways of photodecomposition are indicated in Scheme 3.

The final product is cyanuric acid. Interesting enough, cyanuric acid has also been detected as the final product of atrazine photodecomposition with TiO_2 and sonolysis. This is another indication that photodecomposition of organic compounds by POM and metal oxide particulates (TiO_2) takes place via a common reagent, OH radicals.

All photocatalytic processes with POM follow first order kinetics (figures 6 and 9).

4.2. Selective vs. non-selective oxidations
Despite the complete photocatalytic decomposition of organic compounds in the presence of POM, selective oxidations have been reported.

Photoreactions with POM in inert organic solvents seem to be more under control compared to reactions in aqueous solutions.

Various schemes for the dehydrogenation, alkylation, vinylation, carboxylation, acylation and oxidation of alkanes have been reported. Some general rules on the fate of the radical R formed from the reactions of an excited POM with a substrate RH, as mentioned earlier, have been provided by Hill (18).

$$POM^* + RH \rightarrow POM_{red} + R + H^+$$
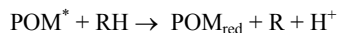
Hill suggests that the radical R. can be reduced by POM_{red} to form a carbanion, or may be oxidized by POM_{ox} to form a carbocation, depending on the redox potential of POM. The radical may also dimerize or undergo radical cross coupling with another radical, or dehydrogenation (18).

Selectivity has been reported also to take place in aqueous media. Thus, primary alcohols have been selectively photooxidized to aldehydes and secondary to ketones (6).
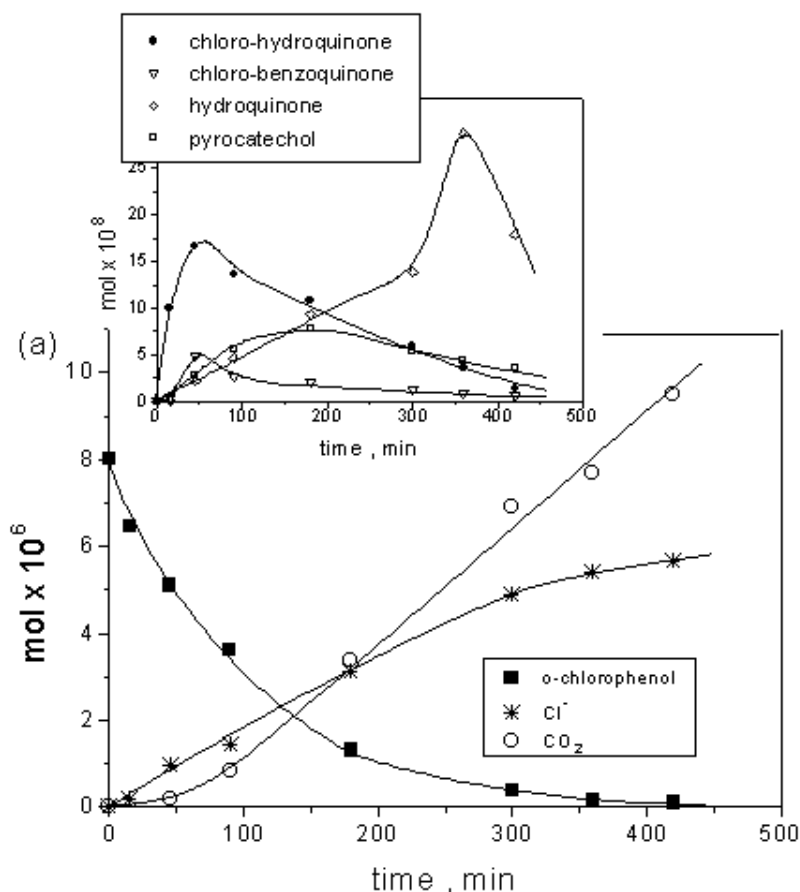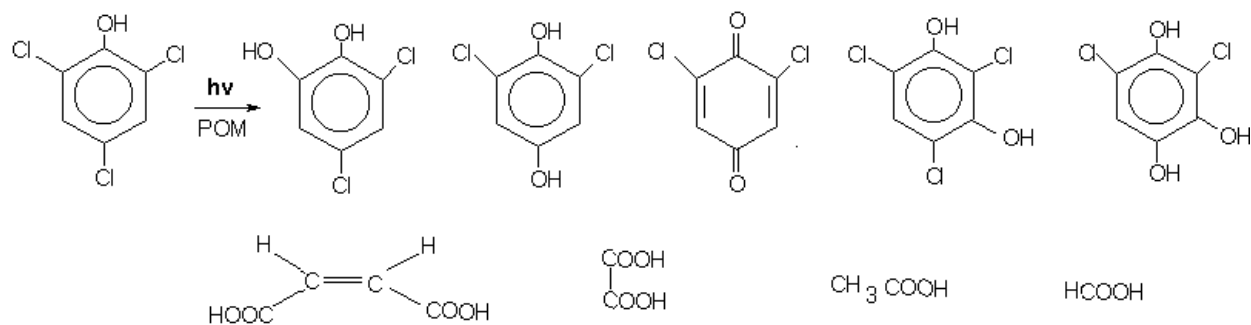
$$(CH_3)_2CHOH + 1/2O_2 \xrightarrow{hv, POM} (CH_3)_2CO + H_2O$$
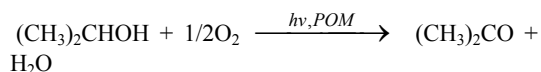
Figure 7. Photodecomposition of ortho-chlorophenol (2.0 mM), formation of CO_2 and Cl^- and (insert) formation and decay of some intermediates, upon photolysis of substrate in the presence of $W_{10}O_{32}^{4-}$ (0.7 mM); $\lambda > 320$ nm, pH 2.5 (HClO$_4$), T 20 ^{0}C. (Reprinted with permission from ref. 13).


Scheme 2. Intermediates detected during photolysis of 2,4,6-TCP in the presence of $PW_{12}O_{40}^{3-}$. Experimental conditions as in figure 8. (Reprinted with permission from ref. 17).

In addition, allyl $CH_2=CHCH_2OH$ and prop-2-ynyl (propargyl) $CH\equiv CCH_2OH$ alcohols result in oxidation only of the alcoholic moieties, leaving the double and triple carbon-carbon bonds intact (6).

In view of the formation of the highly oxidizing OH radicals in the photocatalytic process, selective oxidation seems rather strange. However, detail examination of the photo-oxidation of propan-2-ol to propanone in the presence of $PW_{12}O_{40}^{3-}$ ($\lambda > 320$ nm), showed that selectivity is, as ought to be, kinetically controlled (9). For instance, the rate of photo-oxidation of propan-2-ol is two orders of magnitude faster than the rate of photo-oxidation of propanone. This, by the way is, in agreement with the differences in the rates of reactions of OH radicals with these two species. Prolonged

820
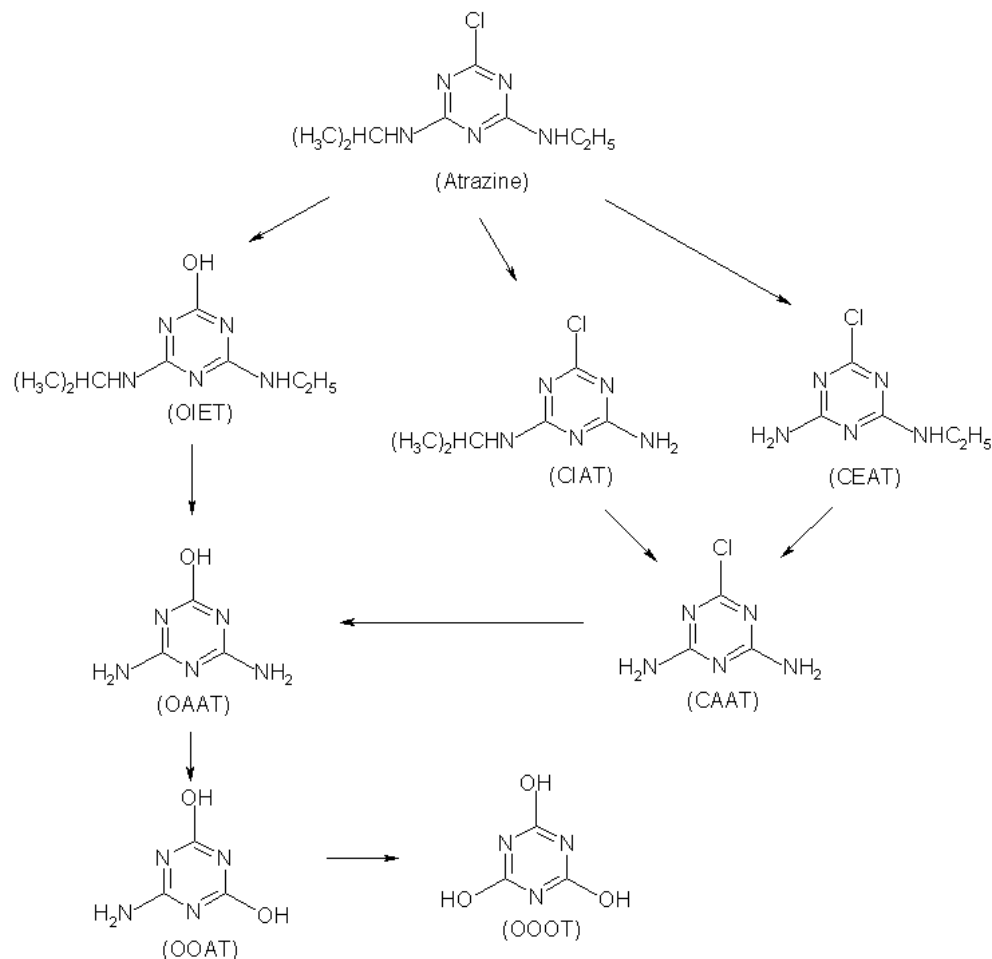
Scheme 3. Degradation pathways of atrazine upon photocatalytic treatment in the presence of $SiW_{12}O_{40}^{4-}$ or sonochemical treatment. (Reprinted with permission from ref. 16).
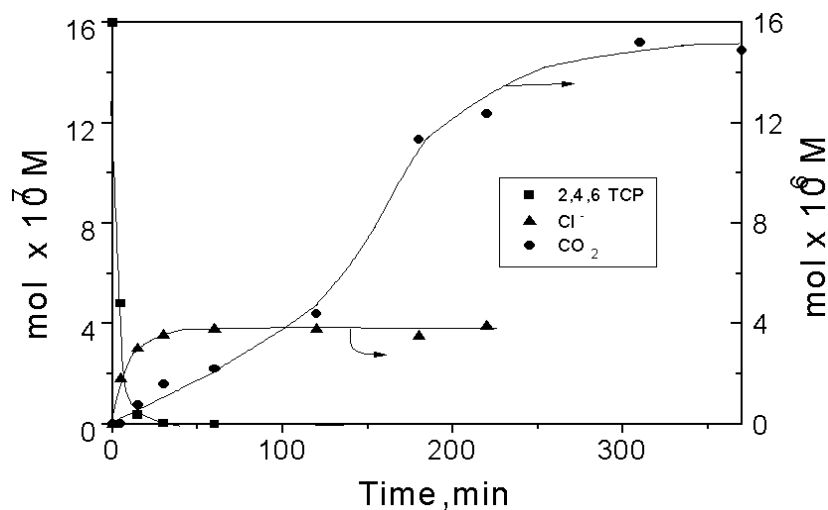

Figure 8. Formation of CO_2, Cl^- and decay of 2,4,6-TCP upon photolysis of aqueous oxygenated solution of substrate, in presence of catalyst: 2,4,6-TCP 0.4 mM, $PW_{12}O_{40}^{3-}$ 0.7 mM, pH 1 ($HClO_4$), $\lambda > 320$ nm, T~20° C. (Reprinted with permission from Ref. 17).
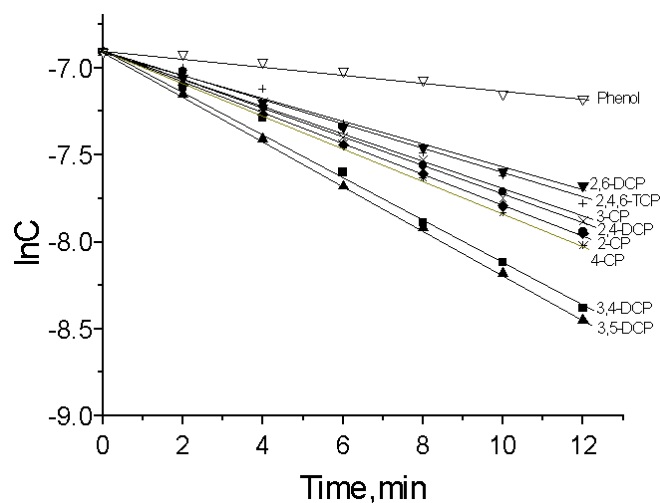
Figure 9. First order plot for the photodecomposition of phenol and various chlorophenols, in the presence of catalysts. Substrates 1 mM, $PW_{12}O_{40}^{3-}$ 0.7 mM, oxygenated solutions, pH 1 ($HClO_4$), $\lambda > 320$ nm, T 20 ^{0}C. (Reprinted with permission from ref. 17)
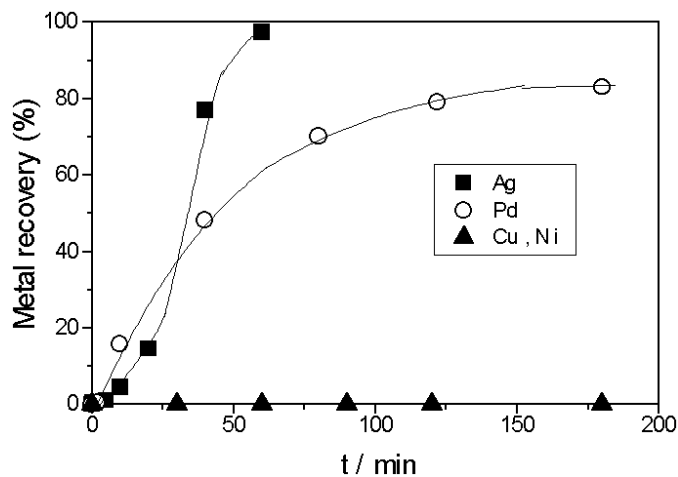
Figure 10. Recovery of metals through photolysis of a solution containing $PW_{12}O_{40}^{3-}$ 0.7 mM, 2,4-DCP 1 mM and M^{n+}, 1.2 mM. pH 1 ($HClO_4$), $\lambda > 345$ nm, T 20 ^{0}C. (Reproduced by permission of The Royal Society of Chemistry (RSC) on behalf of the Centre National de la Recherche Scientifique (CNRS) from Ref. 21).

Figure 11. Diminishing of Cu^{2+} concentration in deaerated aqueous solutions containing propan-2-ol 0.5M, $K_4SiW_{12}O_{40}$ 0.07 mM, Cu^{2+} 2 mM at pH 5, $NaClO_4$ 0.1 M ($\lambda > 320$nm, T 18^0), as a function of illumination time. (Reprinted with permission from Ref. 24).

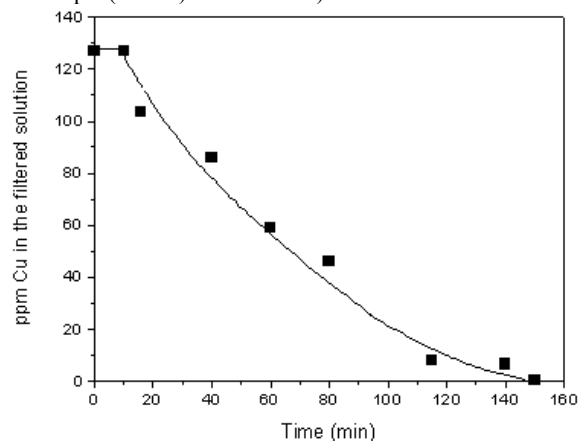illumination of propan-2-ol in the presence of POM leads to CO_2 as has been the case for numerous aliphatic and aromatic compounds (9).

5. REOXIDATION-REGENERATION OF CATALYSTS

5.1. Diversified oxidants, dioxygen

Illumination of organic species in the presence of POM results in oxidation of organic compounds and reduction of POM. Continuous illumination keeps accumulating electrons on the catalyst (figure 3) driving the redox potentials to more negative values until a species in the solution is able to accept the electrons (6). The reduced POM are now capable of reducing a diversified number of chemicals. It should be emphasized that an advantage with POM is that the photochemical and thermal redox reactions, in other words the photoreduction and thermal reoxidation of POM, are discrete processes that can be separated by time and space according to our will. Thus, in the absence of dioxygen, the redox potential reach negative enough values to reduce, from a thermodynamic point of view, H^+ to hydrogen. At this point a steady state is obtained at which the rate of photoreduction of POM is matched by the rate of its reoxidation by H^+ (H_2-evolution). The same holds true for other oxidants (eqn. 2). Unfortunately, the quantum yield for hydrogen production is only about 1%, and it is far from being of any practical value (6).

$$POM(e^-) + H^+ \rightarrow POM + 1/2H_2$$
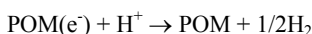
Dioxygen is the most effective oxidant. Its presence restores the catalyst to the original oxidized form thus closing the photocatalytic cycle

$$2POM (e^-) + 1/2O_2 + 2H^+ \rightarrow 2POM + H_2O$$
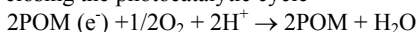
Dioxygen in the process undergoes reductive activation forming superoxy radical, O_2^-, that can cause further oxidation to the organic species in solution as mentioned earlier, (figures 2, 4).

$$POM(e^-) + O_2 \rightarrow POM + O_2^-$$
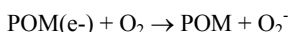
Electrons accumulated on POM can be delivered to other species, as mentioned earlier, producing interesting products. Thus, various para substituted nitrobenzenes have been reduced to the corresponding anilines by photochemically reduced POM in CH_3CN (19)

$$6\ POM(e^-) + p\text{-}XC_6H_4NO_2 \rightarrow 6\ POM + p\text{-}XC_6H_4NH_2 + 2\ H_2O$$
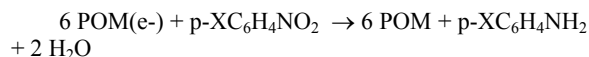
Other examples involve the important reduction of CO_2 to CH_4 roported by Yamase and coworkers by photolysis of $(PTi_2W_{10}O_{40})^{7-}$ in the presence of CH_3OH (20). In this process the catalyst serves as multielectron relay, in that it is photoreduced by CH_3OH, as has been described previously and then delivers the electrons to CO_2 reducing it to CH_4, H_2, etc.

$$(PTi_2W_{10}O_{40})^{7-} + CH_3OH + CO_2 \rightarrow \ldots CH_4 + H_2 + HCHO$$
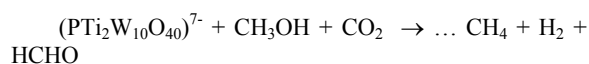
5.2. Metal ions
5.2.1. Reduction precipitation

Recently, a novel photocatalytic method for the selective reduction and recovery of several metal ions from their aqueous solutions based on POM has been reported (21).

By suitable choice of POM and organic substrate, several metal ions can be reduced to a lower or zero oxidation states via the thermal reaction 2 in which the oxidant are in this case metal ions.

$$POM(e^-) + M^{n+} \rightarrow POM + M^{(n-1)+}$$
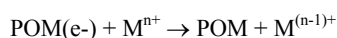
This is in analogy to what has been observed with TiO_2 and other metal oxide particulates (23). Metal ions, M^{n+}, such as Ag^+, Cu^{2+}, Pd^{2+}, Au^{3+}, Hg^{2+} etc., precipitate out from aqueous solutions through a cyclic process that involves, overall, light induced ($h^+ + e^-$) separation in TiO_2, followed by hole oxidation of the organic species and electron reduction of metal ions. An advantage offered by POM relative to TiO_2, we might say, is that, by selecting POM with appropriate redox potentials and organic substrates whose intermediates do not interfere with the process, selective reduction of metal ions can be obtained.

The homogeneous, polyoxometalate-based process exhibits some benefits in comparison with the semiconductor-based (heterogeneous) recovery of metals: The final zero state metal particles are obtained in pure form. No separation from the catalyst is needed and, moreover, the process is catalytic as the photodeposited metal particulates do not hinder the photocatalytic action of polyoxometalate anions.

This way, photocatalytic decontamination of aqueous solutions, from organic pollutants and metal ions can take place, upon illumination in the presence of POM

Figure 10 shows the recovery of metals through illumination of a solution containing $PW_{12}O_{40}^{3-}$ and 2,4-dichlorophenol (21).

Thermal (eqn. 2) between POM and M^{n+} follows thermodynamics, i.e., it depends on the redox potential of the species involved. Thus 12-tungstophosphate with a redox potential $E^0(PW_{12}O_{40}^{3-/4-}) = 0.221$ V vs NHE reduces and precipitates out silver and palladium but not copper (figure 10), whereas, 12-tungstsilicate, $E^0(SiW_{12}O_{40}^{4-/5-}) = 0.057$ V vs NHE recovers copper from a Cu^{2+} aqueous solution, figure 11 (24).

Despite the fact that dioxygen is an effective oxidant for reduced polyoxotungstates, its presence hardly affects the removal of Ag^+ from an illuminated solution $(SiW_{12}O_{40}^{4-}/\text{propan-2-ol}/Ag^+)$. On the contrary, thiosulphate, the fixing reagent in photographic processes which complexes silver ions, lowers the potential of, for instance $Ag(S_2O_3)_2^{3-} / Ag^0$ to 0.01 V vs. NHE preventing thoroughly the reduction of Ag^+.
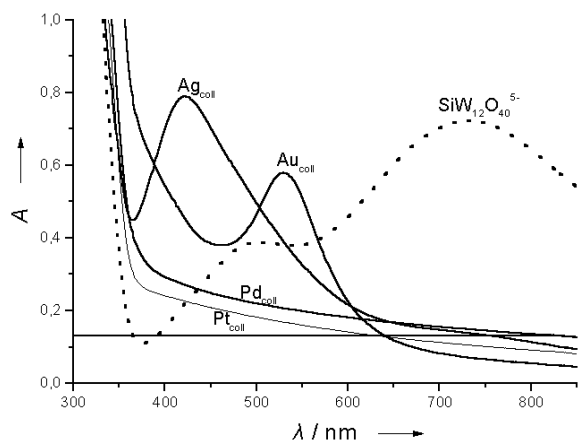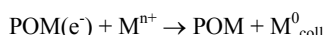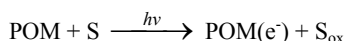
Figure 12. Absorption spectra of metal nanoparticles (Ag, Au, Pd, Pt) in solution, obtained after thermal reaction of photogenerated 1-equivalent reduced POM, $SiW_{12}O_{40}^{5-}$, ca 0.35 mM (spectra also shown), with the corresponding metal ions (Ag^+, Pd^{2+}, $PtCl_6^{2-}$ (0.1 mM) or $AuCl_4^-$ (1 mM)); pH 5. (Reprinted with permission from Ref. 29).

5.2.1. Formation of metal nanoparticles

The formation of metal nanoparticles is a challenging process from fundamental and practical point of view. Metal nanoparticles have been obtained by various methods, i.e., thermal (25), photochemical (26, 27), radiolytic (28), etc., using various reagents.

The diversified redox chemistry of POM and the fact that the reactions

$$POM + S \xrightarrow{h\nu} POM(e^-) + S_{ox}$$

$$POM(e^-) + M^{n+} \rightarrow POM + M^0_{coll}$$

can be separated in time and space or take place in one pot system, makes these compounds capable of functioning as new multifunctional mediators showing both reducing and stabilizing ability in the synthesis of metal nanoparticles.

Figure 12 shows the absorption spectra of metal nanoparticles (Ag, Au, Pd, Pt) obtained after thermal reaction of photogenerated 1-equivalent reduced 12-tungstosilicate $SiW_{12}O_{40}^{5-}$ with the corresponding metal ions (29).

6. PERSPECTIVES

POM are important photocatalysts functioning as electron and multielectron relays for a variety of redox reactions that involve: (a) selective oxidation of organic compounds, (b) non-selective oxidation (i.e., mineralization to CO_2, H_2O and inorganic anions) of a great variety of organic pollutants and (c) reduction of several organic and inorganic species. This indeed rich photochemical behavior has not as yet been accompanied by any commercial exploitation. The reason is that POM like metal oxide particles, carry several inherent problems. Firstly, they have a small absorption in the visible, i.e., they

are poor antennas for harvesting solar energy and secondly their recovery is not an easy task. Whereas, the first problem is an ever-present challenge, several recent reports on the effective immobilization of POM on various surfaces appear very encouraging. Other promising areas of research seem to be the exploration of selective redox reactions mediated by the great variety of POM as well as their photocatalytic role as reducing reagents and stabilizers in the formation of metal nanoparticles.

7. ACKNOWLEDGEMENT

8. REFERENCES

1. See special issue devoted to POM Chemistry, Guest Editor C.L. Hill, *Chem. Rev.* 98, 1-390 (1998)

2. Rindl M, A Reversible Photochemical Reaction. *S. Afr.. J. Sci.* 11**,** 362-366 (1916)

3. Chalkley L, The Extent of the Photochemical Reduction of Phosphotungstic Acid. *J. Phys. Chem.* 56**,** 1084-1086 (1952)

4. Pope M.T. and E. Papaconstantinou, unpublished data.

5. Mizuno N & M. Misono: Heterogeneous Catalysis. *Chem. Rev.* 98, 199-217 (1998)

6. Papaconstantinou E: Photochemistry of Polyoxometallates of Molybdenum and Tungsten and/or Vanadium. *Chem. Soc. Rev.* 16, 1-31 (1989)

7. Hiskia, A., A. Mylonas, E. Papaconstantinou: Comparison of photoredox properties of polyoxometallates and semiconducting particles, *Chem. Soc. Rev.* 30**,** 62-69. (2001)

8. Hiskia, A, E. Papaconstantinou: Photocatalytic Oxidation of Organic Compounds by Polyoxometalates of Molybdenum and Tungsten. Catalyst Regeneration by Dioxygen, *Inorg. Chem.*31*,* 163-167 (1992)

9. Mylonas, A, A. Hiskia, E. Androulaki, D. Dimotikali & E. Papaconstantinou: New aspect of the mechanism of photocatalytic oxidation of organic compounds by polyoxometalates in aqueous solutions. The selective photooxidation of propan-2-ol to propanone: the role of OH radicals. *Phys. Chem. Chem. Phys.*1, 437-440 **(**1999)

10. Yamase, T. & T. Kurozumi: Photoreduction of Polymolybdates(VI) in Aqueous solutions Containing Acetic Acid, *J. Chem. Soc., Dalton Trans.* 2205-2209 (1983)

11. Maldotti, A, R. Amadelli, G. Varani, S. Tollari & F. Porta: Photocatalytic Processes with Polyoxotungstates:

Oxidation of Cyclohexylamine, *Inorg. Chem.*, 33, 2968-2973 (1994)

12. Einaga, H. & M. Misono: Photocatalysis of $H_3PW_{12}O_{40}$ for 4-Chlorophenol Decomposition in Aqueous Media. *Bull. Chem. Soc. Jpn.*, 69, 3435-3441 (1996)

13. Mylonas, A & E. Papaconstantinou: On the Mechanism of Photocatalytic Degradation of Chlorinated Phenols to CO_2 and HCl by Polyoxometalates, *J. Photochem. Photobiol. A: Chem.* 94, 77-82 (1996) and references therein.

14. Texier, I, J.A. Delaire & C. Giannotti: Reactivity of the Charge Transfer Excited State of Sodium Decatungstate at the Nanosecond Time Scale, *Phys. Chem. Chem. Phys.*, 2, 1205-1212 (2000)

15. Hiskia A, E. Androulaki, A. Mylonas, S. Boyatzis, D. Dimotikali, C. Minero, E. Pelizzetti & E. Papaconstantinou: Photocatalytic mineralization of chlorinated organic pollutants in water by polyoxometalates. Determination of intermediates and final degradation products. *Research Chem. Intermediates*, 26, 235-251 (2000)

16. Hiskia, A, M. Ecke, A. Troupis, A. Kokorakis, H. Hennig & E. Papaconstantinou: Sonolytic, Photolytic and Photocatalytic Decomposition of Atrazine in the Presence of Polyoxometalates. *Environ. Sci. Technol*. 35, 2358 – 2364 (2001)

17 Androulaki E, A. Hiskia, D. Dimotikali, C. Minero, P. Calza, E. Pelizzetti & E. Papaconstantinou: Light induced elimination of mono- and polychlorinated phenols from aqueous solutions by $PW_{12}O_{40}^{3-}$ The case of 2,4,6-trichlorophenol. *Environ. Sci. Technol* 34, 2024-2028 (2000)

18. C.L Hill, & C.M. Prosser-McCartha: Photocatalytic and photoredox properties of polyoxometalate systems, in Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds, Eds. Kalyanasundaram K Gratzel M, Kluwer Academic Publishers, Dordrecht, 307-330. (1993)

19. Amadelli, R, G. Varani, A. Maldotti & V. Carassiti: Reduction of Nitroaromatic Compounds by Photoreduced Heteropolytungstates. *J. Mol. Catal.* 59, L9-L14 (1990)

20. Yamase T, & M. Sugeta: Photoreduction of CO_2 to CH_4 in Water Using Dititanodecatungstophosphate as Multielectron Transfer Catalyst. *Inorg. Chim. Acta* 172, 131-134 (1990)

21. Troupis, A, A. Hiskia, & E. Papaconstantinou: Reduction and Recovery of Metals from Aqueous Solutions with Polyoxometallates, *New J. Chem.* 25, 361-363 (2001)

22. Serpone, N, D. Lawless, R. Terzian, C. Minero & E. Pelizzetti: Heterogeneous photocatalysis. Photochemocal conversion of inorganic substances in the environment: hydrogen sulfide, cyanides and metals, in Photochemical Conversion and Storage of Solar Energy, Eds. Pelizzetti, Sciavello, M, Kluwer Academic Publ., the Netherlands, 451-475 (1991)

23. Litter, M.I.: Heterogeneous photocatalysis. Transition metal ions in photocatalytic systems *Appl. Catal. B: Enviromental.* 23, 89-114 (1999)

24. Troupis, A, A. Hiskia, & E. Papaconstantinou: Photocatalytic Reduction and Recovery of Copper by Polyoxometalates. *Environ. Sci. Technol*., 36, 5355-5362 (2002)

25. Aiken, J.D. III, R.G. Finke: A Review of Modern Transition-Metal Nanoclusters: Their Synthesis, Characterization, and Applications in Catalysis. *J. Mol. Catal.*, 145, 1-44 (1999) and references therein

26. Yonezawa Y. T. Sato, M. Ohno & H. Hada: Photochemical Formation of Colloidal Metals. *J. Chem. Soc. Faraday Trans.* 83, 1559-1567 (1987)

27. Sahyun M.R.V & N. Serpone Primary Events in the Photocatalytic Deposition of Silver on Nanoparticulate TiO_2. *Langmuir* 13, 5082-5088 (1997)

28. Belloni, J, M. Mostafavi, H. Remita, J-L. Marignier & M-O. Delcourt: Radiation induced synthesis of mono- and multi-metallic clusters and nanocolloids. *New J. Chem.*, 1239-1255 (1998)

29. Troupis A, A.Hiskia & E. Papaconstantinou: Novel Synthesis of Metal Nanoparticles Using Polyoxometalates as Photocatalysts and Stabilizers. *Angew. Chem., Int. Ed. Engl.* 41, 1911-1914 (2002)

Send correspondence to: Elias Papaconstantinou, Ph.D. Institute of Physical Chemistry, NCSR Demokritos, 153-10 Athens, Greece, Tel.: 30-210-6503642-3, Fax: 30-210-6511766, E-mail: epapac@chem.demokritos.gr