Contribution to water purification using polyoxometalates. Aromatic derivatives, chloroacetic acids

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Abstract

Polyoxometalates appear to be effective photocatalysts for a variety of organic pollutants, leading to their decomposition to CO_2 and H_2O and Cl^- in case of chlorinated hydrocarbons. Various aromatic derivatives and chlorinated acetic acids, undergo mineralization upon photolysis with near visible and UV light, in presence of $W_{10}O_{32}^{4-}$, $PW_{12}O_{40}^{3-}$, and $SiW_{12}O_{40}^{4-}$. These catalysts are, at least, as effective as TiO_2. The main oxidant appears to be OH radicals formed by the reaction of the excited polyoxometalates with H_2O. At the initial stages of photoreaction, dioxygen has a profound effect (up to eighteen times faster) on the photodegradation of chloroacetic acid, whereas, it has minor effect on chlorophenols. On the contrary, at the final stages of photodegradation of chlorophenols, the rates were an order of magnitude faster in presence than in absence of dioxygen. Substitution of W–O moiety of $SiW_{12}O_{40}^{4-}$ for transition metals, namely, $[H_2OMn^{II}SiW_{11}O_{39}]^{6-}$ and $[H_2OCu^{II}SiW_{11}O_{39}]^{6-}$ reduced, by about an order of magnitude, the effectiveness of the catalyst.

Keywords: Aromatic hydrocarbons; Chloroacetic acids; Photodegradation; Photocatalysis; Polyoxotungstates

1. Introduction

Uncontrollable population growth, energy consumption and industrial development, has become a serious problem that leads to an ever increasing contamination of land, water and air. It is, at least, hopeful that the industrial world, that bears the main responsibility for the earth's pollution, has recognized the problem and already works in two directions: (a) to find new industrial nonpolluting methods (green technology) and (b) to find methods to clean the environment. This paper addresses the second part.

Various methods have been used for the degradation of pollutants [1]. Those that involve electromagnetic radiation are: (a) Treatment with ^{60}Co-γ-radiation [2], (b) UV light [3,4], (c) UV light in presence of H_2O_2, or O_3 [5], and (d) UV and near visible light in presence of TiO_2 [6–8]. Methods (a), (c) and (d) lead, more or less, to decomposition to CO_2 and H_2O.

The chemistry of polyoxometalates (POM) is among the fastest growing [9–11], especially in the field of catalysis [12,13]. A recent review by Hill on a specific category of POM, namely catalysis by transition metal substituted and mixed POM, numbers over two hundred papers for the last three years [14]. Undoubtedly, the very specific properties of POM and the modern analytical instrumentation are key factors to this progress. POM can function as very strong acids, stronger than perchloric acid and participate in redox reactions as electron and oxygen relays.

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This paper addresses the issue of decontamination of water from some representative aromatic and aliphatic compounds, mainly chlorinated hydrocarbons, presenting new data on the mineralization of chlorinated acetic acids in presence of three representative POM $W_{10}O_{32}^{4-}$, $PW_{12}O_{40}^{3-}$, and $SiW_{12}O_{40}^{4-}$. The stability of these catalysts in aqueous solution is as follows: $W_{10}O_{32}^{4-}$ is stable for days at pH = 2.5, whereas, the stability of $PW_{12}O_{40}^{3-}$, and $SiW_{12}O_{40}^{4-}$ is, practically, unlimited at pH = 1 and at the pH range 1–6, respectively. Limited work was also performed with two transition metal substituted $SiW_{12}O_{40}^{4-}$, namely $[H_2OMn^{II}SiW_{11}O_{39}]^{6-}$ and $[H_2OCu^{II}SiW_{11}O_{39}]^{6-}$.

Early work by Yamase and Kurozumi has indicated formation of CO_2 methane and succinic acid, upon photolysis of polymolybdates in aqueous solutions containing acetic acid [15].

2. Experimental

$K_4W_{10}O_{32}$, $H_3PW_{12}O_{40}$, and $H_4SiW_{12}O_{40}$ were prepared according to literature methods [16,17]. The transition metal substituted POM (TMSP) $K_6[H_2OMn^{II}SiW_{11}O_{39}]$ and $K_6[H_2OCu^{II}SiW_{11}O_{39}]$ were prepared from the lacunary α-$K_6SiW_{11}O_{39}$ [18], by addition of $MnSO_4H_2O$ and $CuSO_45H_2O$ respectively [19,20]. All chemicals were of analytical reagent grade and used, unless otherwise stated, without further purification.

Photolysis was performed with an Oriel 1000 W Xe arc lamp, equipped with a cool water circulating filter to absorb the near IR radiation and a 320 nm cut-off filter (Schott, Mainz) to avoid direct photolysis of substrates.

Analysis of the products was performed with a JASCO HPLC equipped with (a) a Uvidec-100-VI detector monitored at 280 and 254 nm for chlorophenols, 254, 270 and 290 nm for phenol and p-cresol and 230 nm for chloroacetic acids and (b) a Lichrospher RP-1885 μm column using 35 vol% CH_3CN in H_2O as eluent for chlorophenols, 7 vol% CH_3COOH in H_2O

as eluent for phenol, 20 vol% CH_3CN in H_2O for p-cresol and 35 vol% CH_3CN in H_2O, pH 2.5 (H_3PO_4) for chloroacetic acids. Products were recognized by comparison with reference standards. Products, mainly, with no reference standards, were recognized with a FISONS TRIO 1000 GC-MS equipped with a DB-5 (60 × 0.25 mm) column using NIST/ NBS and Wiley MS libraries software. Chloride ions were analyzed spectrophotometrically [21]. Gas samples were analyzed for CO_2 in a VARIAN 3300 GC with a TCD and a 2 m Porapack Q column. Carbon dioxide was calculated from a standard curve, made under identical conditions using known quantities of CO_2.

The degree of reduction of POM in photolyzed deaerated solutions was calculated from the known extinction coefficients of the reduced catalysts using a HITACHI U-2000 spectrophotometer.

A typical experiment was as follows: To a 8 mL spectrophotometric cell, 1.0 cm length, covered with a serum cup, 4.0 mL solution of 0.7 mM catalyst, and 2 mM substrate was introduced. Photolysis was performed at constant stirring at 20°C, pH was adjusted with $HClO_4$. Deaerations and oxygenations were performed with extra pure Ar and dioxygen.

3. Results

3.1. Aromatic hydrocarbons

Fig. 1a summarizes the already published results of the photodegradation of three representative aromatic pollutants, namely, p-chlorophenol, phenol, and p-cresol in presence of $PW_{12}O_{40}^{3-}$, whereas, the evolution of CO_2 is shown in Fig. 1b. Similar results have been obtained in presence of $W_{10}O_{32}^{4-}$, and $SiW_{12}O_{40}^{4-}$. Mineralization of these pollutants is also obtained in the absence of oxygen. There are, however, differences in the rates of photodegradation at the initial and final stages in presence and absence of oxygen [22,23].
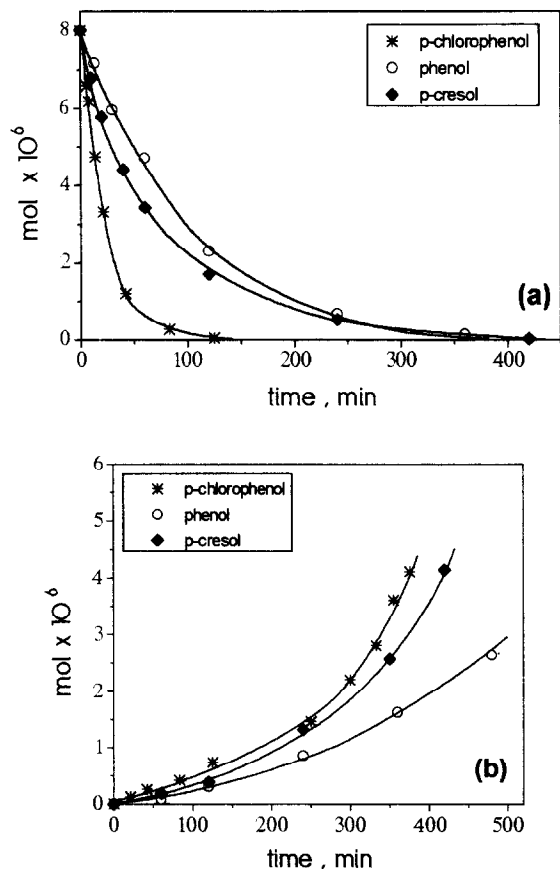
Fig. 1. (a) Photodegradation of p-chlorophenol, phenol, and p-cresol, and (b) evolution of CO_2, upon photolysis of oxygenated aqueous solutions in presence of $H_3PW_{12}O_{40}$. Solution volume 4 mL; catalyst, 0.7 mM; substrate, 2 mM; pH, 1.0 ($HClO_4$); $\lambda > 320$ nm; T, 20°C.

Fig. 3. Comparison of photodegradation of (a) chloroacetic acid, and (b) trichloroacetic acid, upon photolysis of oxygenated aqueous solutions of $H_3PW_{12}O_{40}$. Solution volume, 4 mL; catalyst, 0.7 mM; substrate, 2 mM; pH, 1.0 ($HClO_4$); $\lambda > 320$ nm; T, 20°C.

3.2. Chlorinated acetic acids

3.2.1. In presence of oxygen

Fig. 2 shows the photodegradation of chloroacetic acid and the concomitant evolution of CO_2 and Cl^- in presence of $SiW_{12}O_{40}^{4-}$. Similar results were obtained with the other two catalysts; see below.

Fig. 3 compares the results of photodegradation of monochloro- and trichloroacetic acids the corresponding CO_2 and Cl^- formation in presence of $PW_{12}O_{40}^{3-}$ The considerable slower rate of photodegradation of trichloroacetic acid is noticed.

3.2.2. In deoxygenated solutions

Fig. 4 compares the $W_{10}O_{32}^{4-}$ assisted photodegradation of chloroacetic acid and CO_2 and
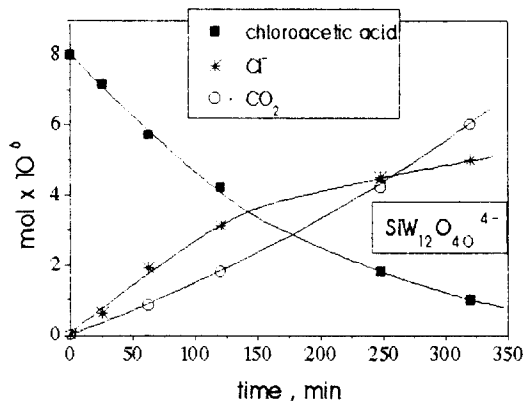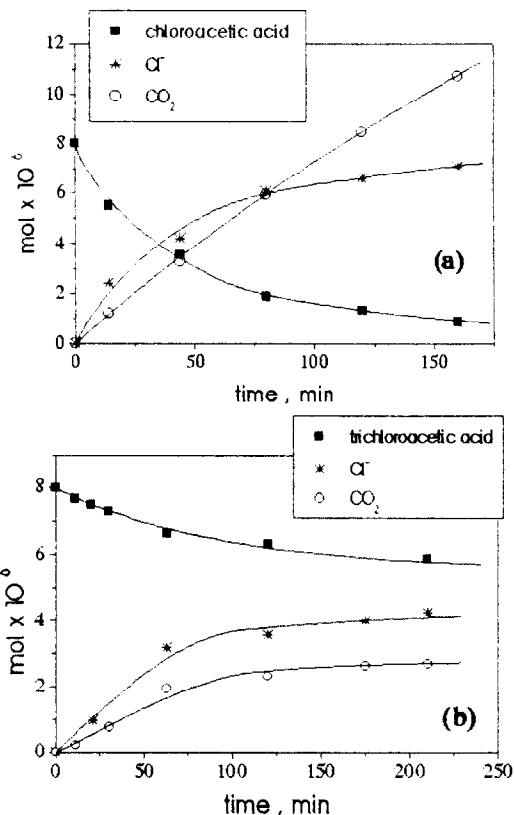

Fig. 2. Photodegradation of chloroacetic acid, and the concomitant evolution of CO_2 and Cl^-, upon photolysis of oxygenated aqueous solution in presence of $H_4SiW_{12}O_{40}$. Solution volume, 4 mL; catalyst 0.7 mM; substrate, 2 mM; pH, 3.0; $\lambda > 320$ nm; T, 20°C.

Cl^- formation in presence (Fig. 4a) and absence of oxygen; Fig. 4b. In deoxygenated solutions the characteristic blue color of reduced POM ($W_{10}O_{32}^{5-}$) is formed and monitored from its known spectra [17,24]. The considerable slower rate of the initial photodegradation in the absence of oxygen is noticed.

Fig. 5 shows the maximum percent of reduction, of the three catalysts in presence of chloroacetic acid obtained in deaerated solu-
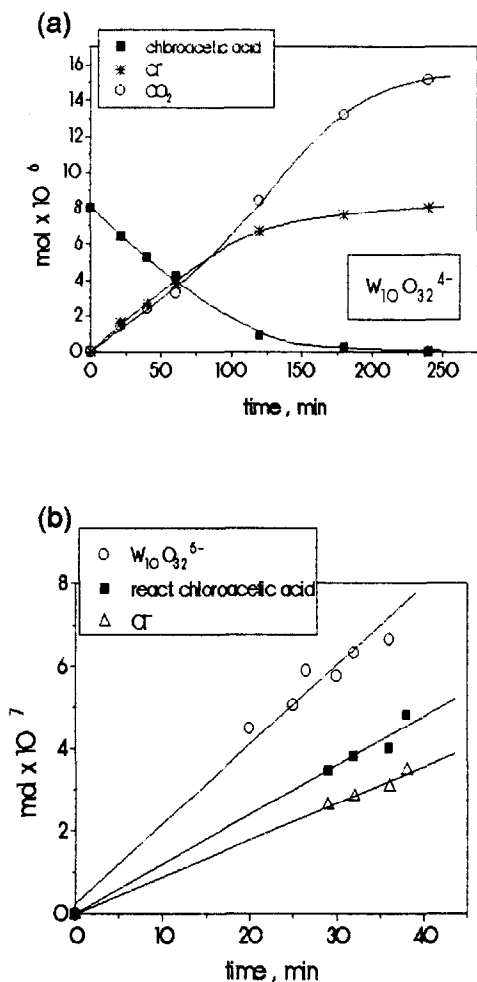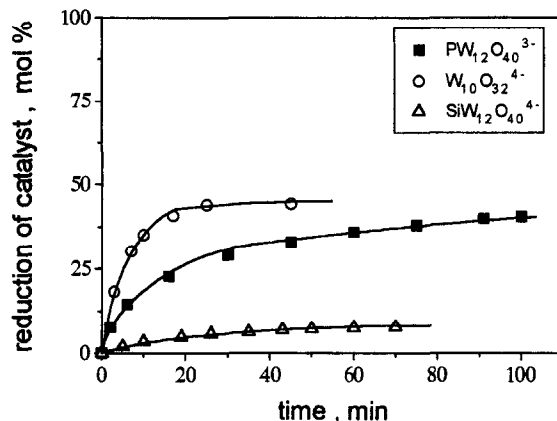

Fig. 5. Variation of maximum percent of reduction of POM (mol%) versus photolysis time, upon photolysis of deaerated aqueous solutions of chloroacetic acid in presence of POM catalysts. Solution volume, 4 mL; catalyst, 0.7 mM; substrate 2 mM; $\lambda > 320$ nm; T, 20°C. pH, 1.0, 2.5, and 3.0 for $PW_{12}O_{40}^{3-}$, $W_{10}O_{32}^{4-}$, and $SiW_{12}O_{40}^{4-}$, respectively (100% reduction means complete by one-electron reduction of catalyst).

tions. Maximum percent reduction denotes a steady state in which the electrons accumulated on the catalyst via the photoreaction can be scavenged, thermally, by an oxidant.

3.3. Further developments. Mineralization of various pollutants by a variety of POM catalysts

Table 1 gives more data on the mineralization of a variety of pollutants upon photolysis, for a certain period of time, and compares the effectiveness of POM and TiO_2. POM catalysts used were the three POM employed throughout this work, plus the two characteristic TMSP derived from $SiW_{12}O_{40}^{4-}$.

The comparative CO_2 evolution of $W_{10}O_{32}^{4-}$, $PW_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$ and TiO_2 from the photodegradation of 4-nitrophenol, 2,4-dimethylphenol, acetic acid, and 1,1,2-trichloroethane is noticed, as well as the practical inactivation of $SiW_{12}O_{40}^{4-}$ upon substitution of one W–O group for Cu^{II}–H_2O and Mn^{II}–OH_2. A comparison of oxidative degradation of thioethers by POM and semiconductors, in aprotic solvents, has been reported by Hill [25].

Fig. 4. The effect of dioxygen in the photodegradation of aqueous solutions of chloroacetic acid in presence of $K_4W_{10}O_{32}$. (a) Oxygenated solution; the decomposition of chloroacetic acid, and the formation of CO_2 and Cl^- are shown. (b) Deoxygenated solution; the formation of the one-electron reduced decatungstate ($W_{10}O_{32}^{5-}$), Cl^-, and the moles of decomposed chloroacetic acid are shown. Solution volume, 4 mL; catalyst, 0.7 mM; substrate, 2 mM; pH, 2.5 ($HClO_4$); $\lambda > 320$ nm; T, 20°C.

4. Discussion

The basic reactions representing redox catalysis by POM are as follows:

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

$$POM_{red} + oxidant \rightarrow POM + oxidant\ products \qquad (2)$$
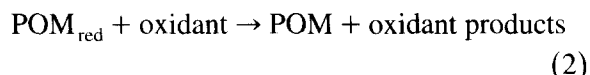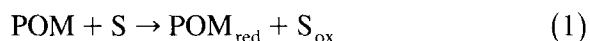
where S = substrate.

Eq. (1) is known to proceed by electron transfer ET and/or hydrogen transfer [26], or oxygen transfer [13], whereas, Eq. (2) restores the catalyst. In case of ET electrons keep accumulating on POM until they can be delivered to various oxidants in solution.

Dioxygen, among others, is a very fast and effective oxidant, Eq. (2), regenerating the catalyst and, as will see below, through reductive activation may participate further in the process.

Absorption of light at the near visible and UV area, i.e., at the oxygen to metal charge transfer (O → M CT) band of POM, enhances their redox capability [26]. For instance absorption of 400 nm light increases the oxidizing ability by ~ 3 eV. Thus continuous photolysis with a cut-off filter 320 nm to avoid possible direct photolysis of substrates, results in mineralization of a great variety of pollutants. This takes place in presence and absence of dioxy-gen, although there are differences discussed below.

The main oxidant seems to be OH radicals generated by the reaction of excited POM with water, as has been the case with TiO_2.

We will present below an overall account of mineralization of various pollutants, providing a step by step explanation of the reactions that take place. We will also compare the behavior of chlorinated acetic acids to the known behavior of some representative aromatic hydrocarbons. Although there are unanswered questions concerning the mode of photodegradation, there are, nevertheless, some points that are well documented.

4.1. POM substrate preassociation

Addition of substrate into a solution results, in all known cases, in a preadsorption of substrate in semiheterogeneous systems like, for instance, TiO_2, or in a preassociation in homogeneous systems like POM.

$$POM + S \leftrightarrow [POM\ldots S] \qquad (3)$$
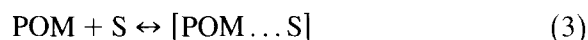
This is deduced, among other observations [26], from the fact that the rates of photoreactions of POM with substrates, follow Langmuir–Hinshelwood behavior, or Michaelis–Menten kinetics [22,27].

Table 1
Percent of CO_2 produced relative to total substrate carbon [a], upon photolysis of various pollutants in presence of catalysts

Catalyst [b]	CO2/mol% of the substrate [a]			
	4-nitro-phenol	2,4-dimethyl-phenol	acetic acid	1,1,2-trichloro-ethane
Time (min) [c]	(180)	(120)	(90)	(150)
$K_4W_{10}O_{32}$ [d]	81.0	50.2	78.1	70.6
$H_3PW_{12}O_{40}$ [e]	75.6	62.0	73.1	70.0
$H_4SiW_{12}O_{40}$ [f]	32.3	13.2	28.9	59.6
$K_6SiCu^{(II)}W_{11}O_{40}H_2$ [g]	16.2	1.3	4.0	4.0
$K_6SiMn^{(II)}W_{11}O_{40}H_2$ [g]	5.7	1.1	4.5	2.9
TiO_2 [g]	89.0	58.6	62.6	55.1

[a] Substrate concentration: $2 \cdot 10^{-4}$ M, [b] catalyst concentration: $7 \cdot 10^{-4}$ M, [c] photolysis time, [d] pH = 2.5, [e] pH = 1, [f] pH = 3, [g] pH = 5.7 (only for acetic acid [f,g]: pH = 3), cut-off filter 320 nm, $T = 20°C$.
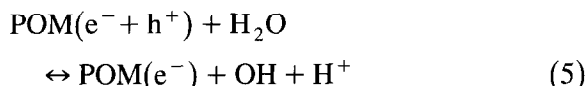
4.2. Excitation

Avoiding, for clarity reasons, to use the pre-associated complex in the reactions that follow and using semiconductor notation, excitation at the $O \rightarrow M$ CT bands results in hole (h^+), electron separation:

$$POM \overset{h\nu}{\leftrightarrow} POM^* \text{ or } POM(e^- + h^+) \qquad (4)$$
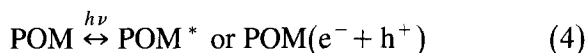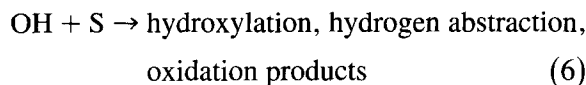
4.3. Reaction with water and substrate

Contrary to what was, generally, believed, the excited state reacts, mainly, with water molecules that are also associated with the catalyst, producing OH radicals

$$POM(e^- + h^+) + H_2O$$

$$\leftrightarrow POM(e^-) + OH + H^+ \qquad (5)$$

which, subsequently, react with substrate S

$$OH + S \rightarrow \text{hydroxylation, hydrogen abstraction,}$$

$$\text{oxidation products} \qquad (6)$$

The formation of OH radicals, upon band gap excitation of TiO_2, has been proposed[28–30] and detected by ESR [31–33].

The following evidence substantiate the formation of OH radicals during photolysis with POM in aqueous solutions: (a) OH adducts (hydroxylation products) have been detected throughout photolysis experiments of aromatic hydrocarbons [22,34], (b) Yamase has also detected, by ESR, OH radicals in aqueous solution, upon $O \rightarrow M$ CT photolysis of POM [35,15].

Further evidence arises from the following: hydrogen atom abstraction mechanism has been invoked in this laboratory [26] and further substantiated by numerous publications as the prevailing mechanism of excited POM with organic substrates. However, further insight into the mechanism, in view of numerous new experimental data, suggests that the first reaction, after the initial excitation of POM in aqueous solution, is mostly, but not exclusively, forma-

tion of OH radicals. This finding, however, does not contradict, but rather verifies and supports the H-transfer mechanism, since OH radicals are long known to radiation chemists to react by H-abstraction and/or addition with organic compounds.

As far as the chlorinated acetic acids are concerned, their decomposition, as is deduced from the data in Table 1 and Fig. 3, follows the order $Cl_3CCOOH \ll ClCH_2COOH \sim CH_3COOH$. This is in support of the photodegradation taking place through formation of OH radicals, and H-atom abstraction from α-carbon, as no α-hydrogen exists in Cl_3CCOOH; see further discussion below.

4.4. Direct reaction of excited POM with substrate

$$POM(e^- + h^+) + S \rightarrow POM(e^-) + S^+ \qquad (7)$$

Direct reaction of excited POM with substrate was shown to proceed to a small extent ($< 10\%$) at least with chlorophenols [22]. This is by no means a general case and individual behavior of various pollutants remains to be seen. This will depend on the preassociation or preadsorption constant of POM with substrate and the rates of photoreactions.

Direct reaction of the excited state, $POM(e^- + h^+)$, with electron scavengers, that is to say, oxidation of the excited state, to begin with, is prohibited. The metal ions in POM are in the highest oxidation state (W^{6+}, d^0), and no further oxidation is possible. Thus, dioxygen does not contribute to the inhibition of $(e^- + h^+)$ recombination. However, once POM are reduced in the process of redox reactions, electron scavengers become important; see below.

4.5. In deoxygenated solution

$$POM(e^-) + H^+ \rightarrow POM + 1/2H_2 \qquad (8)$$

In the absence of other oxidants in solution, Eq. (8) proceeds until the number of electrons

accumulated on POM has driven the redox potential to negative values, sufficient to reduce H^+ [36–38].

However, other reactions can take place before H_2-evolution. In all these cases a steady state is created in which the rate of photoreduction of POM is matched by the rate of its thermal reoxidation [26]. Thus, chloride ions are constantly produced while the concentration of reduced 12-tungstosilicate remains constant; Table 2. Fig. 5 shows the maximum number of electrons accumulated on POM in the photodegradation of chloroacetic acid. It is noticed that, at least for $PW_{12}O_{40}^{3-}$, the electrons accumulated on POM are well below to those required for H_2-evolution [36] indicating that other oxidants than H^+ scavenge the electrons; Eq. (2).

4.6. The role of dioxygen

Dioxygen is a very fast and effective oxidizing reagent (photoelectron scavenger) for reduced POM, reacting up to five orders of magnitude faster than H^+ [39,40], undergoing in the process reductive activation that further promotes the oxidizing ability of the system. While the above statement is, generally, true, there are, however, particularities depending on the nature of substrate and the system used. For instance, POM have extensive photochemistry in absence of oxygen, whereas, no evolution of CO_2 is observed in deoxygenated solutions of TiO_2, although, this is not so clear [25,41].

Table 2
Formation of Cl^- upon continuous photolysis of a deaerated solution of chloroacetic acid, at the steady state (see text)

Photolysis time (min)	Cl^- ($\times 10^{-4}$ M)
76	0.88
126	1.20
151	1.33

Catalyst $SiW_{12}O_{40}^{4-}$, 0.7 mM; substrate, 2 mM; pH, 3.0 ($HClO_4$); $\lambda > 320$ nm; T, 20°C. The steady state is created when about 10% of catalyst is reduced by one electron; see Fig. 5.
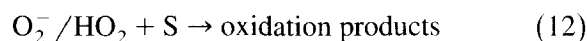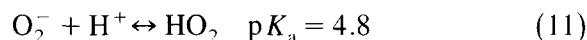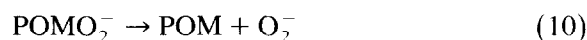
Table 3
The effect of dioxygen on the initial rates of photodegradation of chloroacetic acid (ClAcH), and formation of Cl^-, upon photolysis of aqueous solution of substrate in presence of POM

Catalysts	Initial rates ($\times 10^{-5}$ M min^{-1})			
	oxygenated solutions		deoxygenated solutions	
	decomp. of ClAcH	formation of Cl^-	decomp. of ClAcH	formation of Cl^-
$PW_{12}O_{40}^{3-}$	5.50	4.90	0.30	0.27
$W_{10}O_{32}^{4-}$	1.85	1.80	0.29	0.23
$SiW_{12}O_{40}^{4-}$	0.85	0.84	0.17	0.12

Catalysts, 0.7 mM; substrate, 2 mM; $\lambda > 320$ nm; T, 20°C. pH, 1.0, 2.5, and 3.0 for $PW_{12}O_{40}^{3-}$, $W_{10}O_{32}^{4-}$, and $SiW_{12}O_{40}^{4-}$, respectively.

As far as POM are concerned, the presence of dioxygen at the initial stages of photoreaction has a profound effect on the photodegradation of chloroacetic acid (Table 3 and Fig. 4), whereas, the presence of dioxygen has only minor effect on the photodegradation of chlorophenols [22].

The following reactions that involve the POM catalyst are known to take place in presence of dioxygen [39,42,43]

$$POM(e^-) + O_2 \rightarrow POMO_2^- \qquad (9)$$

$$POMO_2^- \rightarrow POM + O_2^- \qquad (10)$$

$$O_2^- + H^+ \leftrightarrow HO_2 \quad pK_a = 4.8 \qquad (11)$$

$$O_2^- / HO_2 + S \rightarrow \text{oxidation products} \qquad (12)$$

$$2HO_2 \rightarrow H_2O_2 + O_2 \qquad (13)$$

$$H_2O_2 \overset{h\nu}{\rightarrow} 2OH \qquad (14)$$

Eq. (9) and Eq. (10) have been justified from kinetic data [39] in analogy with Cu^+ complexes [44].

Fig. 4 shows the effect of dioxygen on the photodegradation of chloroacetic acid with $W_{10}O_{32}^{4-}$. Table 3 summarizes the results of the initial rates of photodegradation of chloroacetic acid and Cl^- formation in presence of $W_{10}O_{32}^{4-}$, $PW_{12}O_{40}^{3-}$, and $SiW_{12}O_{40}^{4-}$ in oxygenated and deoxygenated solutions. It can be seen that in the oxygenated solutions, the initial photolysis

rates is 5 to 18 times faster than in the absence of dioxygen, as mentioned earlier, and that dechlorination follows the same pattern; Table 3.

On the contrary, the presence of dioxygen had a minor effect on the initial stages of photodegradation of chlorinated phenols, whereas, when the reaction was allowed to proceed to mineralization, the rates were an order of magnitude faster in presence than in absence of dioxygen [22].
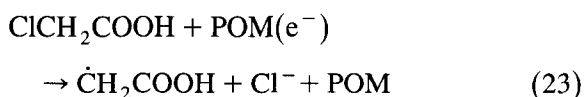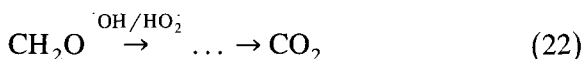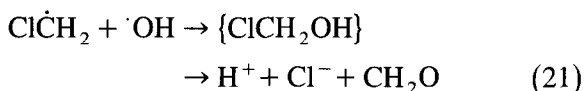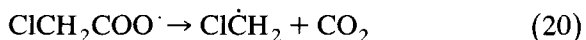
It should be noted that in measuring the rates of photoreactions at the initial stages, in the absence of dioxygen, the reaction was allowed to proceed to less than 20%, so that the catalyst retained its maximum performance. It is noted, that in going, generally, from the oxidized to the one-electron reduced form of POM, the effectiveness of the catalyst drops to about 10% [26].
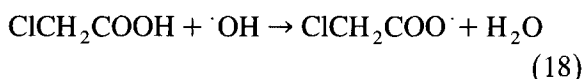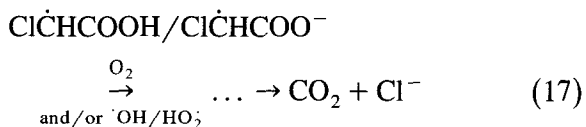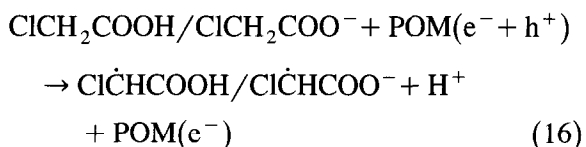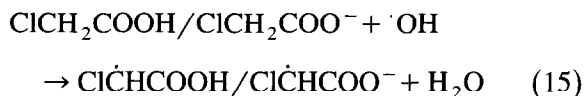
The role of dioxygen in chloroacetic acids, must be different from that in chlorophenols. Specifically, the main function of dioxygen in chlorophenols seems to be the reoxidation (regeneration) of the catalyst and, most probably, oxidation of intermediates that do not affect the initial rates of decomposition. On the other hand, in chloroacetic acids, dioxygen seems to participate in the degradation process from the initial stages of photoreaction by reacting fast with the intermediate radicals formed, which also explains why the formation of Cl^- goes parallel to its decomposition; Table 3. Dechlorination by superoxide generated by reaction of reduced POM with dioxygen [45], as well as radical chain autoxidation of several hydrocarbons [46], in aprotic solvents, have been reported by Hill.

For chloroacetic acid no intermediates were detected, only the final products CO_2 and Cl^-, as has been the case with TiO_2 [47,48]. Therefore, a mechanistic discussion is, mainly, hypothetical.

It is long known though to radiation chemists, that OH radicals cause, primarily, α-carbon hydrogen abstraction in alcohols and carboxylic acids [49]. The following scheme adapted, mainly, from the literature, refers to the first

stages of photodegradation of chloroacetic acid [47,48].

$ClCH_2COOH/ClCH_2COO^- + {}^{\cdot}OH$

$\rightarrow Cl\dot{C}HCOOH/Cl\dot{C}HCOO^- + H_2O$ (15)

$ClCH_2COOH/ClCH_2COO^- + POM(e^- + h^+)$

$\rightarrow Cl\dot{C}HCOOH/Cl\dot{C}HCOO^- + H^+$

$+ POM(e^-)$ (16)

$Cl\dot{C}HCOOH/Cl\dot{C}HCOO^-$

$\xrightarrow[\text{and/or } {}^{\cdot}OH/HO_2^{\cdot}]{O_2} \ldots \rightarrow CO_2 + Cl^-$ (17)

$ClCH_2COOH + {}^{\cdot}OH \rightarrow ClCH_2COO^{\cdot} + H_2O$ (18)

$ClCH_2COOH/ClCH_2COO^- + POM(e^- + h^+)$

$\rightarrow (ClCH_2COO^{\cdot} + H^+)$

$/(ClCH_2COO^{\cdot} + POM(e^-))$ (19)

$ClCH_2COO^{\cdot} \rightarrow Cl\dot{C}H_2 + CO_2$ (20)

$Cl\dot{C}H_2 + {}^{\cdot}OH \rightarrow \{ClCH_2OH\}$

$\rightarrow H^+ + Cl^- + CH_2O$ (21)

$CH_2O \xrightarrow{{}^{\cdot}OH/HO_2^{\cdot}} \ldots \rightarrow CO_2$ (22)

$ClCH_2COOH + POM(e^-)$

$\rightarrow \dot{C}H_2COOH + Cl^- + POM$ (23)
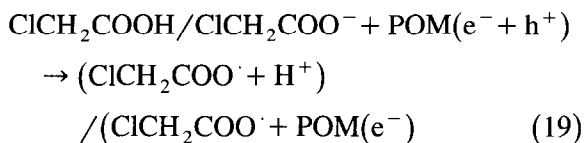
Concerning the mineralization of chlorinated acetic acids, the following observations can be made from the data collected so far.

(a) OH radicals, Eq. (15), as mentioned earlier, and holes (h^+), Eq. (16), react with chlorinated acetic acids by H-atom abstraction from the α-carbon. The lack of α-hydrogen atoms in trichloroacetic acid explains the slow down of its photodegradation; Fig. 3.

(b) Attack on other parts of the molecule, mainly carboxylic hydrogens, ought to take place albeit to a lesser extent; Eq. (18) and Eq. (19) and Fig. 3.

(c) Dioxygen must play an important role in the photodegradation of chloroacetic acid from

the initial stage of photoreaction, by reacting fast with the intermediate radicals formed, Eq. (17), explaining, also, why the formation of Cl^- goes parallel to decomposition of the substrate, as mentioned earlier; Table 3.

(d) Contrary to aromatic hydrocarbons, no induction period is observed for CO_2 evolution [22,23,34]. No opening of the aromatic ring is necessary prior to CO_2 evolution.

In closing this paper, we have summarized and compared in Table 1, further results concerning the effectiveness of various POM and TiO_2 on the mineralization of several other organic pollutants.

The following are general observations:

(a) POM are effective photocatalysts in the near visible and UV area, for a variety of organic pollutant, leading to their photodegradation to CO_2.

(b) POM are, at least, as effective as TiO_2, acting, more or less, in a similar way.

(c) In view of the formation of OH radicals, it appears that in photolysis experiments, selectivity, at least in aqueous solution, reported so far, is a kinetic rather than thermodynamic phenomenon.

(d) Substitution of W–O moiety in $SiW_{12}O_{40}^{4-}$ for copper(II) and manganese(II), i.e., $[(H_2O)Mn^{II}SiW_{11}O_{39}]^{6-}$ and $[(H_2O)Cu^{II}SiW_{11}O_{39}]^{6-}$, results in considerable loss of their photocatalytic effectiveness.

Finally, using as an example chloroacetic acid the mineralization reaction can be presented as follows:
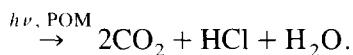
$$ClCH_2COOH + 3/2O_2$$

$$\xrightarrow{h\nu,\ POM} 2CO_2 + HCl + H_2O.$$

Acknowledgements

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