Available online at www.sciencedirect.com
ScienceDirect
Catalysis Today 124 (2007) 149–155
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Photocatalysis by polyoxometallates and TiO_2: A comparative study

P. Kormali, A. Troupis, T. Triantis, A. Hiskia *, E. Papaconstantinou *

Insitute of Physical Chemistry, NCSR Demokritos, 15310 Athens, Greece

Available online 27 April 2007

Abstract

Polyoxometallates (POMs) as a homogeneous photocatalyst and TiO_2 as a heterogeneous photocatalyst seem to exhibit overall similar photocatalytic behavior. Both systems cause photodecomposition of a variety of organic pollutants via the formation and decay of several similar intermediates formed by OH addition (hydroxylation), dehalogenation, deamination, decarboxylation, etc. The final degradation products, for most organic substrates for both systems are CO_2, H_2O and inorganic anions. The similarity of behavior has been attributed to the formation of the common powerful oxidizing reagent, OH radical, from the reaction of the excited catalyst and water molecules.

On the other hand, lately, various laboratories have pointed out differences in reactivity and degradation mechanism between the two photocatalysts. The results are interesting and to a great extent contradictory.

This study compares the photodegradation of four substrates with diversified structures, namely, atrazine, fenitrothion, 4-chlorophenol (4-ClPh), and 2,4-dichlorophenoxyacetic acid (2,4-D) by both $PW_{12}O_{40}{}^{3-}$ and TiO_2 and how their photodegradation is affected by the presence of strong OH radical scavengers, i.e., Br^- and isopropyl alcohol (*i*-prOH).

The results provide substantial evidence that the literature data on the apparent photooxidation mechanism of these two categories of photocatalysts is circumstantial, depending on substrate and the mode of investigation. Overall, though, the action of OH radicals relative to h^+ appears to be more pronounced with $PW_{12}O_{40}{}^{3-}$ than TiO_2.

With respect to thermal (dark) reaction of photoreduced catalysts, both systems can deliver their electrons to a variety of oxidants including metal ions. The advantages of POM relative to TiO_2 relates to the selective reduction precipitation of metal ions and to their unique ability to form metal nanoparticles in which POM serve both as reducing reagents and stabilizers.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Polyoxometalates; TiO_2; Photocatalysis; OH radicals; Metal reduction; Metal nanoparticles

1. Introduction

Polyoxometallates (POM) constitute a large category of well-defined metal oxygen cluster anions, formed by condensation of mainly tungstates and/or molybdates with or without participation of a variety of other elements (Fig. 1) [1,2].

On the other hand, aggregate of various sizes are formed by stirring or sonication, etc. of a variety of metal oxides in aqueous solutions. Particles with diameter over approximately 15 nm behave as bulk semiconductors (SC), whereas, particles smaller than 5 nm have molecular characteristics and are characterized as quantum dots [3].

Thus, POM are well-defined anions that dissolve in water forming homogeneous solutions, whereas, metal oxide particulates, that is SC, disperse in water forming semiheterogeneous solutions. Despite these differences, these two categories of photocatalysts present striking similarities [4].

(a) They both absorb at the near-visible and UV area. For POM this absorption corresponds to O → M CT band (Fig. 1), whereas, for SC (i.e., TiO_2) corresponds to band gap, e.g. (Fig. 2) that is promotion of an electron from the valence band (VB) to conduction band (CB) resulting in electron hole (h^+) separation. Thus, for both systems, the excited state can be described as

$$M \xrightarrow{hv} M(h^+ + e^-)$$

(b) They can be reduced by various means, chemical, electrochemical, photolytic, etc. producing blue species. The similarities of spectra of the reduced species is shown

---

* Corresponding authors.

E-mail addresses: hiskia@chem.demokritos.gr (A. Hiskia), epapac@chem.demokritos.gr (E. Papaconstantinou).

0920-5861/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2007.03.032

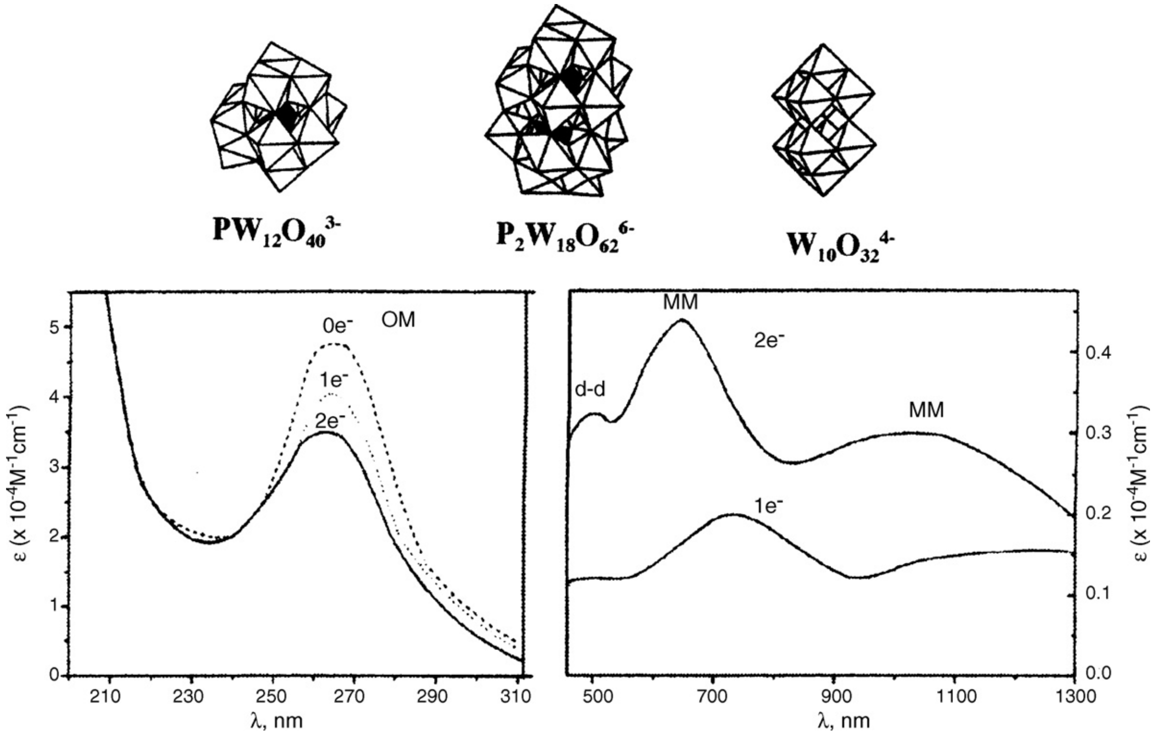


Fig. 1. Typical structures of some POM. $PW_{12}O_{40}^{3-}$ and $P_2W_{18}O_{62}^{6-}$ are composed of PO_4 tetrahedra (dark areas), surrounded by WO_6 octahedra. The spectra in the figure represent the oxidized and reduced (by one and two electrons) forms of $PW_{12}O_{40}^{3-}$. In addition, the O → M CT band, the intervalence electron transfer (M–M CT) and d–d transitions, are indicated on spectra.

in Fig. 3 [5]. For POM there is a stepwise addition of several electrons, whereas, accumulation of electrons takes place also in SC depending on the strength of the reducing reagent.

(c) Excitation at the near vis–UV light, approximately below 400 nm, renders both systems powerful oxidizing reagents able to oxidize and indeed mineralize practically all organic compounds including organic pollutants to CO_2, H_2O and inorganic anions. The process accumulates negative charge on the catalysts until an oxidant is able to scavenge the electrons. Thus both photocatalysts serve as electron relays. On the other hand, accumumulation of negative charge on the catalysts accelerates the $(h^+ + e^-)$ recombination so that the photoreaction is unable to compete.

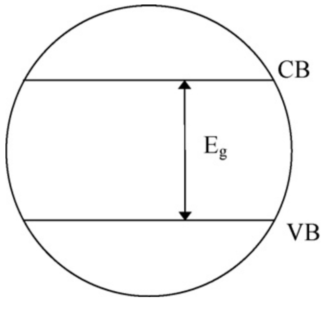


Fig. 2. Schematic representation of a semiconductor (SC) particle. In a SC particle atomic and molecular orbitals coalesce to form energy bands: valence band (VB) and conduction band (CB), E_g = the band gap energy.

(d) Thus, for both systems, accumulation of negative charge drops the efficiency of photoreaction and in addition, drives the redox potential to more negative values.

(e) For both systems the rate-determining step in the photocatalytic reactions is the removal of the electrons [6].

(f) The above-mentioned photooxidation of organic compounds and organic pollutants progresses for both systems, generally, via the same intermediates formed by OH addition (hydroxylation), dehalogenation, deamination, decarboxylation, dealkylation, H-abstraction, breaking of C–C bond in aliphatic and aromatic compounds. The final degradation products, for both systems are CO_2, H_2O and inorganic anions as mentioned earlier. The similarities of behavior, has been attributed to a common oxidant OH radicals produced from the reaction of the excited states of both systems with water molecules

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

where $M(h^+ + e^-)$ represents the excited state of $PW_{12}O_{40}^{3-}$ or TiO_2.

(g) Furthermore, the electrons accumulated on both systems can be delivered to a variety of electron acceptors such as H^+, metal ions and various other oxidants, leading to the formation of H_2, metal reduction–precipitation, etc.

The common photocatalytic cycle of both systems is shown in Fig. 4.

The above has been accounted for the overall similar picture presented by these two categories of catalysts. Several research groups have undertaken the task to elucidate the main oxidant

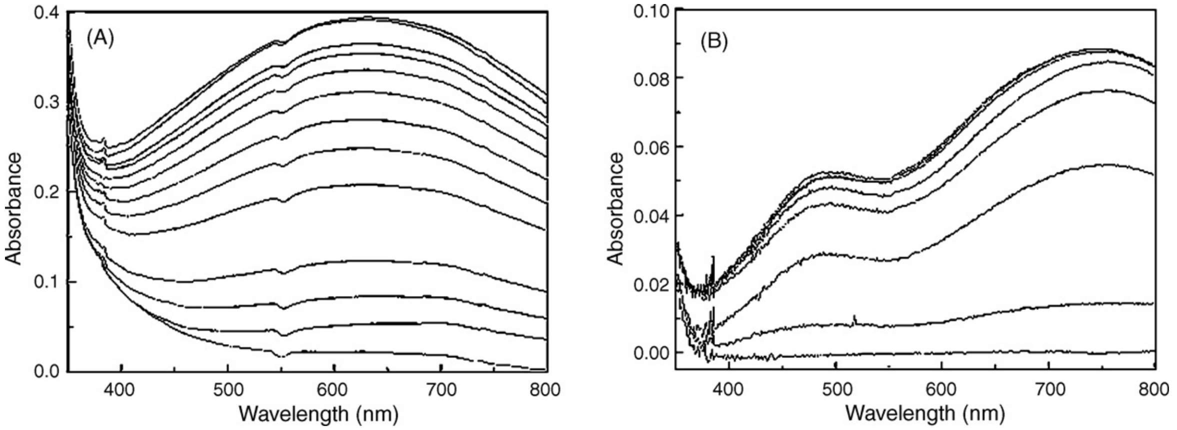


Fig. 3. Gradual photoreduction of TiO_2 (A) and $PW_{12}O_{40}^{3-}$ (B) upon UV–near visible illumination of deaerated aqueous solutions of catalysts in the presence of propan-2-ol. Curves from bottom to top correspond to the UV irradiation time of 0, 5, 15, 25, 45, 55, 65, 75, 85, 100, 122, 124, 180 min and 0, 3, 8, 13, 23, 33, 43, 53 min in the spectra (A) and (B), respectively. (Reprinted from Ref. [5].)

in the primary photochemical reaction, i.e., whether it is exercised via OH radicals or holes or both. A common oxidant, i.e., OH radicals will explain the similar behavior, whereas, the opposite will produce diversified results.

The results, so far have been interesting and to a great extent contradictory. For instance, to mention a few, Ozer and Ferry suggest that various POM of the 1:12 series (Keggin structure) operate via electron transfer, i.e., holes rather than OH radicals [7]. Texier et al. using laser flash photolysis suggest that $W_{10}O_{32}^{4-}$ operates exclusively via holes [8], whereas, Choi and coworkers report that the sole dominant oxidant for POM regardless of substrates is OH radicals, while both h^+ and OH radicals take part in TiO_2 photocatalysis [9]. On the other hand Ishibashi et al. suggest that TiO_2 photocatalyst operates exclusively via holes [10].

These are a few scattered and contradictory results from the literature.

This paper compares the primary photochemical reaction of $PW_{12}O_{40}^{3-}$ and TiO_2 with a variety of substrates atrazine, fenitrothion, 4-chlorophenol (4-ClPh) and 2,4-dichlorophenoxyacetic acid (2,4-D) and how their photodecomposition is affected by the presence of strong OH radical scavengers, namely bromide and propan-2-ol (*i*-prOH). It also compares briefly the thermal (dark) reaction of the reduced species of both systems with various oxidants.

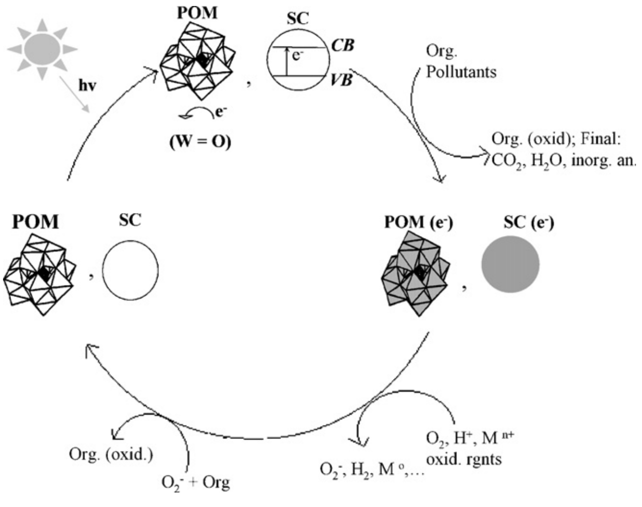


Fig. 4. The common photocatalytic cycle exercised by both systems.

2. Experimental

2.1. Instrumentation

Irradiation was performed with a laboratory constructed ‘‘illumination box’’ equipped with four F15W/T8 black light tubes (Sylvania GTE, USA). The maximum emission of these tubes is around 375 nm, emitting 71.7 μW cm^{-2} at a distance of 25 cm. Alternatively, illumination was performed with an Oriel 1000 W Xe arc lamp equipped with cool water circulating filter to absorb the near IR radiation and a 320 nm cut-off filter in order to avoid direct photolysis of substrates, using a quartz cell of 1 cm path length. The total photonic flux (320–345 nm) determined by ferrioxalate actinometer was 7.9×10^{-6} einstein min^{-1}, which is about ten times higher than the photon flux in the ‘‘illumination box’’.

HPLC analysis was carried out using an HPLC apparatus consisted of a Waters (Milford, MA, USA) model TM 600 gradient pump.

GC–MS analysis was performed using an Agilent 6890 Series gas chromatograph interfaced to an Agilent 5973 mass selective detector (Wilmington, DE, USA). Data acquisition, processing and instrument control were performed by the Agilent MSD Chem-Station software. In cases where quantification was not possible for lack of standard reagents, the relative quantities of intermediates were given in arbitrary units.

The concentration of metal ions was determined with a GBC flame atomic absorption spectrometer monitored at 253.7 nm after filtration of the photolysed solutions with a 0.45 μm Millipore filter.

2.2. Photolysis experiments

The experiments with OH radical scavengers were performed in cylindrical pyrex cells in the ''illumination box''. Fortified aqueous solutions of atrazine (6.95×10^{-5} M), fenitrothion (5.41×10^{-5} M), 4-chlorophenol (11.7×10^{-5} M) and 2,4-D (6.78×10^{-5} M) in presence of the photocatalysts, $H_3PW_{12}O_{40}$ (7×10^{-4} M), TiO_2 (0.2 g/L) and OH radicals trapping reagents KBr (10^{-2} M), isopropyl alcohol (10^{-2} M) were made by dissolving certain quantities of substrates in water (pH $\approx$ 5.5 for TiO_2) or in $HClO_4$ 0.1 M (in the case of $PW_{12}O_{40}{}^{3-}$). Illumination was performed with the ''illumination box'' mentioned earlier.

For the reduction–precipitation of metals a typical experiment was as follows: 4 mL of aqueous metal ion solution containing propan-2-ol and POM catalyst was added to a spectrophotometer cell (1 cm path length), deaerated and covered with a cerum cap. The pH was adjusted at pH 1 with $HClO_4$ whenever necessary. Photolysis was performed with an Oriel 1000 W Xe arc lamp mentioned earlier.

The degree of reduction of POM in photolysed deaerated solutions was calculated from the known extinction coefficient of reduced catalyst at ca. 750 nm using a Perkin-Elmer Lambda19 Spectrometer.

The initial rate of metal recovery was determined by monitoring the concentration of metal ion in the photolysed filtered solutions and calculating the slope of the curve obtained.

Thermal reduction of metal ions by reduced POM was performed as follows: 1 equiv. reduced tungstate, say $PW_{12}O_{40}{}^{4-}$, ca. 0.17 mM is produced upon illumination of

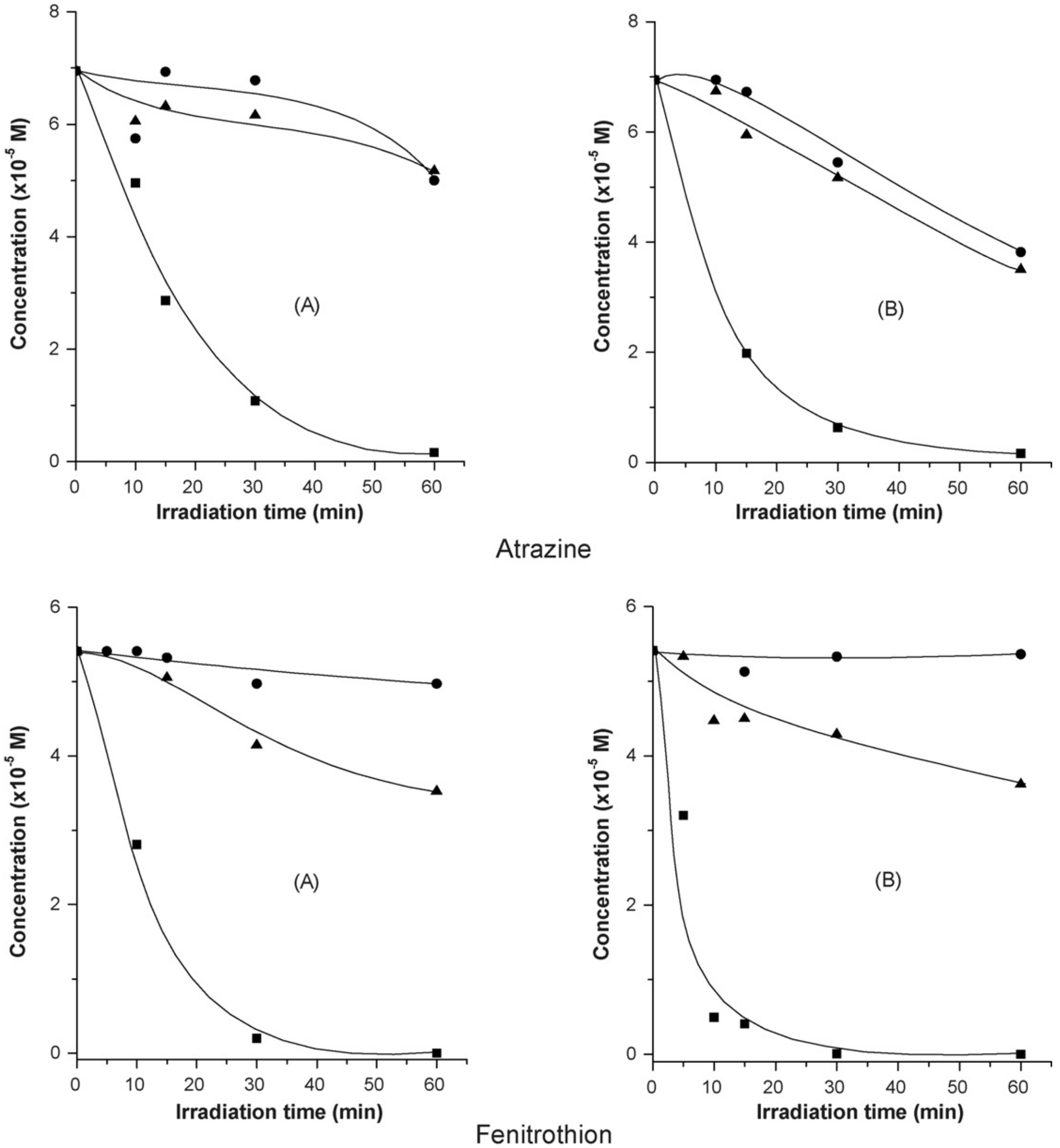
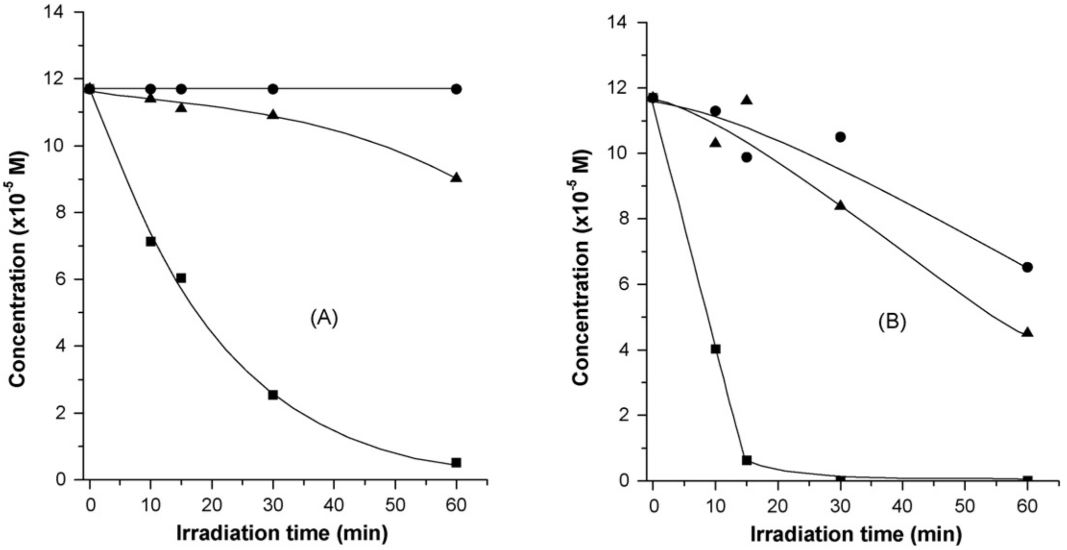
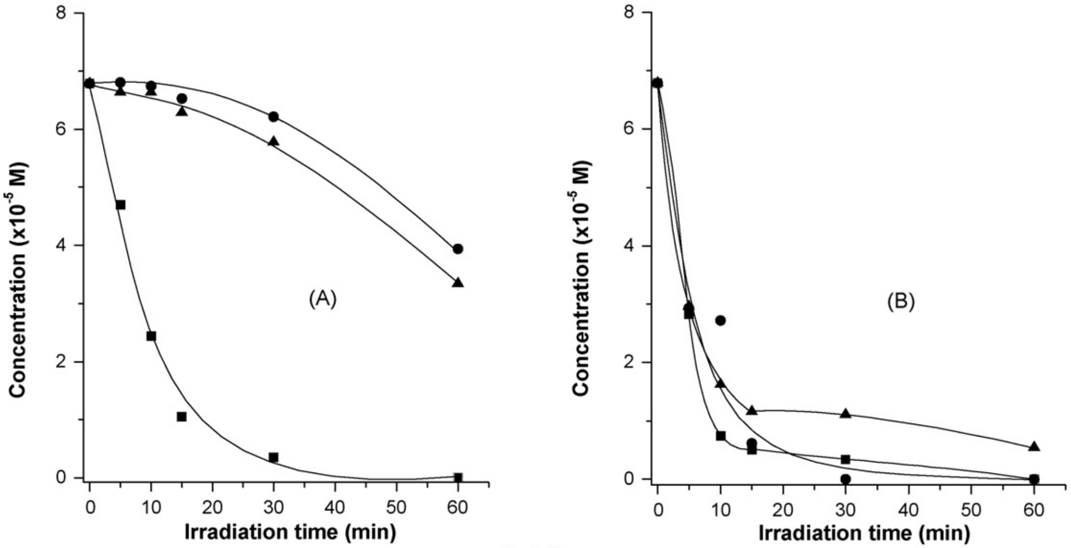


Fig. 5. Photodecomposition of atrazine and fenitrothion by $PW_{12}O_{40}{}^{3-}$ (A) and TiO_2 (B), in the absence (■) and presence of OH radicals scavengers Br^-, (●); *i*-prOH (▲).



4-ClPh



2,4-D

Fig. 6. Photodecomposition of 4-ClPh and 2,4-D by $PW_{12}O_{40}^{3-}$ (A) and TiO_2 (B), in the absence (■) and presence of OH radicals scavengers Br^-, (●); *i*-prOH (▲).

4 ml aqueous solutions of propan-2-ol 0.5 M, $PW_{12}O_{40}^{3-}$ 0.7 mM, $HClO_4$ 0.1 M. To this solution microlitres of deaerated solution of metal ions is added and the drop of the absorbance is monitored at 752 nm (the characteristic absorbance of the one-equivalent reduced tungstate).

3. Results and discussion

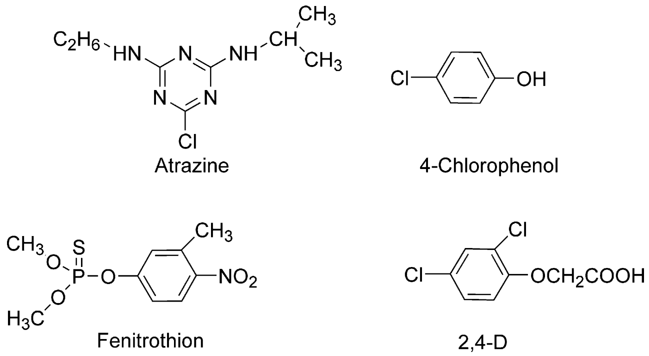
The structures of the four substrates in question are shown in Scheme 1.

Three possibilities have to be considered for the elucidation of the mechanism of the primary photochemical reaction

$$M + S \xrightarrow{hv} M(red) + S(oxid)$$

where M = $PW_{12}O_{40}^{3-}$ or TiO_2, S = substrate. (i) Charge transfer (e^- + h^+), (ii) H-atom transfer, (iii) OH mediated reactions.

The photodecomposition of all substrates by both $PW_{12}O_{40}^{3-}$ and TiO_2 was performed in parallel experiments under the same conditions in the absence and presence of the scavengers. The results are shown in Figs. 5 and 6.



Scheme 1. The structures of four substrates.

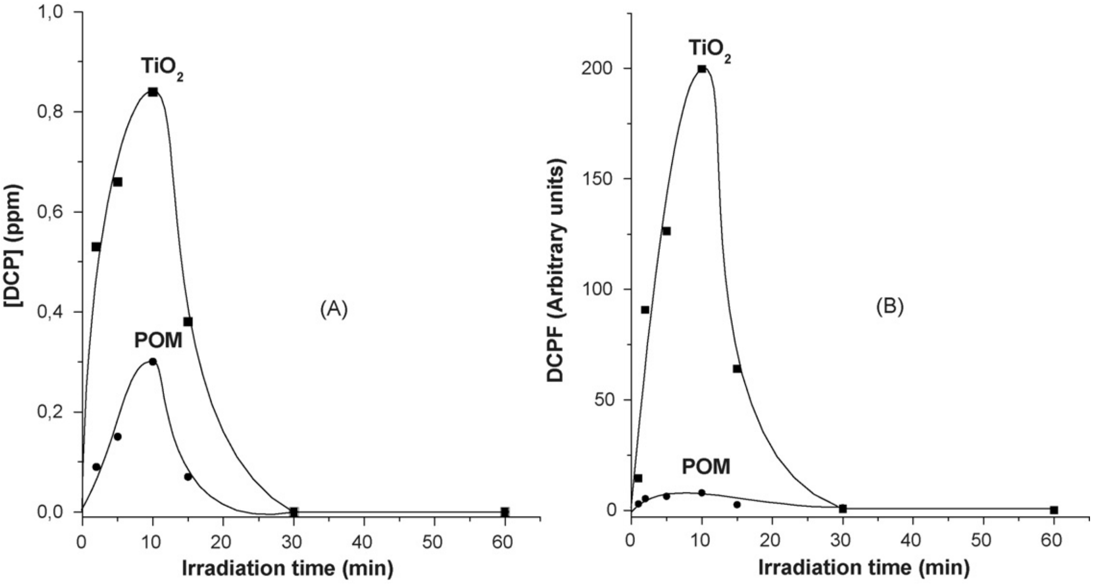


Fig. 7. Photocatalytic formation and decay of DCP (A) and DCPF (B), upon illumination of 2,4-D in the presence of $PW_{12}O_{40}^{3-}$ (●) and TiO_2 (■).

Two groups depending on their response to photochemical decomposition can be considered. The group (atrazine, fenitrothion) whose photodegradation shows similar response to the presence of OH radical scavengers by both photocatalysts (Fig. 5) and the group (4-ClPh, 2,4-D) whose photodegradation by $PW_{12}O_{40}^{3-}$ shows different response in the presence of OH radical scavengers than that of TiO_2 (Fig. 6).

It is to be noted that in the first category (atrazine and fenitrothion), in which we have similar behavior by both $PW_{12}O_{40}^{3-}$ and TiO_2, atrazine suggests that the main oxidant is OH radicals. This suggestion is drawn from the fact that when either one of two strong OH radicals scavengers (Br^-, propan-2-ol) is present the photodegradation slows down but is not eliminated (Fig. 5), indication that holes participate in the photodegradation as well. On the other hand, the presence of the above scavengers eliminates, for all practical purposes, the photodegradation of fenitrothion caused by either $PW_{12}O_{40}^{3-}$ or TiO_2 (Fig. 5). This tends to suggest that for fenitrothion both photocatalysts operate almost exclusively via OH radicals. Previous detail investigation involving intermediates and final products of $PW_{12}O_{40}^{3-}$ and TiO_2 mediated photooxidations of atrazine and fenitrothion have shown the similarities of these processes [11,12].

In the second category (4-ClPh and 2,4D), both substrates suggest that $PW_{12}O_{40}^{3-}$ operates essentially via OH radicals, whereas, TiO_2 operates mainly via holes and to a lesser extent OH radicals (Fig. 6).

Preassociation or preequilibrium constants between the photocatalysts and the substrates calculated from the well-established Langmuir–Hinselwood behavior of these systems,

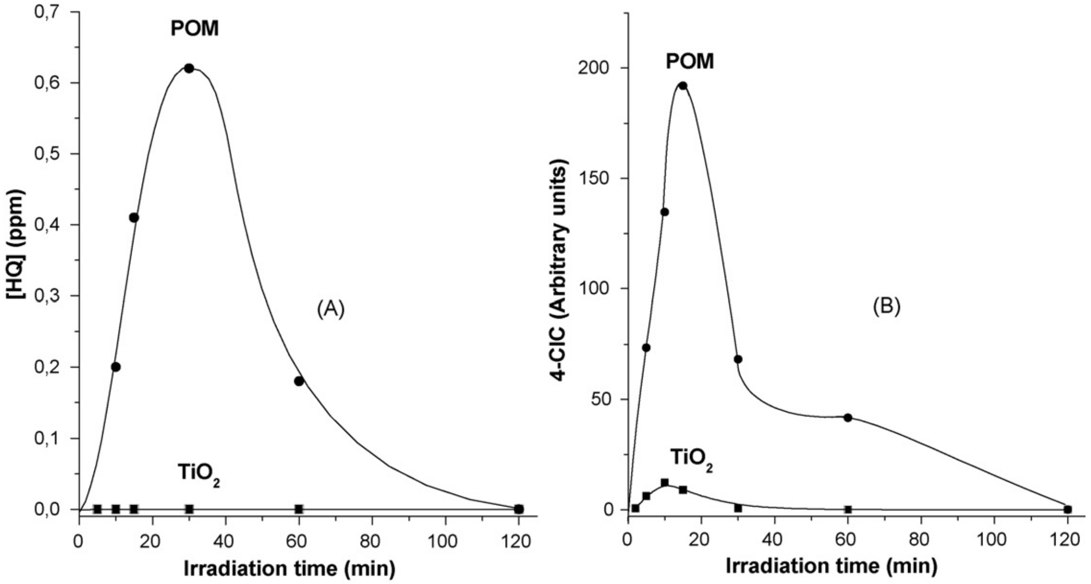


Fig. 8. Photocatalytic formation and decay of hydroquinone (A) and 4-chlorocatechol (B) upon illumination of 4-ClP in the presence of $PW_{12}O_{40}^{3-}$ (●) and TiO_2 (■).

gave no suggestion for the diversified behavior. The same holds true for the Pow values of these substrates [13]; (Pow values represent the *n*-octanol–water partition coefficient, that is the hydrophobic–hydrophilic character, of substrates).

Now, these four substrates have diversified structures. One of the parameters that differentiate the nature of (4-ClPh and 2,4-D) from (atrazine and fenitrothion) seems to be the existence of polar moieties.

In our previous investigations concerning the behavior of the group atrazine and fenitrothion, the results have indicated similar photocatalytic behavior for both TiO_2 and $PW_{12}O_{40}{}^{3-}$. The intermediates detected and final degradation products were, overall, the same (cyanuric acid for atrazine [11,14] and CO_2, $PO_4{}^{3-}$, $SO_4{}^{2-}$, $NO_2{}^{-}$ and $NO_3{}^{-}$ for fenitrothion [12]).

We have extended, in part, this investigation into the other group (4-ClPh and 2,4-D), which shows different photocatalytic behavior in the presence of TiO_2 versus $PW_{12}O_{40}{}^{3-}$, suggested by OH radical scavengers experiments. First of all, analysis for TOC, Cl^- and CO_2 at illumination time intervals have shown that complete mineralization of both substrates is obtained with both catalysts, though TiO_2 is more effective than $PW_{12}O_{40}{}^{3-}$. However, analysis for some of the intermediates supports the different photodegradation mode for TiO_2 versus $PW_{12}O_{40}{}^{3-}$. For instance, for the system (2,4-D/TiO_2, pH 5.5), acting via (h^+), a photo-Kolbe reaction ($h^+ + COO^-$) supports the formation of 2,4-dichloroformate (DCPF) and 2,4-dichlorophenol (DCP) via decarboxylation, followed by dealkylation. On the other hand, the system (2,4-D/$PW_{12}O_{40}{}^{3-}$), acting mainly via OH radicals, forms DCP to a lesser extent and traces of DCPF (Fig. 7).

As far as 4-ClPh is concerned, some of the intermediates detected for the system (4-ClPh/ $PW_{12}O_{40}{}^{3-}$) are hydroquinone (HQ) and 4-chlorocatechol (4-ClC), in agreement with OH radicals being the main oxidant. Thus, addition of OH radicals on the aromatic ring provides 4-ClC, whereas, displacement of Cl atoms by OH radicals forms HQ. On the other hand, no HQ and only traces of 4-ClC are detected for the system (4-ClPh/ TiO_2) acting mainly via (h^+) as OH radical scavengers experiments have suggested (Fig. 8).

Thus, this study verifies further the controversial results reported in the literature [13]. The data obtained concerning the mechanism of the primary photooxidation of $PW_{12}O_{40}{}^{3-}$ and TiO_2 (i.e., whether it is exercised via holes and/or OH radicals) depends on the substrate and the mode of investigation.

3.1. Thermal (dark) reactions of reduced catalysts

The comparison of both systems concerning the thermal (dark) reactions of the reduced photocatalysts with various oxidants is more straight-forward. As mentioned earlier both systems are capable of accumulating photoelectrons that can be subsequently delivered to various oxidants depending on the redox potentials (Fig. 4). However there are several differentiations and it may be said advantages for POM relative to TiO_2 [15]:

- The rate of reduction of M^{n+} by POM follows thermodynamics, (selective precipitation) [16].
- M^0 are obtained in pure form.
- No contamination of catalyst (POM) by M^0.
- The process is photocatalytic.
- The process can also synthesize metal nanoparticles in which reduced POM serve both as reducing reagents and stabilizers [17].

4. Conclusions

Concerning the photooxidizing mode exercised by the two photocatalysts $PW_{12}O_{40}{}^{3-}$ and TiO_2 (i.e., OH radicals versus h^+), it appears that it is circumstantial depending on the nature of substrate and the mode of investigation. However, this and earlier studies agree that, overall, the action of OH radicals relative to h^+ appears to be more pronounced with $PW_{12}O_{40}{}^{3-}$ than TiO_2.

Concerning the thermal (dark) reactions, there are several advantages of POM relative to TiO_2 in that reduction–precipitation of metals can be controlled with the redox potentials of POM and besides metal nanoparticles can be obtained by slightly modifying the precipitation method.

Acknowledgments

We thank the Ministry of Development, General Secretariat of Research and Technology of Greece for supporting part of this work.

References

[1] L.C.W. Baker, D.C. Glick, Chem. Rev. 98 (1998) 3.
[2] M.T. Pope, in: C.K. Jorgensen, et al. (Eds.), Heteropoly and Isopoly Oxometalates in Inorganic Chemistry Concepts, vol. 8, Springer-Verlag, West Berlin, 1983.
[3] A.P. Alivizatos, Science 271 (1996) 933.
[4] A. Hiskia, A. Mylonas, E. Papaconstantinou, Chem. Soc. Rev. 30 (2001) 62.
[5] C. Chen, P. Lei, H. Ji, W. Ma, J. Zhao, H. Hidaka, N. Serpone, Environ. Sci. Technol. 38 (2004) 329.
[6] H. Gerischer, A. Heller, J. Phys. Chem. 95 (1991) 5261.
[7] R.R. Ozer, L.J. Ferry, J. Phys. Chem. B 104 (2000) 9444.
[8] I. Texier, J.A. Delaire, C. Giannotti, Phys. Chem. Chem. Phys. 2 (2000) 1205.
[9] S. Kim, H. Park, W. Choi, J. Phys. Chem. B 108 (2004) 6402.
[10] K.-I. Ishibashi, A. Fujishima, T. Watanabe, K. Hashimoto, J. Photochem. Photobiol. A: Chem. 134 (2000) 139.
[11] A. Hiskia, M. Ecke, A. Troupis, A. Kokorakis, H. Hennig, E. Papaconstantinou, Environ. Sci. Technol. 35 (2001) 2358.
[12] P. Kormali, D. Dimoticali, D. Tsipi, A. Hiskia, E. Papaconstantinou, Appl. Catal. B 48 (2004) 175.
[13] P. kormali, T. Triantis, D. Dimotikali, A. Hiskia, E. Papaconstantinou, Appl. Catal. B: Environ. 68 (2006) 139.
[14] C. Minero, V. Maurino, E. Pelizzetti, Res. Chem. Intermed. 23 (1997) 291 (and references therein).
[15] M.I. Litter, Appl. Catal. B: Environ. 23 (1999) 89.
[16] E. Gkika, A. Troupis, A. Hiskia, E. Papaconstantinou, Appl. Catal. B 39 (2005) 4242.
[17] A. Troupis, A. Hiskia, E. Papaconstantinou, Angew. Chem. Int. Ed. 41 (2002) 1911.