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Solar photodegradation of pesticides in water by sodium decatungstate

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Abstract

Solar photodegradation in aqueous solutions of phenol, 4-chlorophenol, 2,4-dichlorophenol, bromoxynil, atrazine, imidachloprid and oxamyl, in the presence of two photocatalysts titanium dioxide TiO_2 and sodium decatungstate $Na_4W_{10}O_{32}$ is reported. TiO_2 appears to be the most efficient photocatalyst concerning the rate of photodegradation and mineralization of the pure compounds. However, when the pesticides are used in formulated solutions, the decatungstate anion becomes as efficient or even more efficient than TiO_2. The mechanism of the photodegradation in the presence of $Na_4W_{10}O_{32}$ is investigated by nanosecond flash-photolysis experiments, and is compared to the one proposed for TiO_2. The difference of reactivity between the two photocatalysts is accounted by the different primary processes of the mechanisms. The formulation effect is investigated with two model surfactants SDS and Triton X100, and 2-chlorophenol as a model pesticide. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Polyoxometalates; Photocatalysis; Solar photodegradation of pesticides

1. Introduction

In recent years, research on new methods for water purification is developing in different ways including chemical, electrochemical or photochemical processes. Among all the processes involving light [1], ozonation in combination with UV treatment [2] or photo-Fenton reaction [3–7] have been receiving increased attention. More recently, direct VUV photolysis of water–oxygen gas mixtures [8] has also been proposed as a potential method for degradation of organic pollutants. Solar photocatalytic detoxification of water is technologically and environmentally attractive as it can be applied on a very large scale for industrial or domestic waste water treatment or purification of contaminated ground water.

Dispersed solid particles of TiO_2 have been extensively used as an efficient photocatalyst in the chemical decomposition of many organic substrates [9–11]. It generally leads to the total mineralization of organic compounds in CO_2. Recently, Papaconstantinou et al. showed that polyoxometalates can also be used as photocatalysts to degrade chlorinated phenols in aqueous solution, by irradiation with a UV-lamp [12,13]. In their study, the kinetics of degradation of 4-chlorophenol upon photolysis at $\lambda > 320$ nm in the presence of three polyoxometalates were compared with the kinetics of degradation in the presence of TiO_2. The efficiencies of the different photocatalysts were in the order $H_4SiW_{12}O_{40} < K_4W_{10}O_{32} < TiO_2 < H_3PW_{12}O_{40}$ [12,13].

Although absorbing in the UV with a maximum at 323 nm, $W_{10}O_{32}{}^{4-}$ absorption spectrum overlaps the

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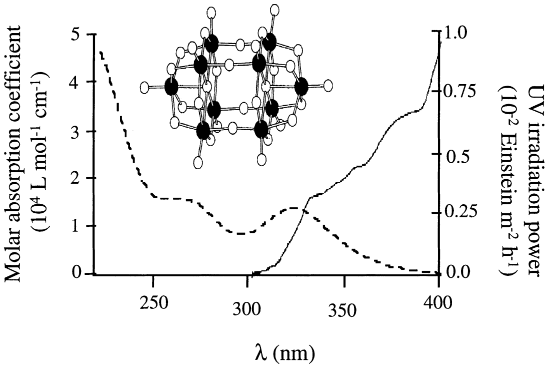


Fig. 1. Overlap of the solar UV emission spectrum (full line) and $Na_4W_{10}O_{32}$ absorption spectrum (dashed line). In the presented structure of $Na_4W_{10}O_{32}$, W atoms are in black, O atoms in white.

solar spectrum (see Fig. 1). It is a better candidate than $PW_{12}O_{40}{}^{3-}$ which absorbs with a maximum at 280 nm. The use of solar light to produce the excited state of the decatungstate anion, which is further able to oxidize organic products, has been demonstrated recently in the case of adamantane [14]. In addition to its possible ability in degrading pollutants under solar irradiation, the decatungstate anion presents two advantages for its potential use in detoxification processes: it has a low toxicity [15] (as TiO_2), and industrial processes involving the supported photocatalyst could be considered. Indeed, contrary to TiO_2 which is heterogeneous, the decatungstate anion is soluble in aqueous solution and not easily separated from the degradation products for recycling. However, the synthesis of decatungstate anion embedded in carbon fibers [16], supported on TiO_2 [17,18] or on silica [19,20], has recently been published.

The work presented here describes the solar photocatalysed degradation of phenol, 4-chlorophenol, 2,4-dichlorophenol, bromoxynil, atrazine, imidachloprid and oxamyl in the presence of sodium decatungstate and TiO_2, which has been studied at Plataforma Solar de Almeria. A comparison will be made between the efficiencies of the decatungstate anion and TiO_2 concerning the kinetics of degradation and mineralization of the substrates under solar irradiation. The mechanism of degradation photocatalysed by sodium decatungstate has also been investigated by nanosecond laser photolysis, and will be compared with the mechanism of degradation by TiO_2.

2. Experimental part

2.1. Solar irradiations (Plataforma Solar de Almeria)

The photoreactor was made of a Liebig cooler type glass tube (two coaxial tubes, forming an inner and outer compartment), fixed at the focus of a Compound Parabolic Collector (CPC) aluminium mirror of 100 cm length and 20 cm width. The thickness of the outer compartment inside which was circulated the solution was about 7 mm. The inner compartment was used for water cooling the solution which went through a centrifugal pump (polypropylene), teflon tubes, the glass tube and a glass reservoir where samples were retrieved. The initial volume of solution was 900 ml and reactions were carried out outdoor under atmospheric oxygen. The parabolic mirror was set with an angle of 37° with respect to the horizontal since the latitude of Almeria is around 37° and this inclination allows the maximum yearly efficiency for this type of solar collectors. The global UV power ($W\,m^{-2}$), which takes into account direct and scattered radiation, was recorded every day. Integration of the UV-power gives the incident energy ($J\,m^{-2}$) received by the sample during the irradiation.

2.2. Laser photolysis

The nanosecond laser was a Q-switched Nd : YAG laser manufactured by BM Industries (model BMI 5011 DNS 10), delivering 7–8 ns pulses at 1064 nm. Q-switching was made with a Pockels cell inside the cavity. The giant pulse was frequency doubled and tripled in KDP crystals. The output energy was 120 mJ at 353 nm. The energy deposited in the sample was lowered to 3 mJ by interposing a diffusing plate in front of the irradiation cell. This energy was measured with a Gentec pyroelectric detector. The excitation beam and the probe beam generated by a pulsed xenon source were perpendicular to each other inside the 1 cm × 1 cm cell. The analyzing beam was spectrally dispersed by a monochromator and converted to an electric signal by a Hamamatsu R928 PM tube. The electric signal was recorded by a digital memory oscilloscope (Tektronix TDS 620 B) connected with a PC computer. The transient signals were analyzed by a home made routine using Igor procedure. Every given rate constant is the mean value of at least five different measurements.

2.3. Chemical products

Sodium decatungstate $Na_4W_{10}O_{32}$ is synthesized [21] and characterized [22] according to literature methods (E.A. cal. for $Na_4W_{10}O_{32}\cdot 7H_2O$: W 71.49%; H 0.55%; found: W 71.50%; H 0.55%; C < 0. 01%; I.R. 1004 cm^{-1} (w); 962 cm^{-1} (s); 912 cm^{-1} (s); 800 cm^{-1} (vs); 580 cm^{-1} (w); 420 cm^{-1} (s); UV $\varepsilon_{323\,nm} = 14{,}700 \pm 300\,l\,mol^{-1}\,cm^{-1}$ in CH_3CN and H_2O). TiO_2 P25 was purchased from Degussa, phenol (98%) from Prolabo, 4-chlorophenol (99%) and standard imidachloprid (1-(6-chloro-3-pyridylmethyl)-*N*-nitroimidazolidin-2-ylideneamine, 99%) from Aldrich, 2,4-dichlorophenol (98%) from Merck, certified bromoxynil (3,5-dibromo-4-hydroxybenzonitrile, 99%) from Cluzeau Info Labo, technical atrazine (6-chloro-2-ethylamino-6-isopropylamino-1,3,5-triazine, 95%) from Ciba Geigy. All these products were used without further purification. Two formulated products were also used: Confidor 20 LS, Bayer, which contains 20% of imidachloprid before dilution and Vydate LS from DuPont, which contains 24% of oxamyl before dilution.

The solutions were made with acidified distillated water ($HClO_4$, pH 2.2), either added with TiO_2 0.2 $g\,l^{-1}$ or with $Na_4W_{10}O_{32}$ $1.5 \times 10^{-3}\,mol\,l^{-1}$. Indeed, above pH 3 the decatungstate anion is in equilibrium with another isomer which only absorbs light under 280 nm, and cannot be excited by solar radiation [23]. The initial concentrations of the solutions were $10^{-3}\,mol\,l^{-1}$ for phenolic substrates, $0.2 \times 10^{-3}\,mol\,l^{-1}$ for imidachloprid, $0.1 \times 10^{-3}\,mol\,l^{-1}$for bromoxynil and atrazine and $0.65 \times 10^{-3}\,mol\,l^{-1}$ for oxamyl.

2.4. Analysis

The concentrations of the substrates were followed by HPLC (injector and variable wavelength detector Hewlett-Packard 1050) equipped with a reverse phase column C-18 (Merck, LiChro-CART RP-18). The eluents (mixture of water/acetonitrile or water/methanol depending on the substrates) were degassed with helium before use. The eluent flux was set to 1 ml min^{-1}. The samples were filtered before injection (Millipore MVLP filters, 0.45 mm).

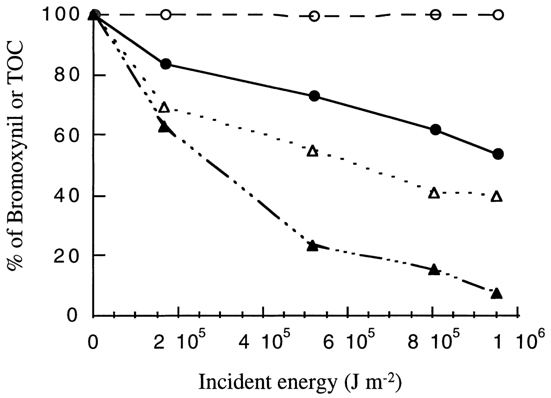


Fig. 2. Solar photodegradation of bromoxynil in the presence of either TiO_2 0.2 $g\,l^{-1}$ (triangles) or $Na_4W_{10}O_{32}$ $1.5 \times 10^{-3}\,mol\,l^{-1}$ (circles). The filled signs represent the evolution of the concentration of bromoxynil, and the open ones the evolution of the TOC. The aqueous solutions were acidified to pH 2.2 ($HClO_4$) and the initial concentration of bromoxynil was $1.3 \times 10^{-4}\,mol\,l^{-1}$.

The determination of Total Organic Carbon (TOC) was performed on a Heraeus-Foss Electric LiquiTOC-2001 model, calibrated every week in the specific range of TOC to be measured by an aqueous solution of potassium hydrogenophtalate.

3. Solar photodegradation and mineralization of pesticides

Fig. 2 shows the evolution of the concentration of bromoxynil and the TOC versus the incident energy of irradiation, for acidic solutions of the pollutant in the presence of either TiO_2 or $Na_4W_{10}O_{32}$. The concentration of TiO_2 is 0.2 $g\,l^{-1}$, which is the concentration usually used at the Plataforma Solar since it is the most efficient for the configuration of its solar reactors. The concentration in sodium decatungstate is $1.5 \times 10^{-3}\,mol\,l^{-1}$. No optimization of the concentration of the photocatalyst $Na_4W_{10}O_{32}$ has been made in the solar reactor. However, up to a concentration of decatungstate of $1.5 \times 10^{-3}\,mol\,l^{-1}$, the rate of the photodegradation of phenol was proportional to the concentration of the photocatalyst. For a concentration of decatungstate of $1.5 \times 10^{-3}\,mol\,l^{-1}$, nearly all the potential photons at 323 nm should be absorbed in 7 mm of solution (thickness of the outer compartment in which the solution was circulated). An increase of the decatungstate concentration should lead to the saturation of the photodegradation rates.

Curves similar to those of Fig. 2 are obtained for the other pesticides. The results are summed up in Table 1, for similar values of the incident energies. Direct photolysis is not reported here but it was checked that for all the compounds, decomposition and mineralization by direct photolysis was slower than decomposition in the presence of either TiO_2 or $Na_4W_{10}O_{32}$ by at least a factor of 5.

For all the phenolic compounds studied (phenol, 4-chlorophenol, 2,4-dichlorophenol, bromoxynil), the solar degradation of the pollutant is twice faster in the presence of titanium dioxide than in the presence of the decatungstate anion, as was observed by Papaconstantinou et al. during irradiation with a UV-lamp [12,13]. Concerning the other pesticides, solar photodecomposition of atrazine and standard imidachloprid in the presence of $Na_4W_{10}O_{32}$ is slower than in the presence of TiO_2. On the opposite, the decatungstate anion becomes the most interesting photocatalyst for the degradation of formulated imidachloprid and formulated oxamyl. The influence of the formulation will be discussed in part 5.

The mineralization of all the pure compounds (phenol, 4-chlorophenol, 2,4-dichlorophenol, bromoxynil, atrazine, imidachloprid) soon followed their degradation in the case of TiO_2. On the contrary, there was nearly no mineralization during 1 day of irradiation in the presence of $Na_4W_{10}O_{32}$ (and also under direct photolysis), even if the pollutant was degraded quickly. It has to be noticed that these results are not consistent with those of Papaconstantinou et al. [12,13], who observed the mineralization of the phenolic compounds during their course of photodegradation in the presence of polyoxotungstate under UV-lamp irradiations.

Absolute comparison between the efficiencies of $Na_4W_{10}O_{32}$ and TiO_2 is difficult. First, sodium decatungstate produces homogeneous aqueous solutions whereas TiO_2 is a heterogeneous photocatalyst. In this last case, it is difficult to estimate the number of photons absorbed by the semi-conductor, since there is an important scattering, and since this number should depends on the configuration of the reactor used [24]. Secondly, if the mechanism of photocatalysis in the presence of TiO_2 has been extensively studied for different types of organic substrates [9–11], the mechanism of photoreactions between $Na_4W_{10}O_{32}$ and phenolic compounds or pesticides is still badly known. It is important to know this mechanism if this photocatalyst is to be used for environmental remediation. Indeed, since the rates of mineralization appear to be quite low (see Table 1), it has to be checked that the photoproducts formed during the degradation of the pesticides are not more toxic than the parent compounds.

4. Mechanism of photocatalysis in the presence of $Na_4W_{10}O_{32}$

A mechanism of photocatalysis by $Na_4W_{10}O_{32}$ involving $OH^\bullet$ radicals has been proposed by Papaconstantinou et al. [12,13]. However, up to now, the formation of $OH^\bullet$ has never been detected in the presence of organic substrates (organic solvents and counter ions can act as substrates [25]). In a recent study on the photodegradation of 4-chlorophenol by $H_3PW_{12}O_{40}$ in aqueous or acetonitrile solution [26], a precomplexation between the 4-chlorophenol and the polyoxometalate was observed. The authors proposed that an electron or H atom transfer can occur either in the excited complex or by diffusional encounter between the excited state of the polyoxometalate and the phenol. In the case of the decatungstate anion $W_{10}O_{32}{}^{4-}$, we did observe neither any shift of the absorption band of the polyoxometalate, nor the coming out of a new absorption band when the concentration of the phenol or chlorophenol added to the solution was progressively increased. We then ruled out the possibility of any precomplexation between the phenols and $W_{10}O_{32}{}^{4-}$.

Previous picosecond and nanosecond flash-photolysis experiments [21,27–29] had lead to a more reliable mechanism in the case of the oxidation of alkanes and alcohols, consecutive to the UV irradiation of solutions in the presence of $W_{10}O_{32}{}^{4-}$. The first step of the reaction is the formation upon light absorption of the excited state $W_{10}O_{32}{}^{4-*}$ of the polyoxometalate. This excited state has a very short lifetime (less than 30 ps [21]) and relaxes in a secondary excited species named X. $W_{10}O_{32}{}^{4-*}$ is less oxidant than $OH^\bullet$, since its redox potential has been estimated by Hill as 1.79 V/NHE in acetonitrile [30]. The nature of the intermediate X is still not clear and no estimation of its redox potential is then possible. It seems that X

Table 1

Percentages of degradation and mineralization obtained for different pesticides under solar photocatalysis either by TiO_2 ($0.2\,g\,l^{-1}$) or $Na_4W_{10}O_{32}$ ($1.5\times10^{-3}\,mol\,l^{-1}$). The solutions were acidified to pH 2.2 ($HClO_4$) and the initial concentrations were $1\times10^{-3}\,mol\,l^{-1}$ for phenolic substrates, $0.2\times10^{-3}\,mol\,l^{-1}$ for imidachloprid, $0.1\times10^{-3}\,mol\,l^{-1}$ for bromoxynil and atrazine and $0.65\times10^{-3}\,mol\,l^{-1}$ for oxamyl

Substrate	Incident energy ($10^5\,J\,m^{-2}$)	TiO_2		$Na_4W_{10}O_{32}$	
		% of Degradation	% of Mineralization	% of Degradation	% of Mineralization
Phenol	5.4	19	14	1	<1
4-Chlorophenol	6.1	68	34	17	<1
2,4-Dichlorophenol	6.4	66	36	18	<1
Bromoxynil	5.2	77	45	27	<1
Atrazine	6.0	100	34	98	7.6
Standard imidachloprid	5.8	100	82	100	3
Formulated imidachloprid[a]	5.1	74	–[c]	94	–[c]
Formulated oxamyl[b]	5.9	80	–[c]	85	–[c]

[a] Confidor 20 LS, Bayer (20% of imidachloprid).

[b] Vydate LS from DuPont (24% of oxamyl).

[c] The added organic compounds (dyes and surfactants) make the TOC measurements unrelevant for the mineralization of the substrate we are interested in.

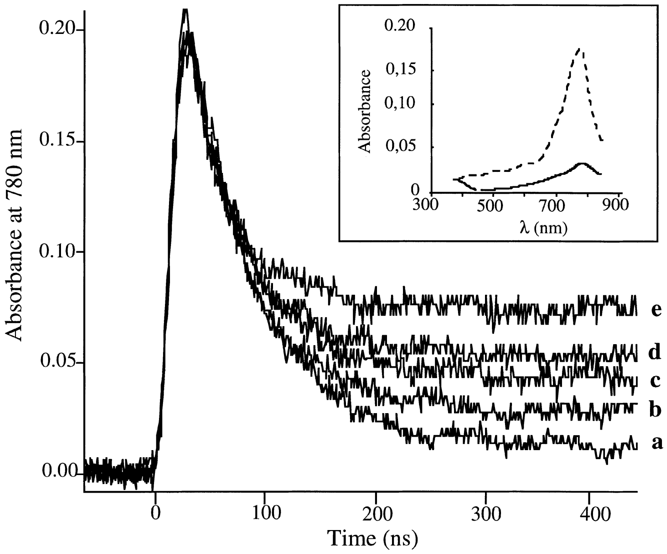


Fig. 3. Absorbance at 780 nm of acetonitrile solutions of $Na_4W_{10}O_{32}$ ($6.1\times10^{-3}\,mol\,l^{-1}$), containing increasing concentrations of imidachloprid. a: $0\,mol\,l^{-1}$; b: $0.41\times10^{-3}\,mol\,l^{-1}$; c: $0.81\times10^{-3}\,mol\,l^{-1}$; d: $1.21\times10^{-3}\,mol\,l^{-1}$; e: $1.98\times10^{-3}\,mol\,l^{-1}$. Insert: Absorption spectrum at the end of the ns laser pulse (dashed line) and 400 ns after the pulse (full line) of an acetonitrile solution of $Na_4W_{10}O_{32}$ ($6.1\times10^{-3}\,mol\,l^{-1}$), with atrazine $5.4\ 10^{-2}\,mol\,l^{-1}$.

could be a charge transfer excited state [21,27–29]. Indeed, its absorption spectrum looks like the spectrum attributed to the reduced $W_{10}O_{32}{}^{5-}$ species (in which the W atom has an oxidation state of 5), but is different in the UV range (see insert of Fig. 3). It has been established in the case of the oxidation of alkanes and alcohols that X reacts with the organic substrates by either electron or H atom transfer [21,27–29], at the nanosecond time scale. We then undertook nanosecond flash photolysis experiments.

4.1. Investigation by nanosecond flash photolysis

These experiments were realised mainly in acetonitrile, due to the better solubility of pesticides in this solvent than in water. However, the observed signals and the mechanisms are similar in water and in acetonitrile. At the end of the nanosecond pulse, the transient X is observed and characterized by its absorption spectrum with a maximum around 780 nm (see insert of Fig. 3). In the absence of any organic substrate, this transient decays exponentially with a lifetime of 35 ns in water and 65 ns in acetonitrile (decay *a* of Fig. 3) [21,27–29]. In the presence of an organic substrate, like imidachloprid, 400 ns after the pulse, the shape of the absorption spectrum has changed (see insert of Fig. 3). There is now two absorption bands of similar intensities, around 780 nm and below 400 nm. This absorption spectrum remains unchanged until the millisecond time range, and is similar to that of the reduced polyoxotungstate $W_{10}O_{32}{}^{5-}$ or its protonated form $HW_{10}O_{32}{}^{4-}$, obtained electrochemically [21]. The kinetics of this H atom abstraction or electron transfer between X and the organic substrate can be followed at 780 nm for different initial concentrations in organic substrates, like imidachloprid (Fig. 3).

Increasing the initial organic substrate concentration has two effects. The first one is to increase the persistent absorption obtained at 780 nm 400 ns after the pulse, since the amount of the produced reduced form of the decatungstate increases. According to Duncan and Fox [29], the presence of this stable reduced form 400 ns after the pulse is the consequence of a H atom abstraction rather than an electron transfer. Indeed, in this latter case, back electron transfer induces low efficiency of the reaction. The second one is a kinetic effect. The decay of the transient X remains pseudo first order, and the plot of the decay constant *k* versus the organic substrate concentration is linear (Fig. 4). The slope gives the bimolecular rate constant k_R of the reaction between X and the organic substrate. The values obtained for the different pesticides are summed up in Table 2. These bimolecular rate constants appear to be lower than the diffusion-limited bimolecular rate constants. For H atom abstraction, the rate constants depend strongly on the Z–H binding energies (Z = C, N, O) and are lower than the diffusion limit. An analogy can be made with H atom abstraction by excited ketones. For both systems, the reactivity increases in the order C–H (alkanes) < C–H (alcohols) < O–H (phenols) [28,29,31], following the order of the binding energies. The bimolecular rate constants for the reaction of decatungstate and alkanes in acetonitrile are around $5 \times 10^7\,\mathrm{l\,mol^{-1}\,s^{-1}}$ [27,29]. For a given substrate, these rate constants are generally higher (by a factor of 2) in water than in acetonitrile.

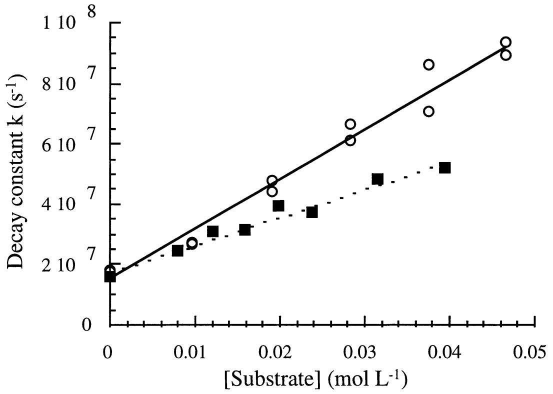
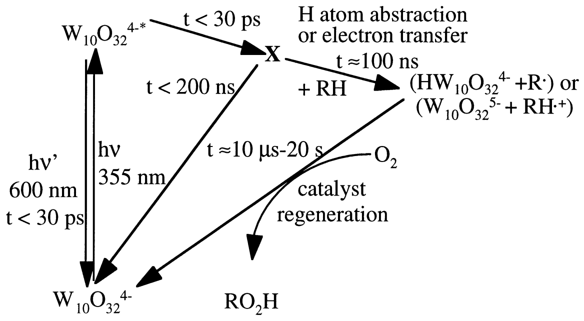


Fig. 4. Decay rate constants *k* in acetonitrile at 780 nm of the transient X vs. the concentration of 2-chlorophenol (open circles) and 3-chlorophenol (filled squares). The concentration of $Na_4W_{10}O_{32}$ was $6.1 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$.



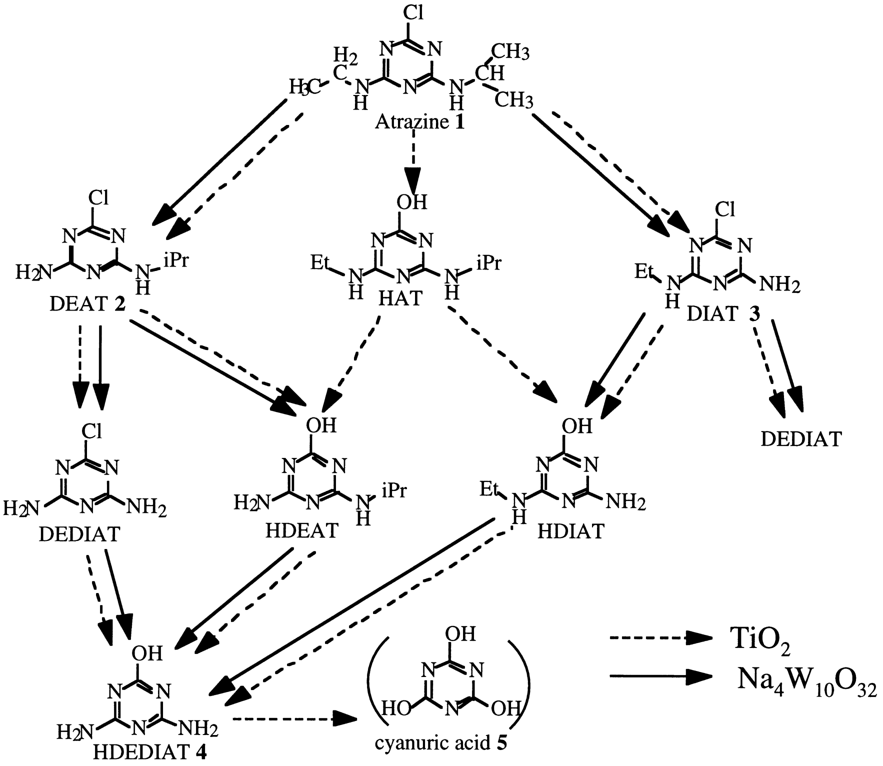
Scheme 1. Proposed mechanism for the photocatalysis by $Na_4W_{10}O_{32}$. RH represents the organic pesticide (adapted from [27]).

On the basis of this results, we propose a reaction mechanism (Scheme 1) similar to the one already proposed in the case of the oxidation of alkanes and alcohols [21,27–29]. X is the key intermediate of the photocatalysis mechanism in the presence of $Na_4W_{10}O_{32}$. It is formed in less than 30 ps. It can decay by physical deactivation or react with the pesticide RH to form either the radical $RH^{\bullet+}$ or $R^{\bullet}$. In the presence of oxygen, the photocatalyst is regenerated on a microsecond to second time range and the photocatalytic cycle is closed, with the formation of hydroperoxides RO_2H [27,28]. These hydroperoxides can be quantified or the subsequent formed products be analyzed by classical analytic methods, like chromatographies.

Table 2
Bimolecular rate constants k_R for the reaction of the transient X and the different pesticides in acetonitrile and water. The solutions were acidified to pH 2.2 ($HClO_4$) and the concentration of $Na_4W_{10}O_{32}$ was 6.1×10^{-3} mol l^{-1}

Substrate	Bimolecular rate constants in acetonitrile (l mol^{-1} s^{-1})	Bimolecular rate constants in water (l mol^{-1} s^{-1})
Phenol	$(1.6 \pm 0.1) \times 10^9$	$(2.4 \pm 0.2) \times 10^9$
2-Chlorophenol	$(1.6 \pm 0.1) \times 10^9$	$(4.0 \pm 0.2) \times 10^9$
3-Chlorophenol	$(9.3 \pm 0.4) \times 10^8$	$(4.9 \pm 0.2) \times 10^9$
4-Chlorophenol	$(1.6 \pm 0.1) \times 10^9$	$(5.5 \pm 0.3) \times 10^9$
Bromoxynil	$(6.6 \pm 0.3) \times 10^8$	–[a]
Atrazine	$(1.2 \pm 0.1) \times 10^8$	–[a]
Standard imidachloprid	$(3.9 \pm 0.2) \times 10^9$	–[a]
Standard oxamyl	$(7.1 \pm 0.3) \times 10^8$	–[a]

[a] Solubility in water is too low to determine the value.



Scheme 2. A simplified scheme of photodegradation of atrazine in the presence of either TiO_2 (dashed arrows) or $Na_4W_{10}O_{32}$ (full line arrows) [32,33].

4.2. Identification of the products of degradation of atrazine

A more detailed study was undertaken in the case of atrazine to identify the products of the solar photodegradation by photocatalysis either by $Na_4W_{10}O_{32}$ or TiO_2[32]. None of the two photocatalysts leads to the mineralization of the aromatic cycle of the pollutant [32,33]. It is then crucial to determine the photodegradation products and to compare their toxicity with that of atrazine. Two reaction pathways are possible: dehalogenation and dealkylation. The phytotoxicity of atrazine is mainly due to the chlorine atom of the triazine cycle, and dehalogenation reactions are environmentally important. A simplified reaction scheme with the different identified products is represented on Scheme 2 [32,33].

In the presence of TiO_2, both reaction pathways (dehalogenation and dealkylation) occur, due to the hydroxyl radical $OH^\bullet$ reactions [32,33]. In the presence of $Na_4W_{10}O_{32}$, dehalogenation will occur consecutively to an electron transfer between the transient X and atrazine 1. This electron transfer has a low efficiency, because of its reversibility by back electron transfer [29,32]. Dealkylation occurs more easily by H atom abstraction, which is not reversible and efficient [29,32]. Competition of both mechanisms-electron transfer and H atom abstraction-favors this last one, which is the only one that can occur on atrazine. Dehalogenation can occur, but only on the dealkylated products 2 and 3. In this study, the most advanced product identified was HDEDIAT 4, observed after 30 h of irradiation with a UV lamp either in the presence of $Na_4W_{10}O_{32}$ or TiO_2 [32]. However, it was shown that photocatalysis of atrazine in the presence of TiO_2 leads to cyanuric acid 5 as a final product [33].

4.3. Comparison of the photodegradation mechanisms in the presence of TiO_2 and $Na_4W_{10}O_{32}$

TiO_2 and $Na_4W_{10}O_{32}$ are two photocatalysts very different in nature (heterogeneous/homogeneous). The primary photoprocesses are not the same. The mechanisms of the photodegradation of organic substrates by photocatalysis on semiconductor particles like TiO_2 have been extensively studied [9–11]. Light absorption induces the creation of an electron-hole pair, which subsequently reacts in aqueous media in the presence of oxygen to form mainly hydroxyl radicals $OH^\bullet$. These hydroxyl radicals are very strong oxidants ($E^\circ(OH^\bullet/H_2O) = 2.58$ V/NHE at pH = 3 [34]). They are the main species responsible for the oxidation of organic substrates and pollutants which can then be degraded. In the case of the decatungstate, the primary reaction is an electron transfer or H atom abstraction.

For most of the substrates, mineralization soon follows the degradation of the pollutant in the case of irradiation in the presence of TiO_2. The decomposition of degradation intermediates occurs rapidly since the hydroxyl radicals being very strong oxidants are not selective. They degrade both the reactions intermediates and the initial substrate. In the presence of $Na_4W_{10}O_{32}$, the reactivity of the products formed can be lower than that of the parent molecule and the total mineralization of the substrates cannot occur, or occur in a longer time range. In this case, the use of decatungstate should be restricted only to the pollutants that produce non toxic intermediates.

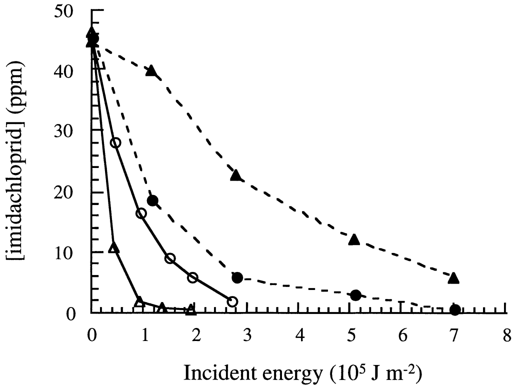


Fig. 5. Solar photodegradation of imidachloprid, as a pure product (open signs) or in diluted formulated solution (filled signs) in the presence of either TiO_2 0.2 g l^{-1} (triangles) or $Na_4W_{10}O_{32}$ 1.5×10^{-3} mol l^{-1} (circles). The aqueous solutions were acidified to pH 2.2 ($HClO_4$) and the initial concentration of imidachloprid was 2×10^{-4} mol l^{-1} (45 ppm) in every solution.

5. Influence of the presence of surfactants

However, $Na_4W_{10}O_{32}$ can be more interesting to use than TiO_2 in order to degrade formulated pesticides. Whereas for all the pure compounds tested, solar photodecomposition was slower in the presence of $Na_4W_{10}O_{32}$ than in the presence of TiO_2, formulated oxamyl degraded at similar rates in the presence of both photocatalysts (see Table 1). The influence of the presence of surfactants was better evidenced in the case of imidachloprid. Fig. 5 reports the degradation of aqueous acidic solutions of imidachloprid versus the incident energy per square meter, for standard and formulated imidachloprid, in the presence of either $Na_4W_{10}O_{32}$ or TiO_2.

As clearly shown in the case of imidachloprid, the presence of surfactants has a drastic effect on the rate of the solar photodegradation of the pollutant in the presence of TiO_2 (and also under direct photolysis), whereas it has only a slight effect in the presence of $Na_4W_{10}O_{32}$. The formulation is conceived to get a better wetting on the plant surface in order to obtain a better efficiency for agricultural treatment. This formulation contains dyes and surfactants since the solution is colored (orange) and foaming, whereas a solution of pure imidachloprid is not. In the presence of titanium dioxide, surfactants, able to adsorb on TiO_2, may affect the rate of the degradation of imidachloprid in two ways. First, by a competition for adsorption on the semi-conductor particles between imidachloprid and the surfactant. The rate of pollutant degradation by TiO_2 generally follows Langmuir-Hinshelwood type kinetics, and decays in the case of competitive adsorption [10]. Secondly, by a kinetic competition between the added formulation products and imidachloprid for the reaction with hydroxyl radicals $OH^\bullet$. These radicals, being very reactive, are not selective and can oxidize both the formulation products and the pesticide. Decomposition of surfactants [35,36] and dyes [37] by photocatalysis with TiO_2 has already been demonstrated, and could be used for the treatment of industrial waste waters of textile industries.

On the other side, the formulation has little effect on the kinetics of degradation of imidachloprid in the presence of $Na_4W_{10}O_{32}$. The reaction mechanism implies in this case the transient excited state X (probably an excited charge transfer state) of the polyoxotungstate. Surfactants and dyes compete kinetically with the pesticide and the important factor to compare the reactivity will be the ratio $(k_{R,\mathrm{surfactant}}[\mathrm{surfactant}])/(k_{R,\mathrm{pesticide}}[\mathrm{pesticide}])$, where ≪pesticide≫ designs the active molecule in the formulation and k_R the bimolecular rate constant of the reaction with the transient X. In formulations, the active molecule usually represents between 10 and 50% (i.e. 100–500 $g\,l^{-1}$) of the product, and the different adjuvants 5% at the most [38]. The ratio [surfactant]/[pesticide] can then be considered to be usually less than 0.1 in weight.

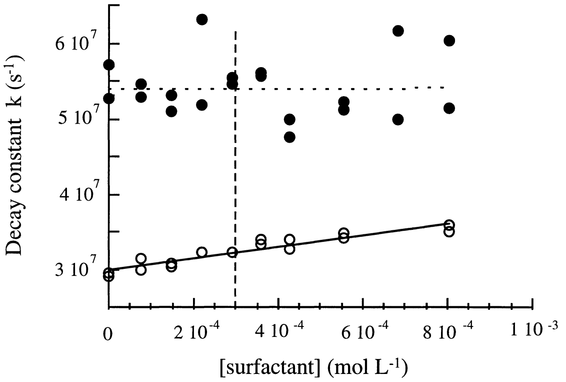


Fig. 6. Influence of the concentration of Triton X100 on the decay constant of the transient X in the absence of 2-chlorophenol (open circles) and in the presence of 2-chlorophenol (filled circles). The solutions were acidified to pH 2.2 ($HClO_4$). The concentration of $Na_4W_{10}O_{32}$ was $6.1\times10^{-3}\,mol\,l^{-1}$ and that of 2-chlorophenol was $3.1\times10^{-2}\,mol\,l^{-1}$. The ratio [surfactant]/[2-chlorophenol] was 0.15 in weight for $[TX100]=8\times10^{-4}\,mol\,l^{-1}$. The dashed line at $3\times10^{-4}\,mol\,l^{-1}$ indicates the critical micellar concentration.

In order to simulate the formulation effect, we used 2-chlorophenol as a model pesticide, and two surfactants: sodium dodecyl sulfate (SDS), model of an anionic surfactant, and Triton X 100 (TX100), model of a neutral surfactant. 2-chlorophenol was chosen because of its high solubility in water in comparison to the other pesticides. In the presence of cetyltrimethylammonium (bromide or chloride) chosen as a model of cationic surfactants, the decatungstate anion precipitates. The concentration of 2-chlorophenol was fixed and the surfactant concentration was increased progressively until the ratio [surfactant]/[pesticide] was around 1 for SDS and 0.1 for TX100 (in weight). Fig. 6 presents the observed decay constants k obtained at 780 nm by nanosecond flash-photolysis, against the concentration of TX100 in the absence of 2-chlorophenol and in the presence of 2-chlorophenol with a ratio [TX100]/[2-chlorophenol] around 0.1 (0.15 at the maximum of [TX100]). Concentrations of TX100 higher and lower than the critic micellar concentration are explored, but no change is observed at the cmc frontier. Curves similar to those of Fig. 6 are obtained for SDS. When the surfactant is alone in solution, we obtain the bimolecular rate constants k_R for the reaction between X and these two surfactants in water: $(8.2\pm1)\times10^{8}\,l\,mol^{-1}\,s^{-1}$ for SDS and $(7.6\pm1)\times10^{9}\,l\,mol^{-1}\,s^{-1}$ for TX100, from the linear plot of k against the concentration of surfactant. These bimolecular rate constants are of the same order to those obtained for the phenolic substrates, also in water (see Table 2). Fig. 6 shows that in the formulated conditions with the ratio [surfactant]/[pesticide] below 0.2 (in weight), there is no influence of the presence of adjuvants on the rate constants k in the presence of pesticide. This unexpected result can be accounted for by either experimental error masking a slow increase of k, or the superposition of two competitive effects: an increase of k due to the increase of the surfactant concentration, counterbalanced by a decrease due to the micellization of the phenol, as shown on Fig. 6. No appreciable change of k is observed at the cmc.

6. Conclusion and perspectives

In this study, we demonstrate the possibility of using a new homogeneous photocatalyst, sodium decatungstate $Na_4W_{10}O_{32}$, for the solar photodecomposition of phenols and pesticides such as bromoxynil, atrazine, imidachloprid and oxamyl. Concerning pure chemical products, the widely used heterogeneous photocatalyst TiO_2 appears to be the most efficient for both the mineralization and the degradation of the substrates. However, when the pesticides are used in formulated solutions, the added organic products have a low effect during photocatalysis in the presence of sodium decatungstate whereas the degradation rate is lowered in the presence of TiO_2. This difference of reactivity is accounted for by the different nature of the active species during both photodegradation processes: $OH^{\bullet}$ in the case of TiO_2, a transient excited state X in the presence of sodium decatungstate. We demonstrate that the reaction between X and the pesticides is an electron transfer or a H atom abstraction occurring on the nanosecond time scale. At the usual concentrations used, the lower reactivity between X and model surfactants than between X and pesticides explains that the presence of formulation has no or a low inhibition effect on the solar photodegradation of pesticides by $Na_4W_{10}O_{32}$, contrarily to TiO_2.

Concerning the practical feasibility of the $Na_4W_{10}O_{32}$ photocatalytic system, the decatungstate anion has been reported as environmentally benign [15]. It is regenerated by atmospheric oxygen and high turnovers can be attained [39]. The problem of the separation of the homogeneous photocatalyst from the treated aqueous wastes can be solved by either precipitation with a counter-cation or fixation on a support. Due to the high solubility of $W_{10}O_{32}^{4-}$ in water (around $250\,g\,l^{-1}$), this latter solution seems to be more adapted. The synthesis of decatungstate anion embedded in carbon fibers [16], supported on TiO_2 [17,18] or on silica [19,20], have been reported. Inclusion of the polyoxometalate in inorganic matrices, such as sol–gel, could be another way of development.

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