

On the mechanism of photocatalytic degradation of chlorinated phenols to CO₂ and HCl by polyoxometalates

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Received 27 March 1995; accepted 11 September 1995

Abstract

Photolysis of homogeneous solutions of polyoxometalates W₁₀O₃₂⁴⁻, PW₁₂O₄₀³⁻, and SiW₁₂O₄₀⁴⁻ with near visible and UV light in presence of chlorophenols, leads to complete decomposition of substrates to CO₂ and HCl. At the initial stages of photooxidation, decomposition rates, in presence and absence of dioxygen, practically compete with each other. On the contrary, at the final stages of decomposition, the rate in presence of dioxygen is an order of magnitude faster than in absence of dioxygen. The main function of dioxygen seems to be the reoxidation (regeneration) of the catalyst. Several hydroxyl intermediates justify the formation of OH radicals. The hydroxyl aromatic derivatives detected are in accordance with the electrophilicity of OH radicals. Hydroxy butanedioic acid and acetic acid were detected in the three monochlorophenols, prior to mineralization.

Keywords: Chlorophenols; Photocatalysts; Photodegradation mechanism; Polyoxometalates

1. Introduction

Contamination of land water and air is an ever increasing problem for the industrial world. To phase this problem the scientific community works in two directions: (a) to find new industrial nonpolluting methods (green technology) and (b) to find methods to clean the environment.

Among the top priority pollutants are chlorinated phenols [1] that find use, among other things, as preservatives of wood and in the manufacture of paper. Unfortunately, they are also byproducts of chlorinated water.

Various methods have been used for their decomposition [2]. Those that involve electromagnetic radiation include mainly: (a) treatment with ⁶⁰Co- γ -radiation [3]; (b) UV light [4]; (c) UV light in presence of H₂O₂ [5] and (d) UV and near visible light in presence of TiO₂ [6,7]. These methods lead, more or less, to decomposition to CO₂ and HCl of which (a) and (d) seem to be quite effective.

Polyoxometalates (POM) have a long and interesting redox chemistry, acting as electron and oxygen relays, that find diversified applications [8]. This ability of POM has been recently employed in commercially important catalytic processes [9].

We have recently reported [10] another catalytic behaviour of POM, namely, the photocatalytic mineralization of chlorophenols (ClPh) to CO₂ and HCl using UV and near

visible light. In this paper we examine the mechanism of mineralization of chlorinated phenols by three representative polyoxometalates, namely, W₁₀O₃₂⁴⁻, PW₁₂O₄₀³⁻, and SiW₁₂O₄₀⁴⁻, as it unfolds through detection of various intermediates and compare it with the behaviour of TiO₂ and semiconductors generally.

2. Experimental

K₄W₁₀O₃₂(I), H₂PW₁₂O₄₀(II), and H₄SiW₁₂O₄₀(III) were prepared according to literature methods [11,12]. 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 to avoid direct photolysis of chlorophenols.

Analysis of the products was performed with a JASCO HPLC equipped with a Uvidec-100-VI detector monitored at 280 and 254 nm, and a Lichrospher RP-1885 μ m column using 35 vol.% CH₃CN in H₂O. Products were recognised by comparison with reference standards. Products with mainly no reference standards, were recognized with a FISIONS TRIO 1000 GC-MS equipped with a DB-5 (60 \times 0.25 mm) column using NIST/NBS and Wiley MS libraries software. Chloride ions were analysed spectrophotometrically [13].

Gas samples were analyzed for CO_2 in a VARIAN 3300 GC with a TCD and a 2 m Porapak 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 blue products using a HITACHI U-2000 spectrophotometer.

Unless otherwise stated, a typical experiment was as follows: to an 8 mL spectrophotometric cell, 1 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 was adjusted with HClO_4 . Deaerations and oxygenations were performed with extra pure Ar and dioxygen. In some deaeration experiments, Ar was purged through V^{2+} solution with identical results.

3. Results

3.1. In oxygenated solutions

3.1.1. Initial degradation of ClPh

Photolysis of o-, m-, and p-ClPh in presence of the three POM with near visible light ($\lambda > 320$ nm) to avoid direct photolysis of chlorinated phenols, results, to begin with, in

degradation of ClPh. Fig. 1 shows the degradation of o-, m- and p-ClPh in presence of POM (I), (II) and (III). The decomposition reactions, under these conditions follow first order kinetics.

3.1.2. Mineralization of ClPh. Identification of intermediates

The photodegradation of ClPh leads to CO_2 and Cl^- as final products. In the process several intermediates, mainly hydroxy radical adducts on the benzene ring, have been identified. Using o-ClPh as an example, the degradation of substrate, the formation of CO_2 and Cl^- , and the build up and decay of several intermediates, upon photolysis ($\lambda > 320$ nm) of aqueous solutions of substrate in presence of the catalysts (I), (II) and (III) are shown in Fig 2. Several other intermediates, see below, not showing in the diagrams have been identified by GC-MS.

3.1.3. Substrate concentration dependence

As is the case with practically all photolysis reactions, at least those that involve semiheterogeneous systems, i.e., semiconductors and substrate, and homogeneous systems (POM and substrate) a plot of initial degradation rate vs. the initial concentration of substrate follows a Langmuir–Hinshelwood behaviour [14] or Michaelis–Menden kinetics. The exem-

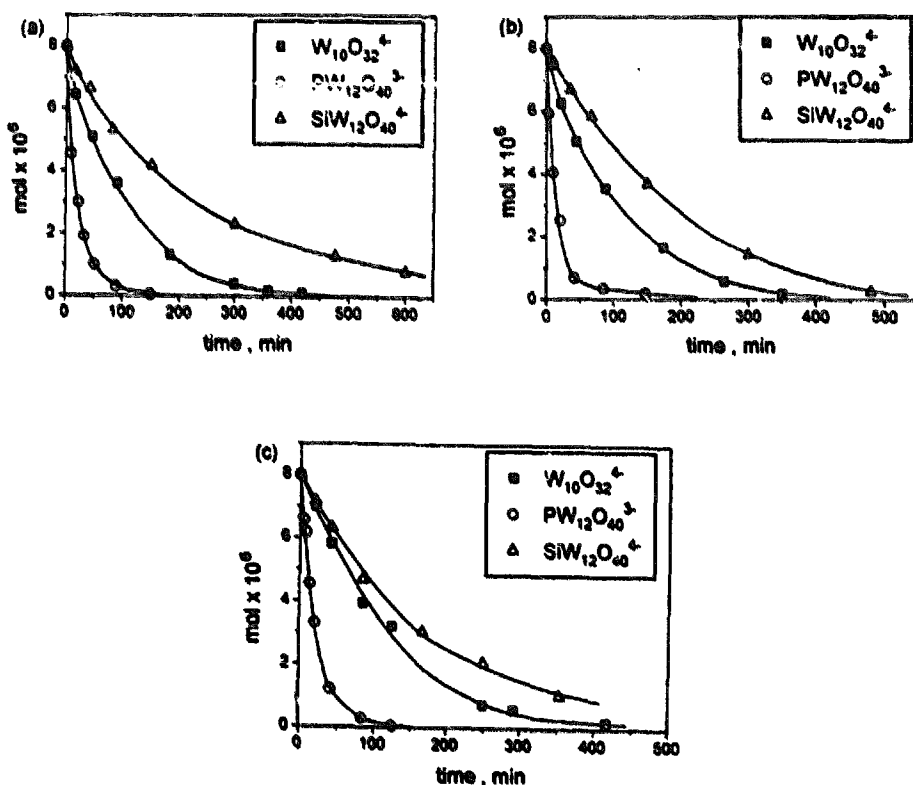


Fig. 1. Photodegradation of oxygenated aqueous solutions of (a) o-ClPh, (b) m-ClPh and (c) p-ClPh with photolysis time in presence of catalysts $\text{W}_{10}\text{O}_{32}^{4-}$, $\text{PW}_{12}\text{O}_{40}^{3-}$, and $\text{SiW}_{12}\text{O}_{40}^{4-}$. Catalyst, 0.7 mM; Substrate, 2.0 mM; $\lambda > 320$ nm, $T = 20$ °C. $\text{W}_{10}\text{O}_{32}^{4-}$, pH 2.5; $\text{PW}_{12}\text{O}_{40}^{3-}$, pH 1.0 and $\text{SiW}_{12}\text{O}_{40}^{4-}$, pH 3.0.

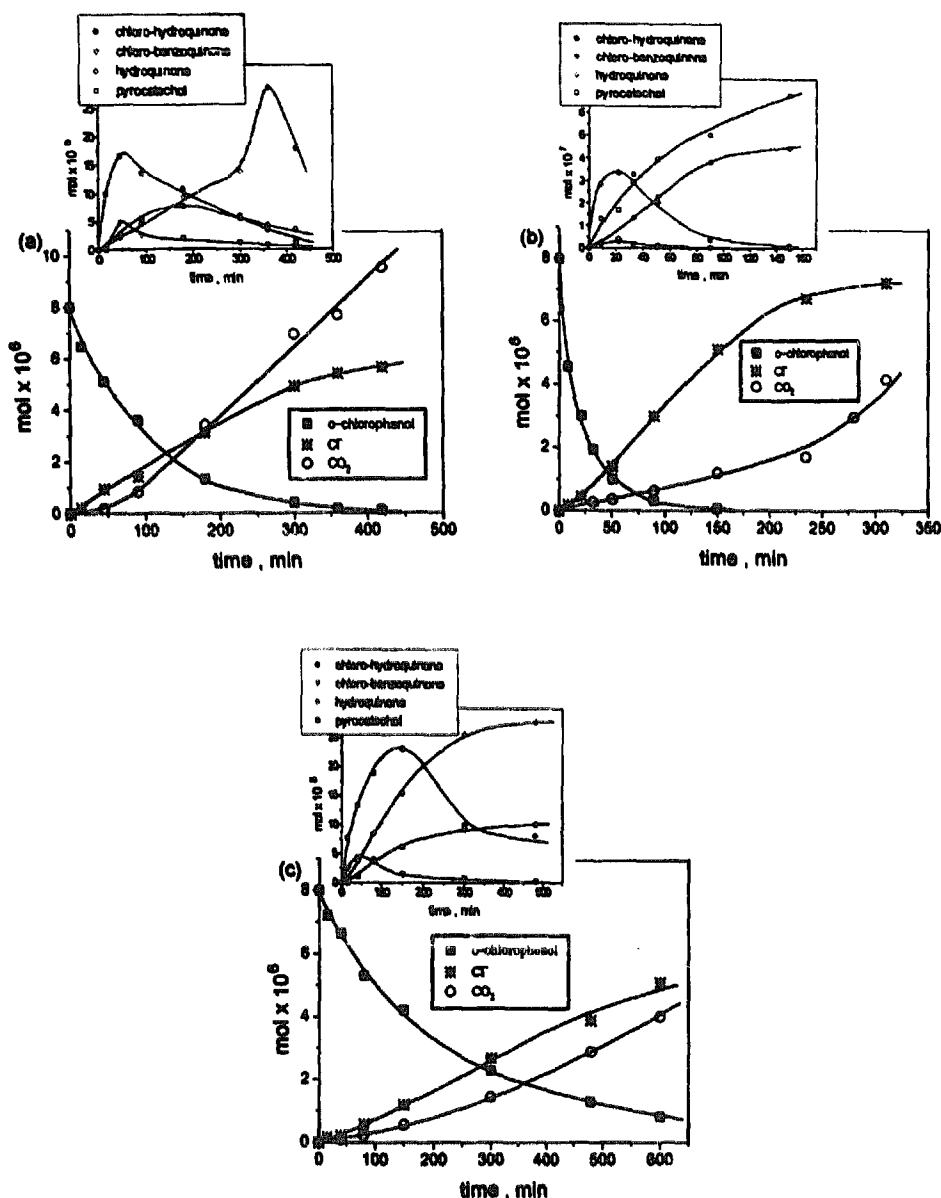


Fig. 2. Mineralization of oxygenated aqueous solutions of *o*-CIPh and formation of CO_2 and Cl^- with photolysis time in presence of (a) $\text{W}_{10}\text{O}_{32}^{4-}$, (b) $\text{PW}_{12}\text{O}_{40}^{3-}$ and (c) $\text{SiW}_{12}\text{O}_{40}^{4-}$. Inset: Formation and decay of some intermediates. Catalyst, 0.7 mM; Substrate, 2.0 mM; $\lambda > 320$ nm, $T = 20^\circ\text{C}$. (a) pH 2.5, (b) pH 1.0, (c) pH 3.0.

play behaviour of *p*-CIPh with the three catalysts is shown in Fig. 3.

3.2. In deoxygenated solutions

3.2.1. Initial degradation of CIPh

To investigate the role of dioxygen in the degradation of CIPh, experiments were carried out under similar conditions except that the solutions were purged with Ar instead of dioxygen. These experiments were a time compromise between: (a) to have the catalyst in the oxidized form where it exhibits its maximum performance, see below, and (b) to

have enough change in the substrate that could be detected by HPLC. Fig. 4 shows the formation of the one-electron reduced (I), i.e., $\text{W}_{10}\text{O}_{32}^{5-}$ and Cl^- , and the moles of degraded *p*-CIPh with photolysis time. Similar results were obtained with the other substrates and catalysts.

3.2.2. Mineralization of CIPh

Similar experiments in the presence and absence of dioxygen, resulted in both cases in mineralization of CIPh. Mineralization, though, in deaerated solutions was an order of magnitude slower than in the presence of dioxygen (see below).

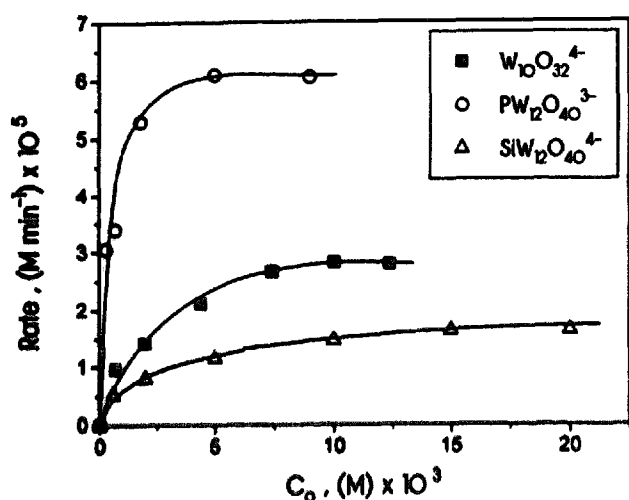


Fig. 3. Variation of the rate of degradation of oxygenated aqueous solution of p-CIPh, with initial concentration of substrate, upon photolysis in presence of the three catalysts. Catalyst, 0.7 mM; Substrate, 2.0 mM; $\lambda > 320$ nm, $T = 20$ °C. $W_{10}O_{32}^{4-}$, pH 2.5; $PW_{12}O_{40}^{3-}$, pH 1.0; and $SiW_{12}O_{40}^{4-}$, pH 3.0

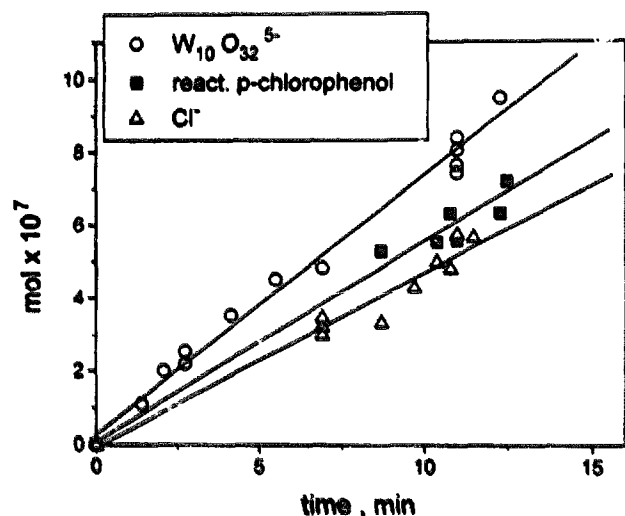
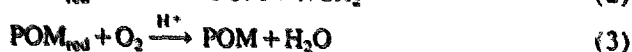
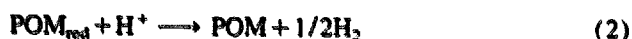


Fig. 4. Formation of the one-electron reduced decatungstate ($W_{10}O_{32}^{5-}$), Cl^- and decomposed p-CIPh, upon photolysis ($\lambda > 320$ nm) of deoxygenated aqueous solutions of p-CIPh with photolysis time. $W_{10}O_{32}^{4-}$, 0.7 mM; p-CIPh, 2.0 mM; pH 2.5, $T = 20$ °C.

4. Discussion

The general scheme of the catalytic action of POM may be presented as follows:



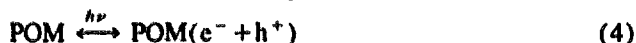
where S is the substrate.

Reduced POM, in the absence of dioxygen can be reoxidized (regenerated) by oxidizing reagents and/or H^+ producing, in the later case, hydrogen, whereas, in presence of

dioxygen, reduced POM are reoxidized through reaction 3. Generally reaction 3 is up to five orders of magnitude faster than reaction 2 [16].

POM on the other hand, absorb strongly in the near visible and UV area. This absorption at the oxygen to metal charge transfer (O-M CT) bands, (< 400 nm) results in enhancement of their redox ability (> 3 eV), thus rendering POM still more powerful oxidizing reagents. The oxidation of substrates results in concomitant reduction of POM, as is the case in thermal reactions, the extent of which depends on the conditions used [15].

Using semiconductor notation, the excitation of POM at the O-M CT bands can be presented as follows:

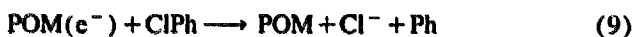
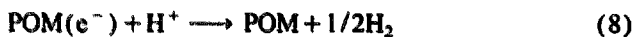


Now, in principle, h^+ cause oxidations and e^- reductions.

We will present below an overall account of the process in deoxygenated and oxygen saturated solutions that mainly involves the inorganic part of the mechanism. Details of the reactions that refer to the organic substrates are given at the end of the discussion.

4.1. In deoxygenated solutions

Reaction 4 is followed by



Reaction 5 is justified by the following reasons: (a) OH radicals have been detected by ESR in photolysis of TiO_2 , exhibiting overall similar behaviour with POM, using spin trapping reagents [17]; (b) Yamase [18], in a publication that somehow has not received so far the appropriate recognition, has also identified OH radicals by ESR upon photolysis of (I); (c) OH adducts to aromatic compounds (hydroxylation products) have been detected throughout the photolysis experiments in this work (see below).

Direct reaction of the excited polyoxometalates, $POM(e^- + h^+)$, reaction 6, was shown to proceed to a small extent. Photolysis in deaerated non aqueous (CH_3CN) solutions to avoid formation of OH radicals, reaction 5, were not conclusive owing to direct reaction with the solvent. Other solvents such as dimethyl sulfoxide are even more reactive. Fig. 5 shows the variation of the rate of formation of the one-electron reduced $W_{10}O_{32}^{4-}$, in deaerated aqueous solution in presence of POM, with increasing ratio of substrate/water. It can be seen that the rate goes through a maximum and falls off to less than 10% of the maximum value in absolute o-CIPh (absence of H_2O).

This tends to suggest that there exist two parallel competitive reactions in which CIPh participates initially: (a) Reac-

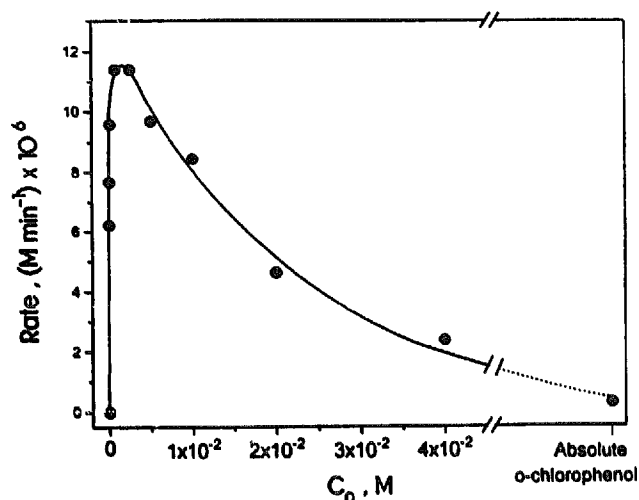


Fig. 5. Variation of the rate of formation of the one-electron reduced decatungstate ($W_{10}O_{12}^{3-}$), upon photolysis of degenerated aqueous solution of *o*-ClPh with increasing concentration of substrate. $W_{10}O_{12}^{4-}$ 0.7 mM; pH 2.5, $T=20^\circ\text{C}$.

tion 7 through OH radicals in aqueous solution, and (b) reaction 6 which seems to take over in absence of H_2O .

Reaction 7 is justified by the detection of several hydroxyl derivatives.

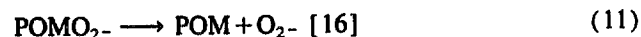
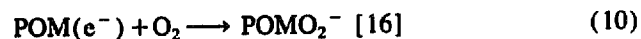
However, a referee has kindly pointed out that the role of OH radicals ought to be considered with some reservation. Hydroxylated intermediates can be formed by other ways. For instance, M.A. Fox et al. [28] have presented evidence that the hole-organic reaction generates cation radical, hydration of which leads, also, to hydroxylation products. Superoxide may also be involved [29].

Reaction 8 proceeds when the number of electrons accumulated on POM has driven the potential to negative values sufficient to reduce H^+ [19].

Reaction 9 is justified by the independent findings of two groups. Hill's laboratory [20] and we [10] have shown that reduced POM (I) and (II) cause carbon-halogen bond cleavage.

4.2. In oxygen saturated solutions

Dioxygen, generally, reoxidizes reduced POM very fast and effectively [16,21]. The following reactions that involve, mainly, the catalyst have been reported:



Reactions 10 and 11 have been justified from kinetic data [16] in analogy with Cu^+ complexes [24]. Reaction 13 has been reported in the literature [22].

4.3. Reaction mechanism

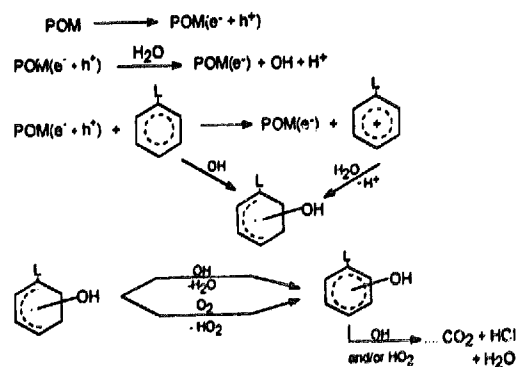
It has been shown that OH radicals are formed in both oxygenated and deoxygenated solutions in analogy with TiO_2 behaviour (reactions 5 and 15).

Dioxygen is known to be an effective electron scavenger inhibiting the recombination of electrons and holes and producing O_2^- / HO_2 ($pK_a 4.8^{25}$) radicals (reactions 10–12).

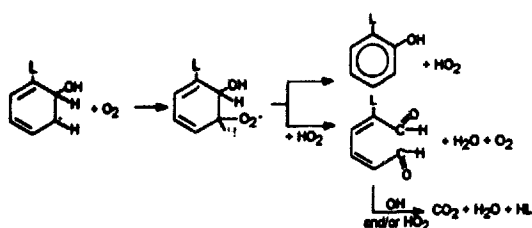
The concerted action of h^+ and the radicals OH, O_2^- and HO_2 is then responsible for mineralization of ClPh. The results have shown that at the initial stages of photolysis, i.e., when the reaction has proceeded less than 20%, so that the catalyst retained its maximum performance, the presence of dioxygen enhanced the degradation of chlorophenols from 20% up to three times at the most. (As is known, in going from the oxidized POM to the one electron reduced product, the catalyst performance drops to less than 10% [15]). On the contrary, when the reaction was allowed to proceed to mineralization, the results were an order of magnitude faster in presence than in absence of dioxygen.

These results tend to suggest that: (a) the reoxidation (regeneration) of the catalyst is the primary function of dioxygen in the mineralization process (reactions 10 and 11) and (b) the inhibition of $h^+ + e^-$ recombination by dioxygen and formation of O_2^- / HO_2 radicals are less significant at least in the first stage of ClPh degradation. They might be important in the degradation and final mineralization of intermediates, but this remains to be seen.

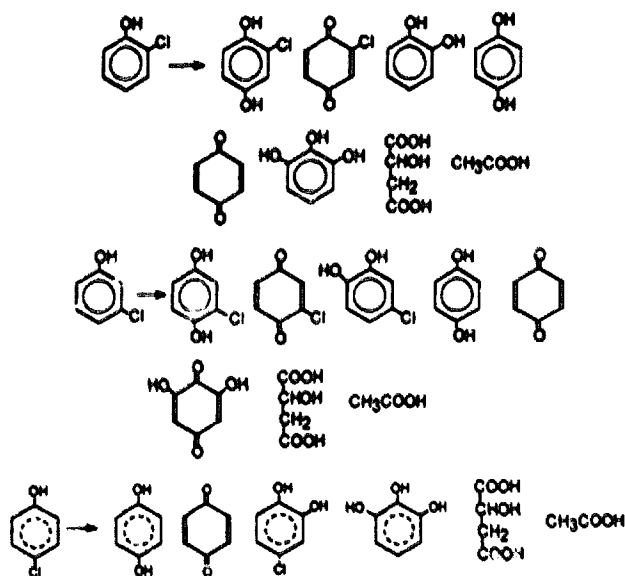
For an L-substituted aromatic compound, the following general scheme, based on known reactions, has been adapted by several workers working with OH radicals generated either by $^{60}Co-\gamma$ -radiolysis of aqueous solutions [26] or TiO_2 photolysis of aqueous solutions [4b,7,22,27]. This scheme which is applicable to POM as well, provides details of the fate of the organic substrate, i.e., mainly reactions 7 and 13 above, accounting for the formation of the hydroxyaromatic derivatives and the overall mineralization process.



For an ortho OH addition in the L substituted benzene ring above, the following reactions explain the mineralization according to Matthews [22].



In the scheme below, we present several intermediates detected during the course of mineralization of ClPh, that are in accordance with the electrophilicity of OH radicals.



Hydroxy butanedioic acid and acetic acid were detected in the three chlorophenols upon opening of the ring prior to mineralization. The overall reaction is



Acknowledgements

We thank V. Roussis for his help with the GC-MS experiments and the Analytical Laboratory for its hospitality.

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