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Chloride anion effect on the advanced oxidation processes of methidathion and dimethoate: Role of Cl_2^- radical

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ABSTRACT

The reaction of phosphor-containing pesticides such as methidathion (MT) and dimethoate (DM) with dichloride radical anions (Cl_2^-) was investigated. The second order rate constants $(1.3 \pm 0.4) \times 10^8$ and $(1.1 \pm 0.4) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ were determined for the reaction of Cl_2^- with MT and DM, respectively. A reaction mechanism involving an initial charge transfer from the sulfide groups of the insecticides to Cl_2^- is proposed and supported by the identified transient intermediates and reaction products. The formation of chlorinated byproducts was determined. The unexpected consequences of an efficient Cl_2^- reactivity towards MT and DM on the degradation capacity by Advanced Oxidation Procedures applied to polluted waters containing the insecticides and Cl^- anions is discussed.

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1. Introduction

Advanced Oxidation Processes (AOPs) are reported to be a promising alternative to remediate effluents which cannot be treated by conventional biological treatments. Most AOPs involve the *in situ* generation of highly reactive species such as hydroxyl and sulfate radicals, which are able to oxidize a wide range of chemicals. Ozone-based oxidation procedures, titanium dioxide heterogeneous photocatalysis and the photo-Fenton process are among the most widely employed AOPs capable of removing toxic pollutants, such as pesticides. However, the presence of phosphates, carbonates, chlorides and surfactants in the water matrix has a remarkable

influence on the process as they may decrease their efficiency (Soler et al., 2009; De Laat and Le, 2006; Machulek et al., 2007; Mora et al., 2009; Dell'Arciprete et al., 2012; Tsuneda et al., 2002; Boncz et al., 2005).

The presence of chloride anions in groundwater and surface water in rural and urban areas is widespread. The input of NaCl from seawater intrusion along coastal areas, animal and human waste in rural areas, leaking landfills, and natural saline seeps, has created progressively worsening problems with water quality (Panno et al., 2002). Therefore, the effect of Cl^- on AOPs pollutant degradation is an important factor to account for, since Cl^- efficiently scavenges $\text{HO}\cdot$ and SO_4^- radicals (Ross et al., 1998) and is able to form Fe^{3+} complexes in

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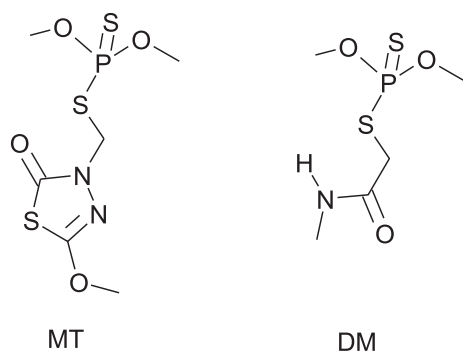
photo-Fenton processes (Machulek et al., 2007). These effects lead to the formation of chlorine-containing radicals, namely Cl_2^-/Cl (Machulek et al., 2007; Liu et al., 2010) and a concomitant reduction in the active oxidant yield. However, organic compounds can also react with Cl atoms and Cl_2^- radicals; hence, the presence of these radicals in the reaction media might produce changes in the photo-oxidative pathways and formation of undesirable toxic chlorinated byproducts (Liu et al., 2010). In fact, reported computer simulations (De Laat and Le, 2006) on the rates of decomposition of H_2O_2 by ferric ion and on the rate of oxidation of an organic solute in the presence of $[\text{Cl}^-] > 10 \text{ mM}$, showed that more than 99% of the generated HO^\bullet are converted into Cl_2^- . Therefore, the formation rate and reactivity of Cl_2^- radicals must be taken into account in the evaluation of the AOP efficiency when applied to systems containing high concentrations of chloride anions. The determination of the kinetic parameters and pathways of the reactions involving Cl_2^- radicals are important input parameters in the development of kinetic models. These models provide a basis for the design and process improvement through facile exploration of diverse processing scenarios (Chong et al., 2010; Peyton, 1990; Susnow et al., 1997).

The removal of phosphor-containing pesticides, such as methidathion (MT) and dimethoate (DM) (see Scheme 1), by photo-Fenton is well reported in the literature (Ballesteros et al., 2009; Oller et al., 2005). The solar photo-Fenton treatment at pilot plant scale of a mixture of four commercial pesticides also containing MT and DM showed similar chemical composition and comparable biocompatibility, though longer irradiation periods were needed to reach the desired mineralization when Cl^- was present (Soler et al., 2009). In the present manuscript we investigate the kinetics and reaction mechanisms of Cl_2^- radical anions with MT and DM and evaluate the importance of these reactions during the AOP treatment of a polluted water containing both, the insecticides and chloride anions.

2. Material and methods

2.1. Reagents

The pesticides employed in this work, MT and DM were purchased from Sigma–Aldrich (Pestanal). Sodium chloride and sodium peroxodisulfate were obtained from Merck. Water



Scheme 1 – Chemical structure of the insecticides methidathion (MT) and dimethoate (DM).

employed in all experiments was Milli Q grade ($>18 \text{ M}\Omega \text{ cm} < 20 \text{ ppb}$ organic carbon). The pH of the samples was measured with a Consort C832 pH-meter.

2.2. Conventional flash photolysis experiments

Flash-photolysis experiments were carried out using a conventional apparatus, Xenon Co. model 720C with modified optics and electronics. Two collinear quartz Xenon high-intensity pulsed flash tubes, Xenon Corp. P/N 890-1128 (FWHM $\leq 20 \mu\text{s}$), with a continuous spectral distribution ranging from 200 to 600 nm and maximum around 450 nm were used. The analysis source was a high pressure mercury lamp (Osram HBO-100 W). The optical path length of the 1 cm internal diameter quartz sample cell was 10 cm. The monochromator collecting the analysis beam (Bausch & Lomb, high-intensity) was directly coupled to a photomultiplier (RCA 1P28), which output was fed into a digital oscilloscope (HP 54600B). Digital data were stored in a personal computer. The emission of the flash lamps was filtered with an aqueous solution highly concentrated in the corresponding organic compound in order to avoid photolysis of the substrate. In fact, flash-photolysis experiments of aqueous solutions of the insecticides in the absence of persulphate showed no transient signals, further supporting that the insecticides photolysis is of no significance under these experimental conditions. The temperature ($20 \pm 3^\circ\text{C}$) was measured inside the reaction cell with a calibrated Digital Celsius Pt-100 Ω thermometer. Freshly prepared solutions were used in order to avoid possible thermal reactions of peroxodisulfate with the substrates. To avoid product accumulation, each solution was irradiated only once.

2.3. Bilinear regression analysis

For each experimental condition, several absorbance decay profiles at different detection wavelengths were taken. Absorbance is thus a function of wavelength and time. Taking advantage of the linearity of the absorbance with both, concentrations and absorption coefficients, a bilinear regression analysis was applied to the experimental absorption matrix in order to retrieve information on the minimum number of species and on their relative concentration profiles and absorption spectra (San Roman and Gonzalez, 1989).

2.4. Computer simulations

The kinetic model for computer simulation is based on component balances and equilibrium equations formulated in terms of a differential algebraic equations system which is solved by Gear's Stiff method and a least squares estimation criterion as described elsewhere (Alegre et al., 2000).

2.5. Determination of byproducts

In order to identify the main reaction products formed after the reaction of Cl_2^- with the insecticides, 250 mL of solutions containing sodium chloride, the pesticide and sodium peroxodisulfate were irradiated using a cylindrical reactor described elsewhere (Dell'Arciprete et al., 2010). An axial immersion low-

pressure mercury lamp Heraeus TNN 15/35 which emits nearly monochromatic radiation at 254 nm was used as irradiation source. Ratios of $[S_2O_8^{2-}] \times \epsilon_{S_2O_8^{2-}} : [Insecticide] \times \epsilon_{(ins)} > 100$, with ϵ the molar absorption coefficient, were used to minimize the photolysis of the pesticides. The latter conditions hold for $[MT] = 3 \times 10^{-4}$ M in solutions containing $[S_2O_8^{2-}] = 0.25$ M, and $[DM] = 1 \times 10^{-3}$ M in solutions containing $[S_2O_8^{2-}] = 0.1$ M, used in these experiments. Chloride concentration was 4 M.

After selected periods of irradiation, the reactor was emptied and the treated solution was concentrated by means of solid phase extraction: 100 mL of the aqueous solution were flown through a LiChrolut EN 200 mg (Merck) cartridge and the adsorbed organics recovered with 3 mL of methanol. A GCMS-QP2010S (Shimadzu) gas chromatograph equipped with a quadrupole mass analyzer was employed to identify major intermediates formed along the process. The temperature program for GC analysis involved an increase from 60 °C to 250 °C at a rate of 5 °C/min rate. A Meta X5 Teknokroma column was used. The determination of the derived intermediates was conducted by interpretation of the mass spectrum and further comparison of the identified product spectrum with those reported in the literature (Evgenidou and Konstantinou, 2006).

3. Results

3.1. Rate constant determination for the reaction of $Cl_2^{\cdot-}$ with MT and DM

Dichloride radical anions, $Cl_2^{\cdot-}$, were formed by reaction of chloride ions with sulfate radical anions, $SO_4^{\cdot-}$, generated upon the UV-photolysis of $S_2O_8^{2-}$ solutions of pH 5.5 ± 0.5 (George and Chovelon, 2002), reaction (1) in Table 1. In the presence of chloride at concentrations $> 10^{-4}$ M (Alegre et al., 2000), $SO_4^{\cdot-}$ radicals are readily depleted yielding chlorine atoms, as shown in reaction (2). Reaction of Cl with $Cl_2^{\cdot-}$ ions reversibly yields $Cl_2^{\cdot-}$ radical ions, reactions (3) and (4). Both, Cl and $Cl_2^{\cdot-}$ radicals absorb below 380 nm with molar absorption coefficients at 340 nm, $\epsilon^{340} = 3800$ M⁻¹ cm⁻¹ (Yu, 2004) and 9600 ± 500 M⁻¹ cm⁻¹ (Nagarajan and Fessenden, 1985), respectively.

Time-resolved experiments with 0.6 M $> [Cl^-] > 0.3$ M and $[S_2O_8^{2-}] = 1.5 \times 10^{-2}$ M performed with the conventional flash-photolysis apparatus show a transient species with an absorption maximum at 340 nm, whose spectrum is in agreement with that reported for the $Cl_2^{\cdot-}$ radical ions (Adams et al., 1995). The concentration of $Cl_2^{\cdot-}$ is expected to be much higher than that of Cl under our experimental conditions, as the equilibrium constant for the reversible reactions (3) and (4) (3) and (4) is $K_{3,4} = 1.4 \times 10^5$ M⁻¹ at 298 K (Buxton et al., 1998). Hence $\epsilon(Cl_2^{\cdot-}) \times [Cl_2^{\cdot-}] / \epsilon(Cl) \times [Cl] > 1.1 \times 10^5$ M⁻¹ is obtained, thus indicating that the absorbance of chlorine atoms is negligible compared to that of $Cl_2^{\cdot-}$.

Flash-photolysis experiments performed with solutions containing 0.6 M $> [Cl^-] > 0.3$ M, $[S_2O_8^{2-}] = 1.5 \times 10^{-2}$ M, and either DM or MT at concentrations lower than 6.25×10^{-5} M also show fast formation of $Cl_2^{\cdot-}$. In the presence of increasing insecticide concentrations, the decay of the transient is accelerated (see Fig. 1 for experiments in the presence and

Table 1 – Manifold of reactions taking place upon UV-light activation of peroxydisulfate in the reaction mixture containing $S_2O_8^{2-}$, Cl^- , and the insecticide. The corresponding rate constants, k , at 25 °C are also shown. The acronym INS stands for MT or DM.

$k/M^{-1} s^{-1a}$		
	$S_2O_8^{2-} + hv \rightarrow 2SO_4^{\cdot-}$	$\nu = I_{abs} \times \phi(SO_4^{\cdot-})^b$ (1)
	$SO_4^{\cdot-} + Cl^- \rightarrow Cl + SO_4^{2-}$	4.7×10^8 at $I = 0.1$ M ^c (2)
	$Cl + Cl^- \rightarrow Cl_2^{\cdot-}$	8.5×10^{9c} (3)
	$Cl_2^{\cdot-} \rightarrow Cl + Cl^-$	$6.0 \times 10^4 s^{-1c}$ (4)
	$Cl_2^{\cdot-} + Cl_2^{\cdot-} \rightarrow Cl_2 + 2Cl^-$	3.3×10^{9c} (5)
	$Cl_2^{\cdot-} + INS \rightarrow$ Organic transient	$k_{6MT} = (1.3 \pm 0.4) \times 10^{8d}$ $k_{6DM} = (1.1 \pm 0.4) \times 10^{8d}$ (6)
	$Cl + INS \rightarrow$ f	(7)
	$Cl + H_2O \rightarrow HO^\cdot + HCl$	$2 \times 10^5 s^{-1c}$ (8)
	$Cl_2^{\cdot-} + H_2O \rightarrow HO^\cdot + 2Cl^- + H^+$	$< 1.3 \times 10^3 s^{-1c}$ (9)
	$Cl_2^{\cdot-} + HO^- \rightarrow HO^\cdot + 2Cl^-$	$4 \times 10^6 M^{-1} s^{-1c}$ (10)
	$HO^\cdot + Cl^- \rightarrow Cl + HO^-$	$4.3 \times 10^9 M^{-1} s^{-1c}$ (11)
	$HO^\cdot + INS \rightarrow$	$k_{12MT} = 7.1 \times 10^{9e}$ $k_{12DM} = 8.5 \times 10^{9e}$ (12)
	$SO_4^{\cdot-} + INS \rightarrow$ f	(13)
	$SO_4^{\cdot-} + H_2O \rightarrow SO_4^{2-} + HO^\cdot + H^+$	$(6.6 \pm 0.4) \times 10^{2g}$ (14)
	$SO_4^{\cdot-} + S_2O_8^{2-} \rightarrow S_2O_8^{\cdot-} + SO_4^{2-}$	$(6.3 \pm 1.5) \times 10^{5g}$ (15)
	$2 SO_4^{\cdot-} \rightarrow S_2O_8^{2-}$	$5 \times 10^{8c,g}$ (16)
	$2 HO^\cdot \rightarrow H_2O_2$	$5.2 \times 10^{9c,g}$ (17)

a Second order rate constants are given unless otherwise indicated.

b ν is the rate of $SO_4^{\cdot-}$ formation, I_{abs} is the absorbed photonic flux and $\phi(SO_4^{\cdot-})$ is the peroxydisulfate photodissociation quantum yield.

c Yu (2004), Alegre et al. (2000), and Ross et al. (1998).

d k values from this work.

e Marin et al. (2011).

f Assumed diffusion-controlled for simulation purposes, in agreement with reported rate constants for the reaction of Cl with organic sulfides (Ross et al., 1998).

g Herrmann et al. (1995).

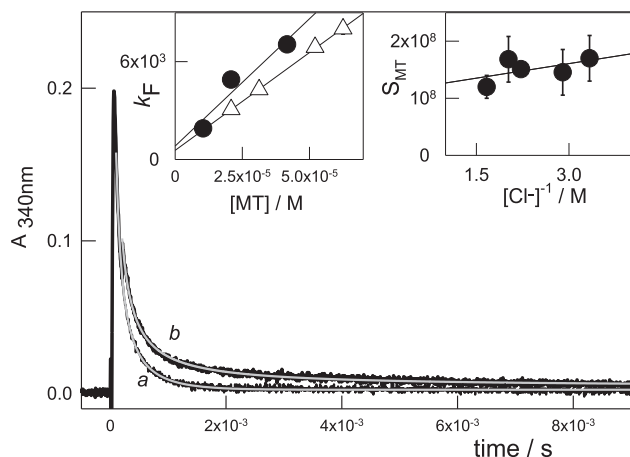


Fig. 1 – Absorbance traces at 340 nm obtained in experiments with solutions containing $[S_2O_8^{2-}] = 1.5 \times 10^{-2} M$ and $[Cl^-] = 0.45 M$ in the presence (curve a) and absence (curve b) of $1.04 \times 10^{-5} M$ of MT. The grey lines stand for the fitting to Eq. (1). Left inset: Plots of k_F vs $[MT]$ for experiments with $[Cl^-] = 0.345 M$ (●) and $0.5 M$ (△). Right inset: Plot of the slopes “S” vs. $[Cl^-]^{-1}$. The fitting to a straight line yields $r^2 = 0.32$. Note that the percentage probability that five data points of two uncorrelated variables give a correlation coefficient $|r| = 0.56$ is $\sim 35\%$ (Taylor, 1982). The symbols size is on the order of the experimental error, unless otherwise specified by the error bars.

absence of MT). For both insecticides, the transient absorbance at 340 nm could be well fitted to a mixed first and second order decay rate law given by Eq. (1), also shown in Fig. 1.

$$A^\lambda(t) = \frac{k_F}{\left(\frac{2 \times k_B}{\varepsilon^\lambda \times l} + \frac{k_F}{A_0^\lambda}\right) \times e^{k_F \times t} - \frac{2 \times k_B}{\varepsilon^\lambda \times l}} \quad (1)$$

$A^\lambda(t)$ in Eq. (1) is the absorbance at time t and wavelength λ ; k_B and k_F stand for the second and the pseudo first-order decay rate constants, respectively; ε^λ is the molar absorption coefficient at wavelength λ , A_0^λ is the absorbance immediately after the flash of light, and l is the optical path length of the cell.

The parameter k_B did not depend on the insecticide concentration, as expected for the recombination of $Cl_2^{\cdot-}$ radical ions (reaction (5)). On the other hand, for each amount of chloride, k_F depends on the insecticide (DM or MT) and on its concentration as shown in Fig. 1 left inset.

The effect of the insecticides on the decay rate of $Cl_2^{\cdot-}$ may be understood if reactions (6) and (7) efficiently compete with the decay reactions of $Cl_2^{\cdot-}$ and Cl, reactions (5), (8), (9), and (10) in Table 1. The efficient removal of HO· radicals by the insecticides (reaction (12)) does not allow the attainment of equilibrium conditions for the complex reversible reaction system of $Cl/Cl_2^{\cdot-}$ with water and hydroxide anions, which may be considered as simple first-order reactions schematized by reactions (8)–(11) (Mártire et al., 2001). For solutions of pH in the range from 3 to 6 and $[Cl^-] > 0.3 M$, the conditions: $K_{3,4} \times [Cl^-] > 1$, $k_{10} \times [HO^-] < k_9$ and $k_8/(K_{3,4} \times [Cl^-]) \ll k_9$ apply (Alegre et al., 2000) (Mártire et al., 2001). With these

considerations, the apparent first-order decay rate constant of $Cl_2^{\cdot-}$, k_F , is given by Eq. (2), for both MT and DM insecticides. The acronym INS stands for MT or DM.

$$k_F = k_9 + \left[\frac{k_{7\text{INS}}}{K_{3,4} \times [Cl^-]} + k_{6\text{INS}} \right] \times [\text{Ins}] \quad (2)$$

Plots of k_F vs. $[MT]$ or $[DM]$ (Fig. 1 left inset) yield straight lines as expected from Eq. (2). The intercepts of these plots yield for both insecticides $k_9 = (750 \pm 350)$, on the order expected for this rate constant (see Table 1). In turn, the slopes “ S_{INS} ” seem to be linearly correlated with $[Cl^-]^{-1}$, in agreement with Eq. (2). The intercept of the linear plots of S_{INS} vs. $[Cl^-]^{-1}$ (as shown in Fig. 1 right inset for MT) yield $k_{6\text{MT}} = (1.3 \pm 0.4) \times 10^8 M^{-1} s^{-1}$ and $k_{6\text{DM}} = (1.1 \pm 0.4) \times 10^8 M^{-1} s^{-1}$. However, the statistical analysis of the data indicates that there is a 35% probability that S_{INS} is not correlated with $[Cl^-]^{-1}$. If this is the case, the data points correspond to independent measures of $k_{6\text{INS}}$, which values are coincident, within the experimental error, with those obtained assuming a linear correlation of the variables. This situation may be understood considering that, even for the extreme case that reaction (7) were diffusion-controlled ($k_{7\text{INS}} \sim 2 \times 10^{10} M^{-1} s^{-1}$), the condition $k_{7\text{INS}}/(K_{3,4} \times [Cl^-]) \ll k_{6\text{INS}}$ (see Eq. (2)) holds for $[Cl^-] > 0.3 M$. Therefore, determination of a reliable value for $k_{7\text{INS}}$ is not possible from our experiments.

The reported rate constants for the reaction of hydroxyl radicals with MT and DM are $7.1 \times 10^9 M^{-1} s^{-1}$ and $8.5 \times 10^9 M^{-1} s^{-1}$, respectively (Marin et al., 2011), reaction (12) in Table 1. These values, ca. 50 times higher than those measured for $Cl_2^{\cdot-}$, might explain the slower removal observed for both pesticides by solar photo-Fenton when performed in the presence of chloride ions under experimental conditions where the more efficient HO^\bullet oxidant has been partly replaced by the milder $Cl_2^{\cdot-}$ radical.

3.2. Organic transients formed after MT and DM reactions with $Cl_2^{\cdot-}$ radicals

A bilinear analysis of the absorption traces obtained in the wavelength interval from 290 to 600 nm in experiments performed with $[S_2O_8^{2-}] = 1.5 \times 10^{-2} M$, $[Cl^-] = 0.45 M$ and either $[MT] = 6.25 \times 10^{-5} M$ or $[DM] = 2.2 \times 10^{-4} M$ showed the formation of two transients for each insecticide with spectra and decay profiles shown in Fig. 2a and b for MT and DM, respectively. Short-lived transients with absorption maxima in the range from 320 to 340 nm and lifetimes of 0.17 and < 0.10 ms were observed for MT and DM, respectively. Considering that the transient spectra resembles that of $Cl_2^{\cdot-}$ radicals (circles in Fig. 2a and b) and the observed lifetimes are on the order of those expected for $Cl_2^{\cdot-}$ radicals under each particular experimental condition, these transients were assigned to $Cl_2^{\cdot-}$ radicals.

The longer lived transients observed for MT and DM absorb in the 280–310 nm range (triangles in Fig. 2a and b). Considering that these intermediates are only observed in flash-photolysis experiments involving both, $Cl_2^{\cdot-}$ radicals and the insecticides, they are expected to be due to organic transients formed after reactions (6). Moreover, the concentration profiles (grey lines in the insets of Fig. 2a and b) show half-rise times $\leq 200 \mu s$ (in the limit of our time window), as expected

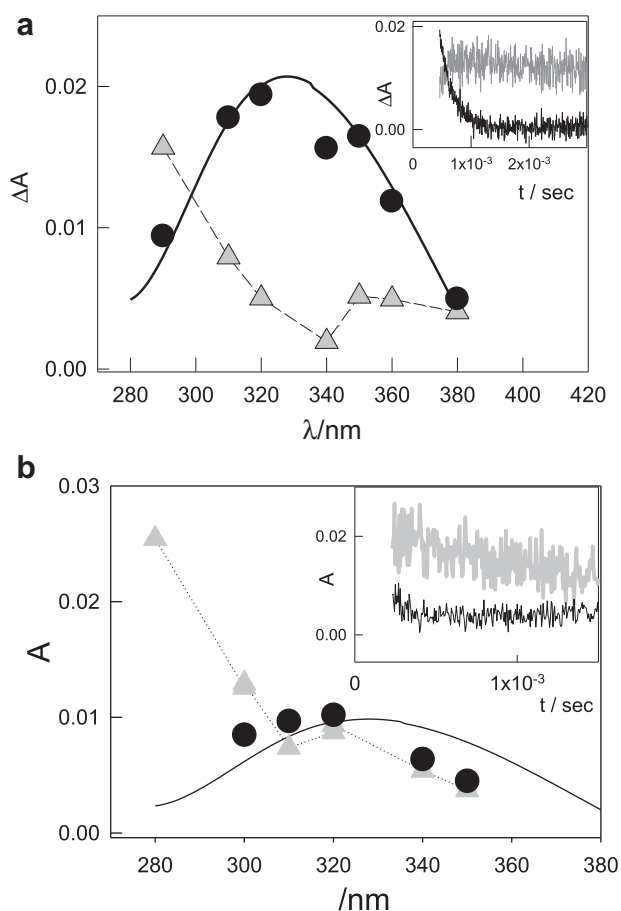


Fig. 2 – Transient spectra retrieved by a bilinear computer analysis of the absorption traces obtained from flash-photolysis experiments performed with air saturated solutions of pH 5.5 containing $[S_2O_8^{2-}] = 1.5 \times 10^{-2} M$, $[Cl^-] = 0.45 M$, and the insecticides: $[MT] = 6.25 \times 10^{-5} M$ (plot a) and $[DM] = 2.2 \times 10^{-4} M$ (plot b). The symbols (●) and (▲) stand for the respective short- and long-lived transients, respectively. The solid line stands for the Cl_2^- radical spectrum obtained in the absence of insecticides. Insets: Contribution of the short- (black curves) and long-lived (grey curves) transients to the absorbance of the traces at 320 and 290 nm, respectively, for the experiments in the figure.

for transient species formed after the insecticide reactions with Cl_2^- radicals. The transients decay is in the ms domain, independent on the presence of molecular oxygen. As will be discussed latter in the text, the long-lived transients are assigned to sulphenyl radical cations. Any contribution of the organic transients formed after reaction (7) to the observed spectra may be neglected under the present experimental conditions since Cl atoms are readily scavenged by Cl^- as the condition $k_3 \times [Cl^-] \gg k_7 \times [Ins]$ holds, even for a diffusion-controlled reaction (7).

3.3. Identification of stable reaction products

Pesticide solutions containing $S_2O_8^{2-}$ and Cl^- anions were continuously irradiated at 254 nm during 10 min and then

analyzed by GC–MS. Table 2 shows the mass to charge ratios, retention times, and assigned chemical structures of the observed byproducts.

Reactive SO_4^- and HO^\cdot radicals are also present in the reaction mixture; SO_4^- radicals as precursors of Cl/Cl_2^- radicals, reactions (1) and (2), and HO^\cdot radicals as a consequence of Cl/Cl_2^- reactions with water, reactions (8)–(11). Since high concentrations of the insecticides were used in the continuous irradiation experiments performed to determine the products of reaction (6), the generation of detectable concentrations of products due to the reaction between the insecticides and HO^\cdot (reaction (12)), SO_4^- (reaction (13)), and Cl radicals (reaction (7)), should not be ruled out. To evaluate the magnitude of this contribution, a computer program was built to simulate the generation of oxidized products formed from the different reactions. To this purpose, reactions (1)–(13) along with the reactions of SO_4^- with water and peroxodisulfate ions (reactions (14) and (15), respectively), and SO_4^- bimolecular recombination (reaction (16)), were taken into account. The reaction rate constants used are those depicted in Table 1. Initial parameters were the analytical concentrations of reactants and the continuous irradiation conditions. To this purpose, SO_4^- radicals were assumed to be formed at a rate of $8.5 \times 10^{-6} M s^{-1}$ as expected for the irradiation with a 15 W low-pressure Hg lamp (incident photonic flux at 254 nm = $6.1 \times 10^{-6} E L^{-1} s^{-1}$) of a 0.25 M $S_2O_8^{2-}$ solution ($S_2O_8^{2-}$ photodissociation quantum yield 0.5–0.7 (Criquet and Karpel Vel Leitner, 2009) contained in a 2.5 cm optical pathway reactor.

The simulation shows that the generation of products from the reactions of the insecticides with SO_4^- and Cl radicals under the experimental conditions used are negligible while those for the reaction of DM and MT with HO^\cdot are 5 and 13%, respectively, as shown in Table 3. Therefore, the identified products are mainly formed after the reaction of the insecticides with Cl_2^- .

3.4. Reaction mechanisms

The Cl_2^- radicals are prone to undergo charge transfer reactions with most substrates, and in particular with organic sulfides (Mishra et al., 2005). In fact, it was early reported by Asmus and Hiller (Asmus et al., 1977; Asmus and Bonifacić, 1980; Hiller and Asmus, 1981) that Cl_2^- radicals are involved in an exchange equilibrium with sulfides yielding chloride anions and neutral radicals comprising a three electron sulfur–chlorine bond (represented as $S\cdot Cl$) and absorbing around 390 nm. The latter radicals may further dissociate to Cl^- anions and sulphenyl radical cations, which exhibit absorption in the 300–400 nm range depending on the substituents (Jonah and Madhava Rao, 2001; Asmus et al., 1977; Varmenot et al., 2001). Formation of sulphenyl radical cations of MT and DM is supported by the nature of the reaction products and the fact that the observed organic transients do not react with O_2 (Glass, 1999). Moreover, MT has been reported to undergo a charge transfer reaction with the organic photocatalysts triphenylpyrylium and triphenylthiopyrylium (Arques et al., 2009).

Scheme 2 shows the proposed mechanism for MT. A charge transfer mechanism between the insecticide and Cl_2^-

Table 2 – Oxidation byproducts formed after the reaction of Cl_2^- with the insecticides. GC retention times, R_t , MS molecular ions (when observed) and characteristic fragmentation ion peaks are given together with assigned products.

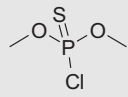
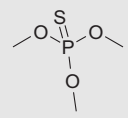
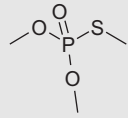
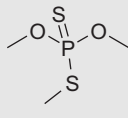
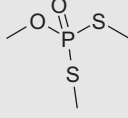
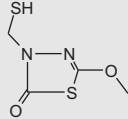
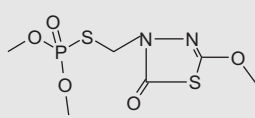
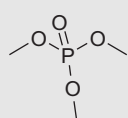
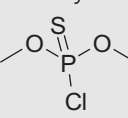
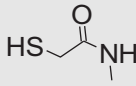
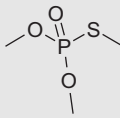
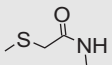
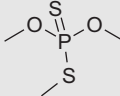
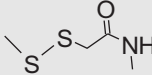
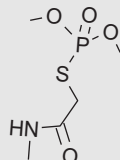
	R_t (min)	MW (characteristic ions, m/z)	Product assignment
MT	6.05	160 (130, 97, 47)	 O,O-dimethyl phosphorochloridothioate, compound <u>1</u>
	6.3	156 (126, 109, 93, 79, 63)	 O,O,O-trimethylthiophosphoroate, compound <u>6</u>
	9.3	156 (141, 126, 110, 95, 79)	 Trimethylphosphoro-thioate, compound <u>5</u>
	11.25	172 (141, 126, 125, 109, 95, 94, 93, 79, 63, 47)	 O,O,S-trimethyl thiophosphorothioate, compound <u>3</u>
	14.3	172 (126, 125, 79, 47)	 O, S, S-trimethylphosphorodithioate, compound <u>7</u>
	17.1	178 (146, 145, 132, 85, 58)	 Compound <u>2</u>
	30.9	286 (145, 142, 109, 85)	 Compound <u>4</u>
DM	32.9	302 (177, 157, 145, 126, 125, 109, 85, 79, 63, 58)	Compound <u>4</u>
	5.45	140 (110, 109, 95, 79, 80)	 O,O,O-phosphoric acid trimethylester, compound <u>11</u>
	6.05	160 (130, 97, 47)	 Compound <u>1</u>

Table 2 – (continued)

R _t (min)	MW (characteristic ions, m/z)	Product assignment
8.8	105 (58, 48)	 Compound <u>8</u>
9.4	156 (141, 126, 110, 95, 79)	 Compound <u>5</u>
9.9	119 (73, 61, 58)	 2-S-methyl-(N-methyl) acetamide, compound <u>10</u>
11.3	172 (125, 93, 79)	 Compound <u>3</u>
16.6	151 (105, 58)	 N-methyl, acetomethyl-di-sulfide, compound <u>9</u>
17.5 and 18.4	(181, 124, 79, 46)	Compound <u>13</u> (CH ₃ O) ₂ PO(SC ₂ H ₂ ONO ₂) DM
25.3	229 (125, 93, 87)	
27	213 (182, 141, 126, 79, 58)	
		 O,O-dimethyl-S-(N-methylcarbamoylmethyl) phosphorothioate compound <u>11</u>

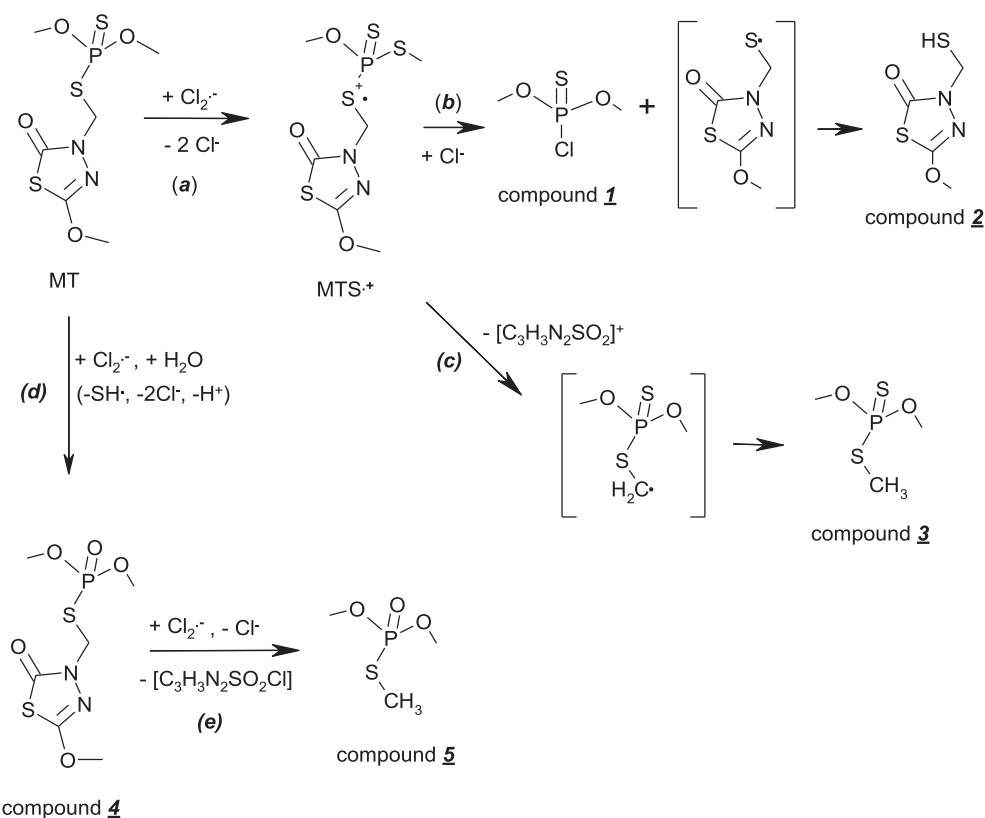
radicals leads to the formation of the sulphenyl radical cation MTS^{•+}, reaction pathway (a). Chloride ions may further induce the heterolysis of S–P bonds of MTS^{•+} to yield compound 1 and an organic radical leading to compound 2 after H-atom

Table 3 – Percentage of products formed by the reactions of the insecticides with HO[•], SO₄^{•-}, Cl[•], and Cl₂^{•-} radicals obtained from the computer simulations of steady state irradiation experiments with [Cl⁻] = 4 M and either [MT] = 3 × 10⁻⁴ M and [S₂O₈²⁻] = 0.25 M or [DM] = 1 × 10⁻³ M and [S₂O₈²⁻] = 0.1 M.

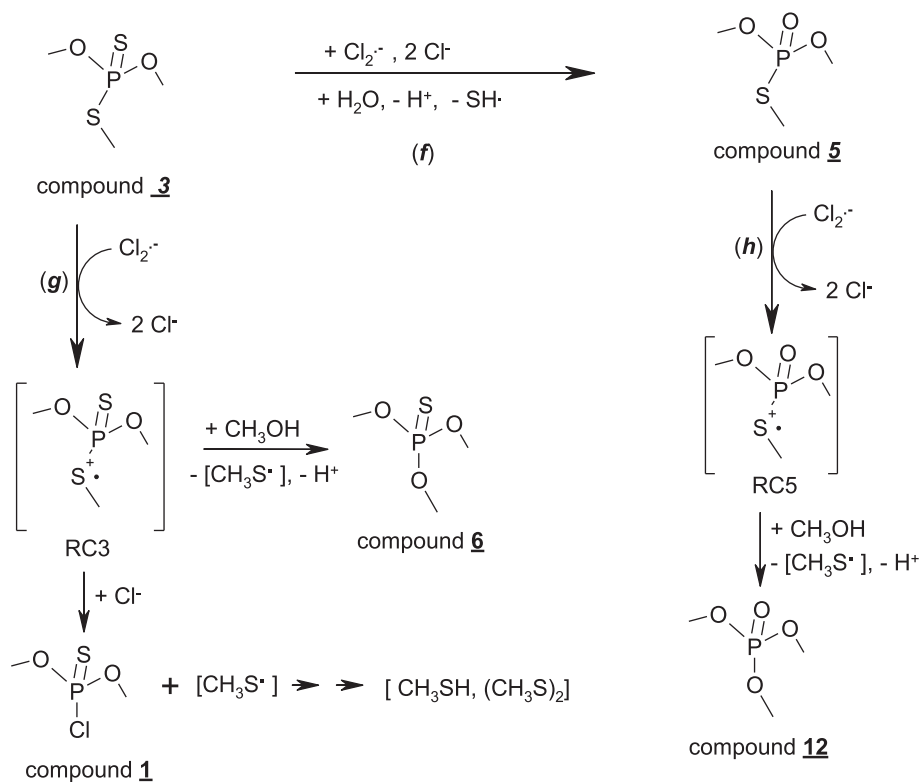
	SO ₄ ^{•-}	Cl [•]	Cl ₂ ^{•-}	HO [•]
DM	0.03	0.19	94.56	5.22
MT	0.01	0.11	86.78	13.10

abstraction, pathway (b). Otherwise, C_α-N fragmentation of MTS^{•+} yields compound 3, pathway (c).

Organophosphorous compounds with the thiono S=P structure are known to hydrolyze to their oxon forms, O=P, via specific base hydrolysis (Rav-Acha et al., 2007) and upon chlorination of their aqueous solutions (Tahara et al., 2006). Hypochlorite anions have also been found to act as a nucleophile accelerating MT hydrolysis (Duirk et al., 2008). No clear evidence on the oxon formation mechanism is obtained from the present study, as for solution pHs of 5.5 and after 10 min irradiation, hydrolysis is expected to be of little significance. Formation of compound 4 probably involves the interaction of Cl₂^{•-} with the S atom of the thiono structure followed by water addition and displacement of S, pathway (d). Further reaction between compound 4 and Cl₂^{•-} involving a sulphide radical



Scheme 2 – Proposed reaction mechanism for the reaction of MT with $Cl_2^{\bullet-}$ radical anions. Transients and stable compounds in brackets are proposed, but not detected.



Scheme 3 – Proposed reaction mechanism for the oxidation of compound **3. Transients and stable compounds in brackets are proposed, but not detected.**

cation leads to the formation of compound 5, as depicted in reaction path (e).

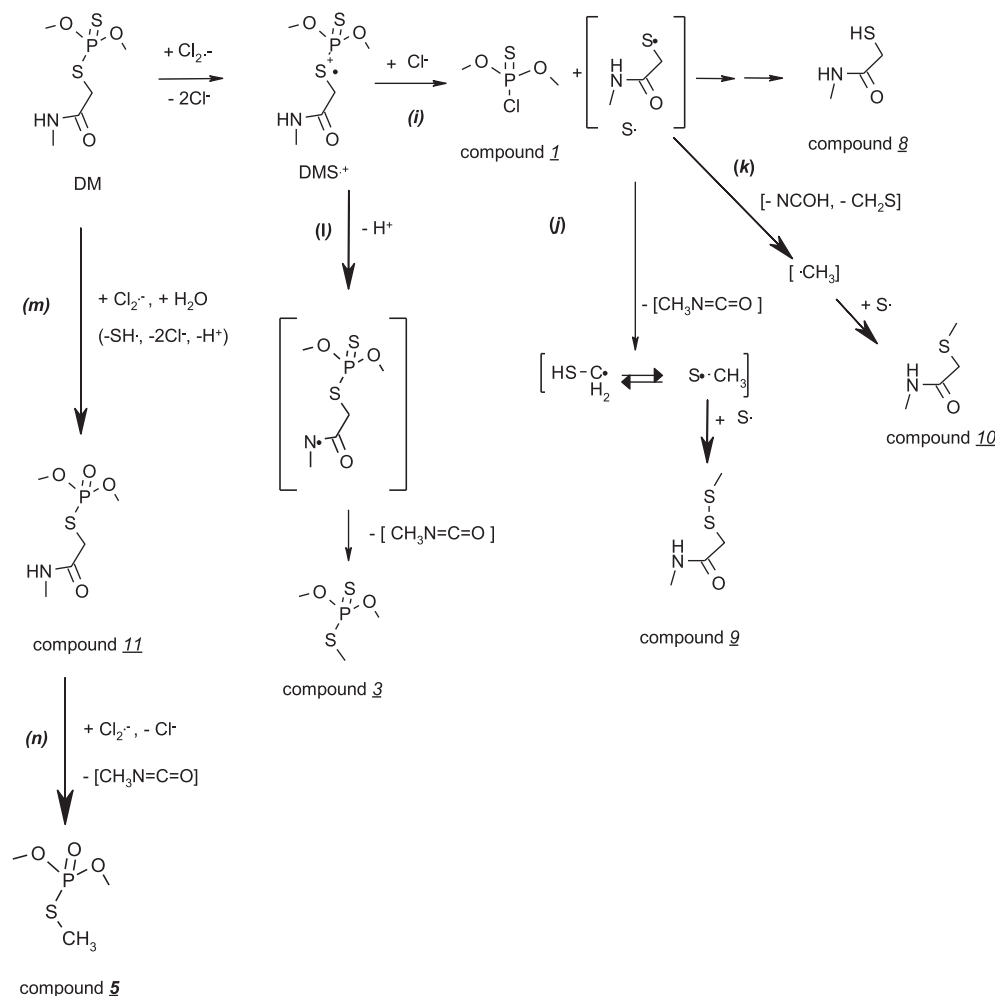
In Scheme 3, pathway (f) shows formation of compound 5, the oxon derivative of compound 3. Further oxidation of compound 3 with Cl_2^- radicals leads to the radical cation RC3, pathway (g), which upon chloride addition yields compound 1 and CH_3SH . Methanol and CH_3SH may be formed as a consequence of the degradation of the phosphoric acid methyl-esters and methylthioates byproducts to phosphate. Methanol is able to react with RC3 to yield compound 6. Generation of SH_2 and CH_3SH in the reaction mixture, as also observed in the Fenton degradation of MT (Ballesteros et al., 2009), facilitates the H-abstraction reactions proposed in Schemes 2–4.

Major degradation products were also detected in the case of DM (see Table 2). It is interesting to note that some of the products are coincident with those detected in MT degradation (compounds 1, 3, and 5), which correspond to the degradation byproducts of the phosphothioester moiety of the pesticides. Compounds 12, 11, 8, 5, and 3 were previously reported in the TiO_2 -mediated photocatalytic decomposition of DM (Evgenidou and Konstantinou, 2006; Calza and Massolino, 2008) and these compounds, together with 11, 10 and 9, in the thermal degradation of DM (Andreozzi et al.,

1999). Similar reaction paths to those observed for MT are likely to take place in the reaction of DM with Cl_2^- radicals.

Scheme 4 shows the charge transfer mechanism between DM and Cl_2^- leading to the formation of the corresponding S-centered radical cation DMS^+ . Formation of compounds 1 and 8 may be explained by the heterolytic cleavage of the S–P bond of DMS^+ involving a sulphenyl radical (S^\cdot), reaction path (i). Rearrangement of radical S^\cdot and further heterolysis yielding a methyl sulphenyl radical and recombination of the latter with S^\cdot leads to the formation of compound 9, reaction path (j). Otherwise, rearrangement of radical S^\cdot and further heterolysis yielding a methyl radical and recombination of the latter with S^\cdot leads to the formation of compound 10, reaction path (k). On the other hand, $\text{C}_\alpha\text{--C}_\beta$ fragmentation (Schöneich et al., 2001) of DMS^+ yields compound 3, reaction path (l). Formation of the oxon derivative of DM, compound 11, is also observed, as depicted in reaction path (m). Further reaction of compound 11 and Cl_2^- radical anions may lead to the formation of compound 5, as depicted in reaction path (n).

As discussed above, compound 3 also leads to the formation of 5 (see Scheme 3). Oxidation of compound 5 with Cl_2^- radicals leads to the radical cation RC5, pathway (h). Addition of methanol to RC5^\cdot may lead to the formation of compound 12.



Scheme 4 – Proposed reaction mechanism for the reaction of DM with chloride radical anions. Transients and stable compounds in brackets are proposed, but not detected.

Schemes 2–4 consider the possible generation of N-, S- and C-centered radicals which are known to efficiently react with molecular oxygen to yield oxidized products (Wlodek, 2002; Neta et al., 1990). Therefore, reactions with O_2 cannot be neglected. In fact, compound **13** has been identified as an N-oxidized product, probably formed after O_2 reaction with N-centered radicals such as those formed after reaction path (i) in Scheme 4. Molecular oxygen reactions involving $\cdot SCH_3$ and $\cdot CH_3$ radicals yield CO_2 , in agreement with the total organic carbon depletion observed during the course of the reaction.

O,O-dimethyl phosphorochloridothioate is the main chlorinated byproduct detected after the reaction of both, MT and DM with Cl_2^- . Because of its toxicity, this compound is environmentally relevant. On the other hand, compounds **4**, **5** and **11** are expected to show an increased toxicity relative to their precursors since the thiophosphate (P=S) moiety is replaced by the more toxic oxon (P=O) group (Tahara et al., 2006; Duirk et al., 2008). As generation of Cl_2^- has been reported in the photo-Fenton process in the presence of chlorides (Machulek et al., 2007), formation of toxic compounds in photo-Fenton reaction under these conditions should not be ruled out. In fact, the small decrease in the biodegradability observed for DM and MT mixtures treated by solar photo-Fenton (Soler et al., 2009) in the presence of Cl^- compared to experiments in its absence may be attributed to the different reaction products formed.

4. Discussion

The presence of chloride anions in polluted waters generally reduces the AOPs depletion efficiency of organic pollutants because of the scavenging of hydroxyl radicals by chloride anions (Fang et al., 2012). Chlorine and Cl_2^- radicals formed in these systems may also initiate the oxidation of pollutants thus minimizing the negative effect of Cl^- on AOP efficiency. In fact, we found here that the insecticides methidathion and dimethoate efficiently react by an electron transfer pathway with Cl_2^- radicals. Therefore, these insecticides might be expected to be degraded by AOPs even in the presence of chloride anions. However, toxic chlorine-containing products may form under these conditions.

Because chlorine, Cl_2^- , and HO^\cdot radicals are interrelated by a complex scheme of reactions (see Table 1), predictions on the effect of Cl^- on the depletion rates of the insecticides are not straightforward. To understand the behavior of the reaction system, the depletion of MD and MT in contaminated waters containing $[Cl^-] = 0.0, 10^{-4}, 10^{-3}, 10^{-2}$, and 0.4 M was modeled assuming an artificial UV/ H_2O_2 procedure producing HO^\cdot radicals at a rate of $8.5 \times 10^{-6} M s^{-1}$. To this purpose, a 10 mM H_2O_2 solution contained in a 2 cm optical pathway reactor irradiated with a 25 W low-pressure Hg lamp, $2 \times 10^{-5} E L^{-1} s^{-1}$ incident photonic flux at 254 nm, was considered. A minimum reaction mechanism consisting of reactions (3)–(12), and HO^\cdot radical recombination, reaction (17), was considered. The system was allowed to evolve until a steady concentration of Cl , Cl_2^- , and HO^\cdot radicals was attained and the concentration of products linearly increased with the reaction time. To compare the amount of products obtained in the presence and absence of chloride ions, an arbitrary value of 100% was assigned to the total molar

concentration of products simulated in its absence. Simulation of high insecticide conversions was avoided, since the number of reactions of unknown rate constants geometrically increases with the increasing number of reaction products.

The effect of pH due to reaction (10) is negligible up to 9. Fig. 3 shows that the presence of chloride anions in the range from 10^{-4} to 0.4 M inhibits the depletion efficiency of 6.25×10^{-5} MT, though it does not follow a linear correlation with $[Cl^-]$. Chloride anion concentrations $> 10^{-4}$ M are already capable of scavenging HO^\cdot radicals. However, the higher $[Cl_2^-]:[Cl]$ ratios established for higher $[Cl^-]$ (reversible reactions (3) and (4)) and the good efficiency of the insecticide reaction with Cl_2^- radicals (reaction (6)) lead to a partial recuperation of MT degradation capacity for $[Cl^-] > 10^{-3}$ M. In fact, for $[Cl^-] = 10^{-3}$ M, MT is depleted by HO^\cdot , Cl and Cl_2^- radicals, while for $[Cl^-] = 0.4$ M, depletion is mainly due to Cl_2^- radicals. Moreover, Fig. 3 inset shows that the extent of inhibition also depends on the concentration of insecticide, as the lower insecticide concentrations show the higher decrease in the degradation efficiency even for $[Cl^-]$ as low as 10^{-4} M. A similar discussion applies to DM. An important consequence of the depletion of MT and DM by Cl_2^- radicals is the detrimental formation of toxic byproducts.

The previous discussion further supports the participation of Cl_2^- radicals unexpected effects on AOPs efficiency. Yang et al. (2005) studied the methylene blue (MB) and orange II (OII) degradation by TiO_2/UV -light in the presence of $[Cl^-]$. These authors reported little influence on the degradation efficiency of both dyes in the presence of $[Cl^-] < 0.01$ mol/L. However, for $[Cl^-] > 0.10$ mol/L they reported opposite effects: a significant degradation inhibition was observed for MB while OII showed an enhanced degradation. Also, Cl_2^- radicals may also be responsible for the increased decolorization of Orange

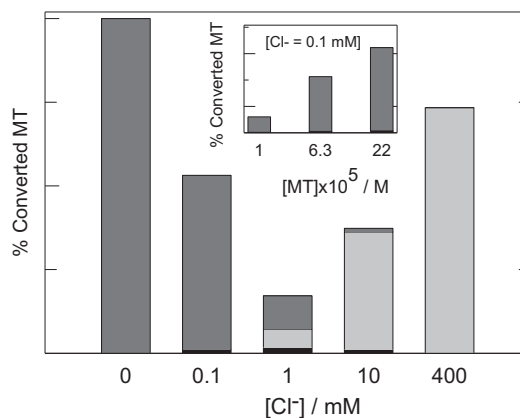


Fig. 3 – Expected consumption efficiency of MT during treatment by an artificial AOP producing HO^\cdot radicals at a rate of $8.5 \times 10^{-6} M s^{-1}$. Polluted waters of pH 3 containing $[MT] = 6.25 \times 10^{-5}$ and different $[Cl^-]$ were considered. The consumption due to the different scavengers is depicted as: dark grey: HO^\cdot , light grey: Cl_2^- , black: Cl . Inset: Expected effect on the consumption efficiency of MT during treatment by the same artificial AOP of polluted waters of pH 3 containing $[Cl^-] = 1 \times 10^{-4} M$ and different $[MT]$. The % converted MT in this plot is normalized to that observed in the absence of chloride anions for the same MT concentration.

7 by peroxodisulfate in the presence of 0.1 M chloride anions (Wang et al., 2011).

5. Conclusion

The phosphor-containing pesticides methidathion (MT) and dimethoate (DM) chemically react with Cl_2^- radical anions with rate constants $(1.3 \pm 0.4) \times 10^8$ and $(1.1 \pm 0.4) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, respectively. The sulfide group of the insecticides is the preferred site of attack initiating the degradation of the insecticides. Chlorinated byproducts were observed among the identified degradation products.

Computer simulation models predict that chloride anions present in polluted waters are able to scavenge the active oxidizing radicals produced by the AOP technologies to generate Cl atoms and Cl_2^- radicals. Because of the efficient reactions of MT and DM with Cl_2^- radicals, these processes are expected to have an important contribution in the AOP treatment of the insecticide's contaminated waters also containing high levels of chloride anions. However, toxic products are formed under these conditions.

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