Chloride promoted oxidation of tritosulfuron by peroxymonosulfate

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Abstract

Tritosulfuron has been eliminated by continuous addition of potassium peroxymonosulfate to an aqueous solution containing the herbicide and chloride ions. The influence of Cl^- content ($6 \cdot 10^{-5}$–$22.5 \cdot 10^{-4}$ M), inlet peroxymonosulfate concentration (0.05–0.2 M), initial tritosulfuron amount (0.5–2.5 mg L^{-1}) and temperature (298–333 K) has been assessed. Tritosulfuron oxidation by HClO has been experimentally calculated to be in the proximity of $4.03 \pm 0.15 \cdot 10^{13} \exp(-7989/T)$ $M^{-1}s^{-1}$. Experimental data suggested the existence of an inefficient peroxymonosulfate decomposition, likely associated to the experimental setup used. A simple mechanism of first order ordinary differential equations is capable of acceptably simulate the profiles of tritosulfuron and peroxymonosulfate accumulated in the reactor, considering the formation of active chlorine species from the interaction of peroxymonosulfate and chloride. First oxidation intermediates have been identified by means of liquid chromatography coupled to high resolution mass spectrometry. The attack by hydroxyl radicals and the addition of chlorine have been appreciated in these generated species. An oxidation mechanism has also been proposed. The evolution of intermediates with reaction time indicates that few compounds are recalcitrant to the peroxymonosulfate/chloride system.

1. Introduction.

Herbicides emerge as a significant contributor to Green Revolution. These substances are used to control and eliminate the growth of a variety of herbaceous pests that, in other circumstances, would diminish the harvest quantity and quality.

Unfortunately, with the benefits of herbicides, some disadvantages have also appeared. Hence, the abusive use and environmental accumulation may threaten the long-term survival of major ecosystems by disruption of predator-prey relationships and loss of biodiversity. Also, pesticides can have significant human health consequences. There is overwhelming evidence that agricultural use of herbicides has a significant impact on water quality and leads to serious environmental consequences [1].

Herbicides can reach natural water sources by gradual accumulation in the soil where they slowly percolate down into underground water or/and heavy rainfall and irrigation wash herbicides off farmland into lakes and rivers.

Amongst the herbicides of recent use, tritosulfuron (TtS) can be cited. This herbicide is a new active substance developed by BASF. The chemical family is sulfonylureas. The formulated product BAS 635 00 H is a water dispersible granules containing 714 g/kg tritosulfuron. It is a systemic herbicide for the post-emergence control of a range of dicotyledonous weeds in cereals (winter and spring wheat, winter and spring barley, winter rye, oats, triticale) and maize. It will be applied as well as a unique product as well as in combination with other herbicidal active substances.

Some reports catalogue this herbicide as "very toxic for aquatic species/can cause long-term concerns in water ecosystems", [2]. Accordingly, technologies aimed at their efficient and environmentally friendly removal from water bodies are always in mind of water treatment practitioners.

Oxidation processes are often considered when dealing with recalcitrant aqueous contaminants at low concentrations. Use of peroxymonosulfate (PMS) is gaining interest due to easy and safe storage, generation of highly reactive sulfate radicals, possibility of activation by different ways, capacity of oxidation in direct reactions, and oxidation through indirect reactions in the presence of halogens. In this study the potential of the system PMS/Cl$^-$ has been investigated. This technology can be an attractive alternative to wastewaters containing chlorides at moderate concentrations.

2. Materials and methods

2.1 Materials

Analytical grade tritosulfuron standard ($C_{13}H_9F_6N_5O_4S$, CAS 142469-14-5) was used as received. Acetonitrile used was HPLC or Mass Spectrometry (MS) grade. Peroxymonosulfate compound (Oxone®, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, CAS 37222-66-5) was technical grade. Chlorides were added in NaCl form. The rest of chemical used were analytical grade. Ultrapure water from Milli-Q® academic device (Millipore®) was used in solutions preparation.

2.2 Experimental setup and procedure

The experimental installation consisted of a 1.0 L borosilicate cylindrical glass vessel magnetically stirred by means of an IKA® RCT stirrer equipped with temperature control (temperature range: 20-60ºC), if necessary (Figure 1). Firstly, the reactor was filled with

1.0 L of aqueous tritosulfuron and the required amount of sodium chloride. Afterwards, a peristaltic pump from Perkin Elmer fed a constant flow of 0.7 mL min^{-1} of a concentrated solution of peroxymonosulfate into the reactor. The initial concentration of PMS and chloride were chosen according to some preliminary tests. A Crison® multimeter was used in order to monitor pH by immersing the electrode into the solution. At different times samples were extracted and the reaction quenched by Na$_2$S$_2$O$_3$ 0.5 M at a ratio of 10 µL per 1 mL of sample for tritosulfuron analysis.
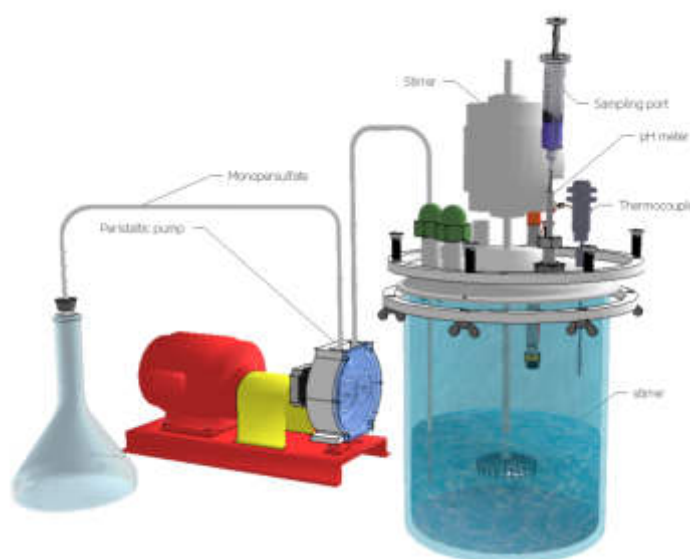
Figure 1. Experimental setup.

2.3 Analytical methods

Aqueous tritosulfuron concentration was analyzed by High Performance Liquid Chromatography (HPLC) coupled to UV detection in an Agilent 1100 apparatus. Chromatographic separation was carried out using a Kromasil 100 5C18 (5µm, 2.1x150mm) as stationary phase. A constant elution grade of 50% acetonitrile and 50% Milli-Q® water acidified with 0.1% H$_3$PO$_4$ was pumped, obtaining a retention time of 7.4 min. UV detection was conducted at 225 nm. The limit of detection was calculated to be 22.01 µg L^{-1} and the relative standard deviation was 0.24%.

Transformation products during the oxidation process were analysed by HPLC coupled to a Quadrupole Time of Flight (HPLC-QTOF). Previous to the analysis, salt content was removed by a Solid Phase Extraction (SPE) carried out with C18 cartridge Oasis HBL 60 mg, conditioned with 4 mL of methanol (MS quality) and 2 mL of Milli-Q®. After that, 4 mL of sample were extracted and eluted to 1 mL of methanol. The extracted samples were injected (5µL) in an Agilent 1260 HPLC coupled to an Agilent 6520 Accurate Mass QTOF LC/MS equipped with ESI electrospray. The chromatographic separation was carried out in a Zorbax SB-C18 column (3.5µm, 4.6x150mm) at 30ºC. Pure Milli-Q® water and acetonitrile were used as mobile phase. An elution gradient at 0.4 mL^{-1} min flow rate was initially increased from 10% of acetonitrile to 90% in 25 min, and kept thereafter for 2 min before equilibration. The QTOF conditions were as follows: ESI(-) mode, gas temperature 325ºC, drying gas 10 mL min^{-1}, nebulization 45 psig, Vcap 3500 V, fragmentation 100V, acquisition m/z range 100-1000. The obtained mass spectra were processed by means of Agilent Mass Hunter Qualitative Analysis B.04.00 software.

Peroxymonosulfate concentration was analyzed spectrophotometrically by a colorimetric method based on N,N-diethylphenylenediamine (DPD) oxidation.

3. Results and discussion

3.1. Preliminary experiments

Before going deeper into the study of the PMS/Cl$^-$ system, some previous experiments were conducted to assess the capacity of peroxymonosulfate to directly oxidise tritosulfuron and the potential of the presence of chlorides to accelerate the process.

Figure 2 reveals several aspects to take into consideration. Hence, PMS is capable of slightly oxidize TtS to some extent in the absence of chloride. An inlet PMS concentration of 0.2 M led to a final TtS conversion of roughly 10% after 120 min. The ability of

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peroxymonosulfate to react with organic substances has been previously reported [3]. The presence of Cl⁻ in the reaction media enhanced the degradation of TtS. Hence, when the PMS inlet concentration was 0.02 M the presence of $1.5 \cdot 10^{-4}$ M and $6 \cdot 10^{-4}$ M in chloride increased TtS conversion from 10% (absence of Cl⁻) to 35 and 65%, respectively. Applying more extreme conditions (C_{PMS_inlet}=0.2 M, C_{Cl^-}=$6 \cdot 10^{-4}$ M), TtS could be totally removed in roughly two hours.
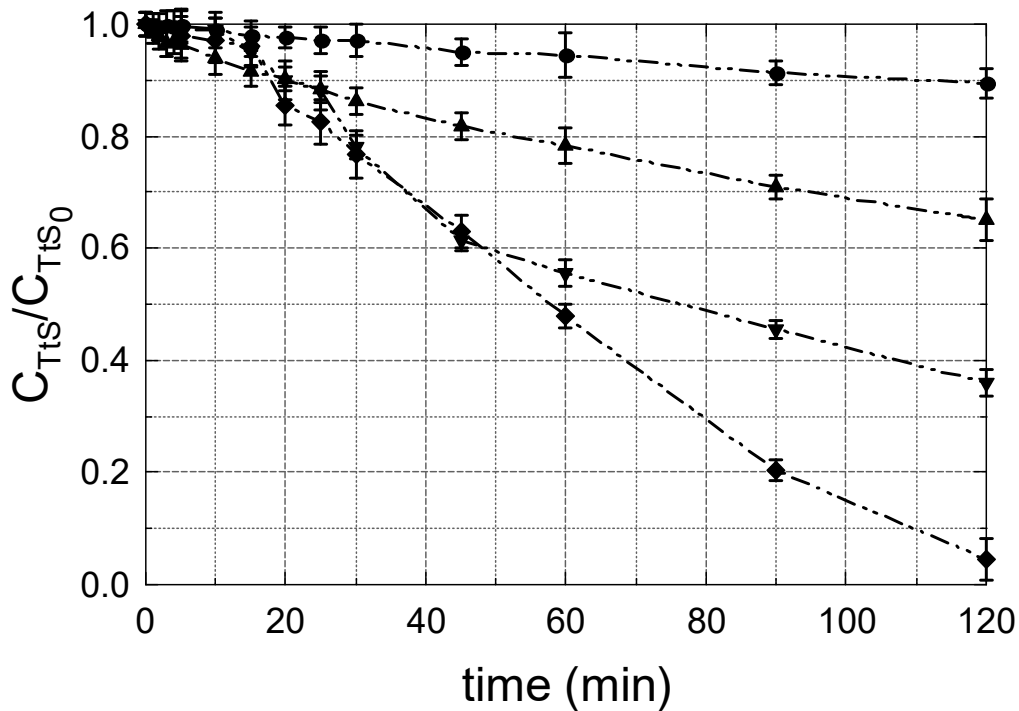
Figure 2. Evolution of the normalized tritosulfuron concentration. Experimental conditions: T=298 K, pH range=3-5, Q_{PMS}=0.7 mL min⁻¹, V_0=1 L, $C_{TtS,0}$=1 mg L⁻¹. ●, C_{PMS_inlet}=0.2 M; ▲, C_{PMS_inlet}=0.02 M, C_{Cl^-}=$1.5 \cdot 10^{-4}$ M; ▼, C_{PMS_inlet}=0.02 M, C_{Cl^-}=$6 \cdot 10^{-4}$ M; ♦, C_{PMS_inlet}=0.2 M, C_{Cl^-}=$6 \cdot 10^{-4}$ M.

The reaction between peroxymonosulfate and chloride ions can lead to HClO formation according to:

$$Cl^- + HSO_5^- \rightleftharpoons HClO + SO_4^{2-} \qquad \text{(slow)} \qquad (1)$$

And further Cl₂ generation:

$$H^+ + Cl^- + HClO \rightleftharpoons H_2O + Cl_2 \qquad \text{(fast)} \qquad\qquad (2)$$

Kinetic data for the reaction under acidic conditions have been reported at various ionic strengths in the order of $k_{Cl}=1.5 - 2.0 \cdot 10^{-3}$ $M^{-1}s^{-1}$ [4].

Chlorine/hypochlorite can further react with tritosulfuron, contributing to its depletion (eq. 3).

$$HClO/Cl_2 + \text{Tritosulfuron} \rightarrow \text{Products} \qquad\qquad (3)$$
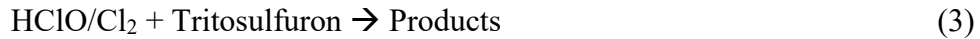
Several authors claim that chloride ions can affect the kinetics of peroxymonosulfate mediated oxidation reactions only when high concentrations are used [5], however, at the sight of the results here obtained, the presence of Cl^- at moderately low concentrations is enough to accelerate the oxidation of some compounds. Similar results were reported by Lei and co-workers when oxidising methylene blue [6].

Once the efficiency of the combination PMS/Cl^- was assessed, next, the influence of some of the most important operating variables was investigated.

3.2. Variables influence

3.2.1. Chlorides concentration influence

Cl^- is oxidized to $HClO/Cl_2$ in the presence of peroxymonosulfate. Accordingly, the concentration of chloride species must play a crucial role in TtS abatement rate. A series of experiments was therefore conducted by varying the concentration of chlorides in the reaction bulk keeping constant the rest of parameters. In all runs the initial pH was in the range 3.3-3.8 given by PMS addition. Figure 3 shows the results obtained.
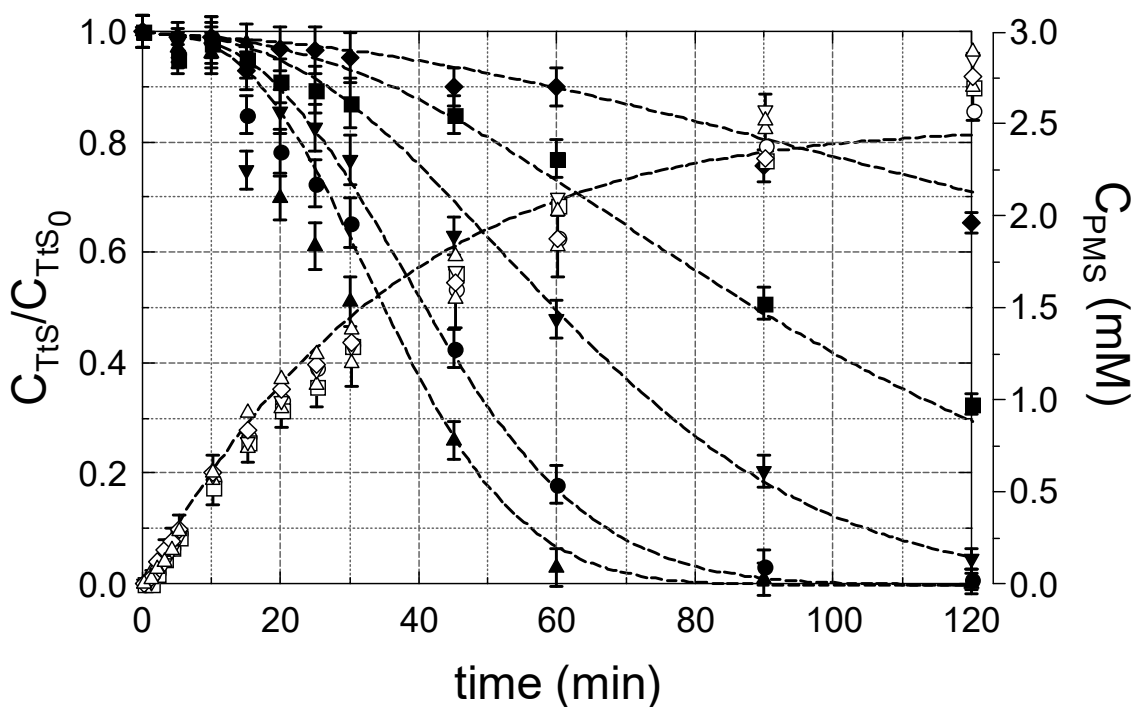
Figure 3. PMS/Cl⁻ system. Evolution of the normalized tritosulfuron concentration and peroxymonosulfate as a function of time. Influence of initial chloride concentration. Experimental conditions: T=298 K, pH range=3.3-3.8, C_{PMS_inlet}=0.1 M, Q_{PMS}=0.7 mL min⁻¹, V_0=1 L, $C_{TtS,0}$=1 mg L⁻¹. C_{Cl^-}: ♦, 6·10⁻⁵ M; ■, 2.5·10⁻⁴ M; ▼, 6·10⁻⁴ M; ●, 15·10⁻⁴ M; ▲, 22.5·10⁻⁴ M. (Open symbols: Peroxymonosulfate concentration, dashed lines: theoretical simulated profiles).

As observed, under the conditions investigated, Cl⁻ always exerted a positive effect on TtS removal rate, in accordance with reaction 3.

The influence of Cl⁻ concentration can be qualitatively estimated by solving a simplistic differential equation system representing the process. Thus, assuming that TtS is eliminated by direct reaction with peroxymonosulfate and also by chlorine active species, from the experimental setup and methodology used, the following set of first order differential equations can be proposed:

$$-\frac{d\left(C_{TtS} \times V\right)}{dt} = V \times k_{TtS\text{-}D} C_{TtS} C_{SO_5^{2-}} + V \times k_{TtS\text{-}Cl} C_{TtS} C_{Cl_2/HClO} \tag{4}$$

Formation of chlorine active species is assumed to follow second order kinetics:

$$\frac{d\left(C_{Cl_2/HClO} \times V\right)}{dt} = V \times k_{Cl} C_{Cl^-} C_{SO_5^{2-}} - V \times k_{TtS\text{-}Cl} C_{TtS} C_{Cl_2/HClO} \tag{5}$$

Also, peroxymonosulfate variation can be described by:

$$\frac{d\left(C_{SO_5^{2-}} \times V\right)}{dt} = Q \times C_{SO_5^{2-}}^{inlet} - V \times k_{TtS\text{-}D} C_{TtS} C_{SO_5^{2-}} - V \times k_{Cl} C_{Cl^-} C_{SO_5^{2-}} \tag{6}$$

Finally:

$$\frac{dV}{dt} = Q \tag{7}$$

Where $C_{SO_5^{2-}}^{inlet}$ is the peroxymonosulfate concentration fed to the reactor and Q is the inlet

flowrate.

The simplistic kinetics represented by equations 4-7 can be numerically solved.

Values of the rate constant corresponding to the direct TtS oxidation by peroxymonosulfate ($k_{TtS\text{-}D}$) were experimentally obtained in discontinuous experiments, $k_{TtS\text{-}D}=2.6\pm0.1\cdot10^{4}\cdot\exp(-6117/T)$ $M^{-1}s^{-1}$. The rate constant $k_{Cl}=10^{32}\cdot\exp(-11394/T)$ $M^{-1}s^{-1}$ was adapted from bibliography data [4]. The rate constant $k_{TtS\text{-}Cl}$ was adjusted to minimize the differences between experimental and calculated TtS concentration evolution with time. The fitting process acceptably simulated TtS profiles under different operating conditions; however, peroxymonosulfate evolution was clearly overestimated. MPS accumulated to a higher extent in theoretical profiles if compared to experimental

data. These results were observed even in the absence of added chlorides. Accordingly, some kind of inefficient PMS decomposition was assumed, likely associated to the experimental setup used. No clear reason can be envisaged to account for this decomposition, although direct reaction with TtS first intermediates or/and decomposition to sulfate and oxygen could partially explain the experimental facts. Hence, eq. 6 was modified to account for this inefficient peroxymonosulfate decomposition by adding a new first order term:

$$\frac{d\left(C_{SO_5^{2-}} \times V\right)}{dt} = Q \times C_{SO_5^{2-}}^{inlet} - V \times \left(k_{TtS-D}C_{TtS}C_{SO_5^{2-}} - k_{Cl}C_{Cl^-}C_{SO_5^{2-}} - k_{ineff}C_{SO_5^{2-}}\right)$$

(8)

At the pH conditions used in this study (3.3-3.8) the main species in solution in equilibrium given by equation 2 is HClO [7]. Consequently, in order to reduce the number of optimized parameters, the rate constant k_{TtS-Cl} was at this point experimentally calculated and k_{ineff} adjusted to fit TtS and peroxymonosulfate theoretical and empirical concentrations.

Dashed lines in figure 3 show an acceptably modelling of the process when completing experiments at different chloride initial concentrations keeping constant the rest of operating variables. Additionally, the model also predicts similar profiles in PMS evolution regardless of the chloride amount in the media, this was also experimentally observed. The value of k_{TtS-Cl} used in the model was $4.03 \pm 0.15 \cdot 10^{13} \cdot \exp(-7989/T)$ $M^{-1}s^{-1}$ while the adjusted k_{ineff} took a value of $4.16 \pm 0.23 \cdot 10^{-4}$ s^{-1} at 25ºC.

3.2.2. Peroxymonosulfate inlet concentration influence

The influence of peroxymonosulfate inlet concentration was assessed in the interval 5–$20 \cdot 10^{-2}$ M. Figure 4 shows the results obtained. As observed, peroxymonosulfate concentration exerts a positive influence within the range of values investigated. Differences are less pronounced than those observed in the case of Cl^- concentration.
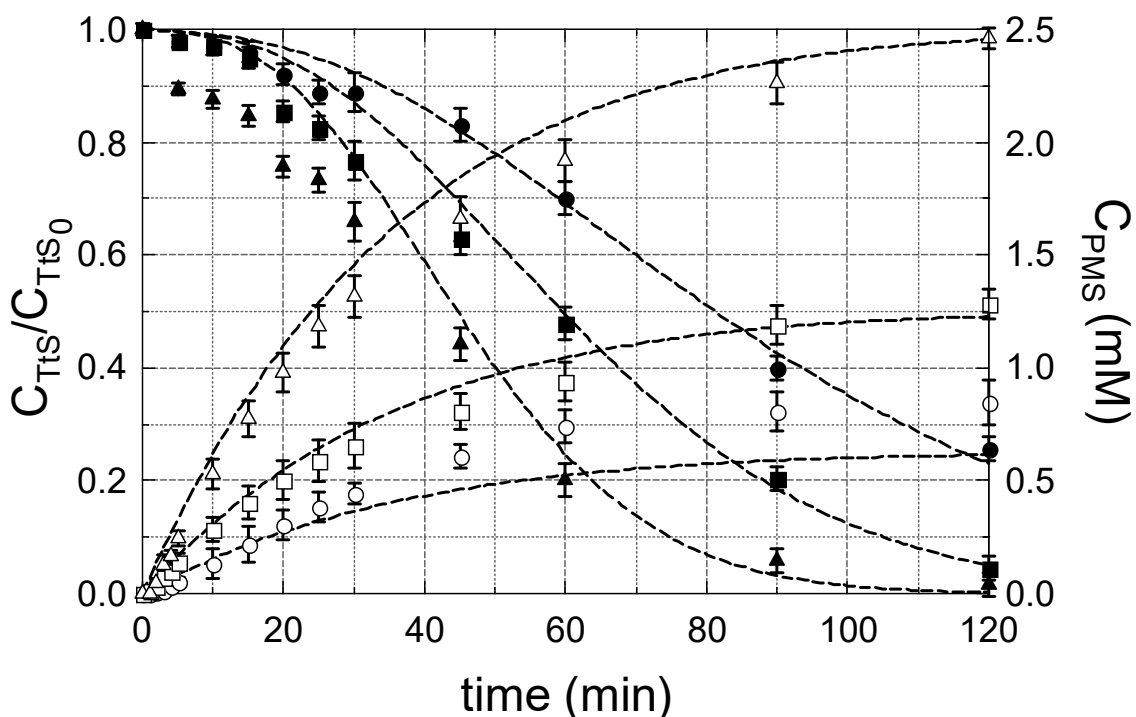

Figure 4. PMS/Cl^- system. Evolution of the normalized tritosulfuron concentration as a function of time. Influence of C_{PMS_inlet}. Experimental conditions: T=298 K, pH range=3.3-3.8, $C_{Cl^-}=6 \cdot 10^{-4}$ M, $Q_{PMS}=0.7$ mL min^{-1}, $V_0=1$ L, $C_{TtS,0}=1$ mg L^{-1}. C_{PMS_inlet}: ●, 0.10 M; ■, 0.2 M; ▲, 0.4 M. (Open symbols: Peroxymonosulfate concentration, dashed lines: theoretical simulated profiles).

The evolution of peroxymonosulfate and tritosulfuron concentrations were adequately simulated by the simplistic mechanism previously proposed (equations 5, 7, 8).

Figure 5 depicts the theoretical influence of reagents initial concentrations in a wider range of values. This figure reveals a sharp influence of initial reagents concentration at increasing values of this parameter until reaching an optimum. From this optimum, increase in system efficacy is less pronounced. Dashed lines in Figure 5 indicates that an optimum in chlorides concentration can be located around $5 \cdot 10^{-3}$ M while a peroxymonosulfate inlet dose of 0.5 M should be adequate to remove 1 mg L^{-1} of TtS in 60-70 min. Obviously, using more severe conditions can reduce the reaction time to reach 100% TtS conversion according to specific needs.
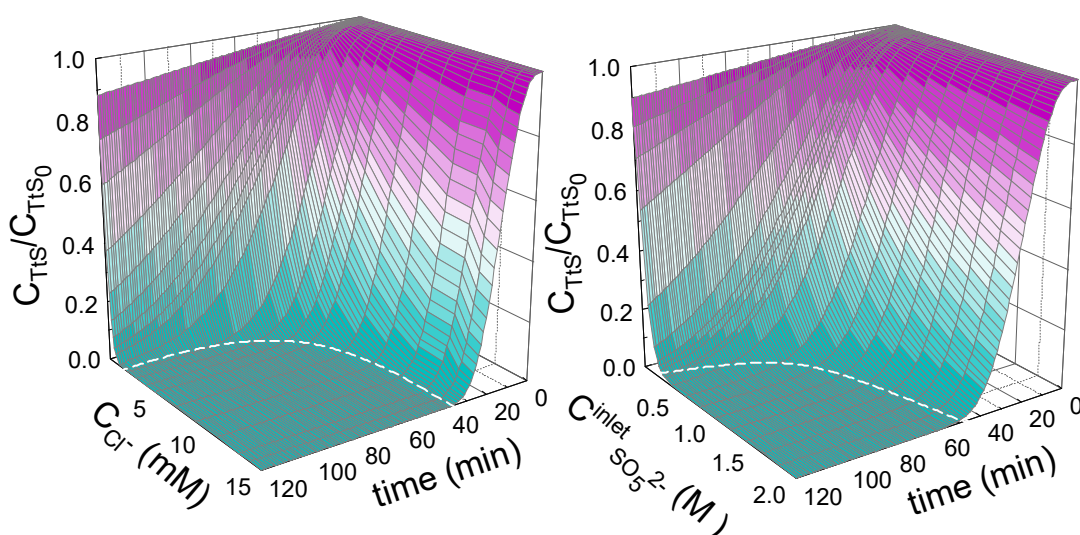
Figure 5. PMS/Cl^- system. Sensitivity analysis of initial chlorides and inlet peroxymonosulfate concentrations. Simulated evolution of the normalized tritosulfuron concentration as a function of time. Modelling conditions: T=298 K, pH range=3.3-3.8, C_{Cl^-}=$6 \cdot 10^{-4}$ M, Q_{PMS}=0.7 mL min^{-1}, V_0=1 L, $C_{TtS,0}$=1 mg L^{-1}, C_{PMS_inlet}= 0.2 M.

3.2.3. Tritosulfuron initial concentration influence

The concentration of tritosulfuron was ranged in the interval 0.5–10 mg L^{-1}, and the obtained results are depicted in Figure 6.

Figure 6 reveals that the process is not first order in TtS concentration, which is a common error found when analyzing the kinetics of oxidation processes. The simplistic mechanism proposed is capable of simulating the profiles obtained at different initial tritosulfuron concentrations. This parameter does not influence the PMS profiles; hence, PMS evolution curves are similar regardless of the initial parent compound concentration. These results were corroborated both experimental and theoretically.
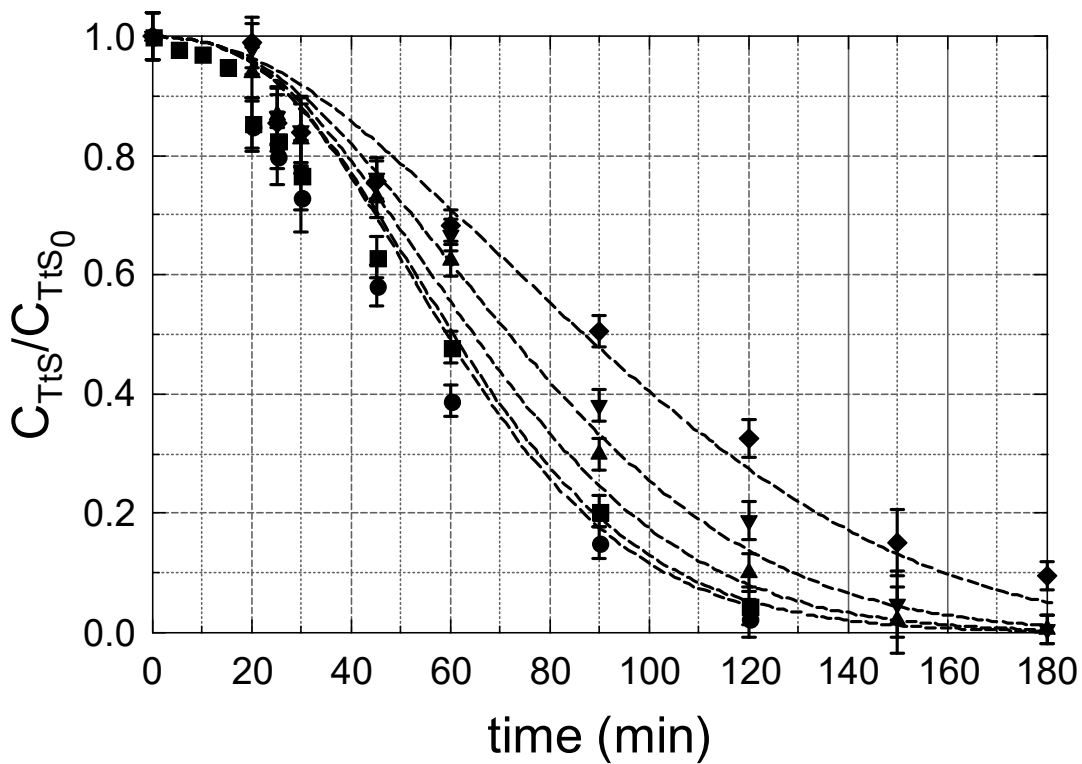

Figure 6. PMS/Cl⁻ system. Evolution of the normalized tritosulfuron concentration as a function of time. Influence of $C_{TtS,0}$. Experimental conditions: T=298 K, pH range=3.3–3.8, C_{Cl^-}=6·10⁻⁴ M, Q_{PMS}=0.7 mL min⁻¹, V_0=1 L, C_{PMS_inlet}=0.2 M, $C_{TtS,0}$: ●,0.5 mg L⁻¹; ■, 1.0 mg L⁻¹; ▲, 2.5 mg L⁻¹, ▼, 5 mg L⁻¹; ◆, 10 mg L⁻¹ (Dashed lines: theoretical simulated profiles).

3.2.4. Temperature influence

Finally, the effect of reaction temperature was investigated in the interval 303–333 K. Figure 7 illustrates the positive action of temperature in TtS removal rate. The only adjustable parameter k_{ineff} followed an Arrhenius trend $k_{ineff} = 4.28 \pm 0.15 \cdot 10^7 \cdot \exp(-7492/T)$. At the sight of Figure 7 the simple model proposed in this study also does a good job when simulating the effect of temperature on tritosulfuron depletion profiles.
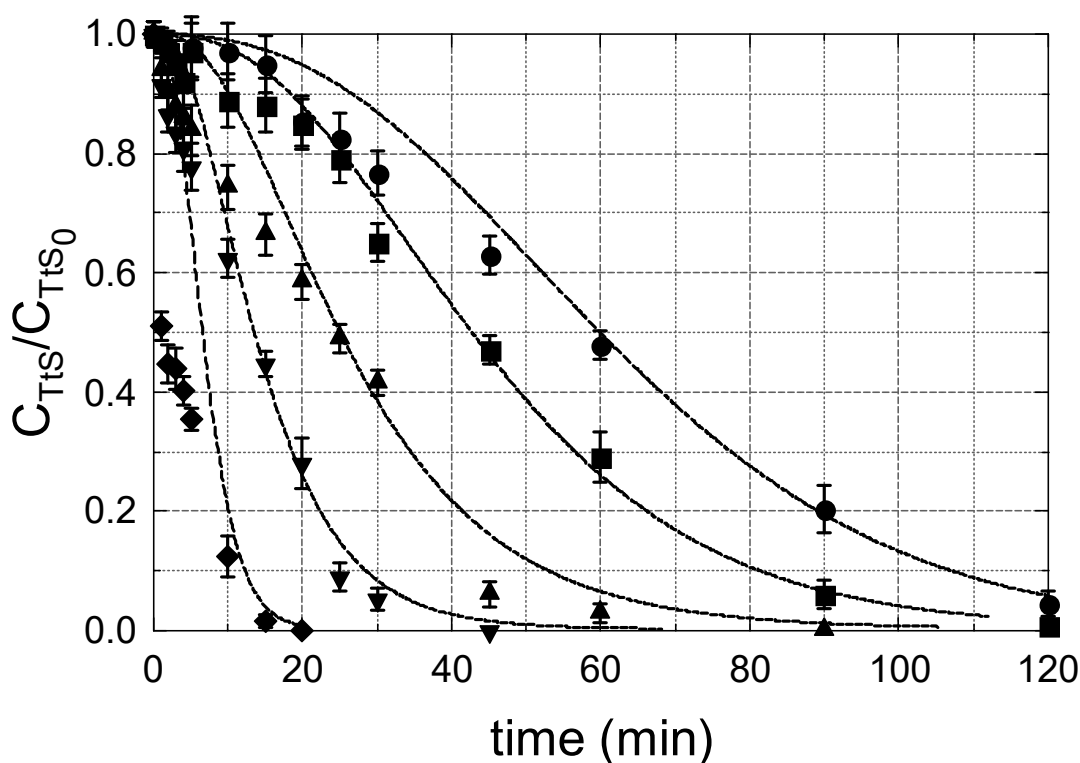

Figure 7. PMS/Cl⁻ system. Evolution of the normalized tritosulfuron concentration as a function of time. Influence of temperature. Experimental conditions: pH range=3.3–3.8, $C_{Cl^-} = 6 \cdot 10^{-4}$ M, $Q_{PMS} = 0.7$ mL min⁻¹, $V_0 = 1$ L, $C_{PMS\_inlet} = 0.2$ M, $C_{TtS,0} = 1.0$ mg L⁻¹. Temperature: ●, 298 K; ■, 303 K; ▲, 313 K; ▼, 323 K; ♦, 333 K. (Dashed lines: theoretical simulated profiles).

To assess the most influencing stages in the mechanism, finally, a sensitivity analysis of the rate constants involved in the mechanism was conducted. Hence, Figure 8 depicts the

aforementioned analysis. As inferred from this figure, k_{Cl} and k_{TtS-Cl} exert a significant influence on TtS conversion, especially at low values of these parameters. Contrarily, k_{ineff} mainly affects the process when high values are used. The direct reaction between peroxymonosulfate and tritosulfuron does not play any significant role in the mechanism within the typical range of values of this constant.
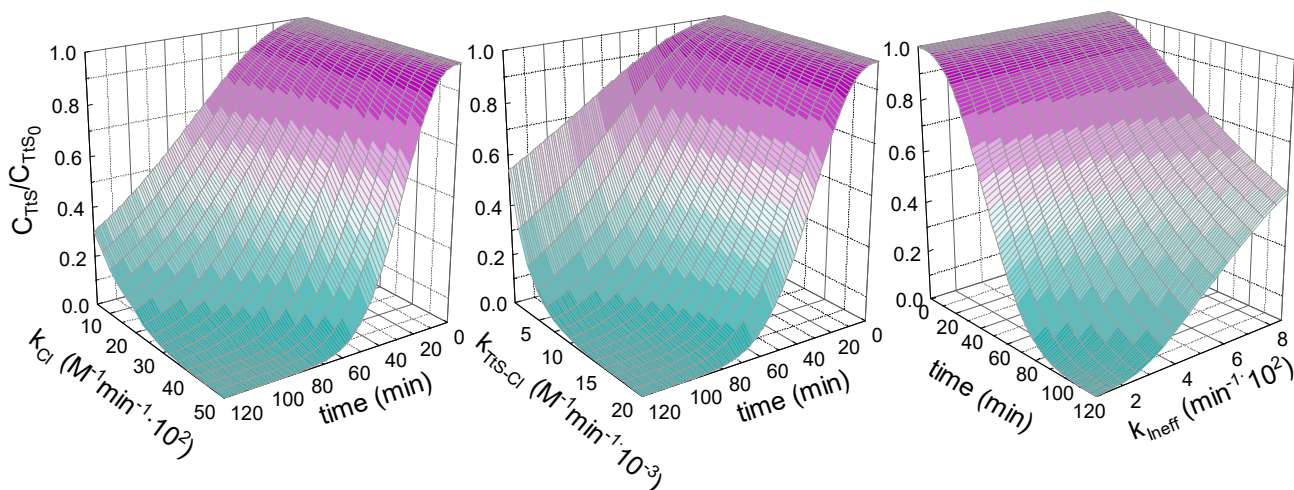

Figure 8. Sensitivity analysis of rate constant values in the proposed mechanism. Simulated evolution of the normalized tritosulfuron concentration as a function of time. Modelling conditions: T=298 K, pH range=3.3–3.8, $C_{Cl-}=6\cdot10^{-4}$ M, $Q_{PMS}=0.7$ mL min^{-1}, $V_0=1$ L, $C_{TtS,0}=1$ mg L^{-1}, $C_{PMS\_inlet}=0.2$ M.

3.3. Intermediates: identification, evolution & proposed mechanism

An attempt was conducted to identify the first intermediates generated in the reaction by analyzing some samples taken at different stages of the process. Total Ion Chromatograms (TICs) at different reaction times are depicted in Figure 9 (0, 24.7, 54.9 & 96.7% of tritosulfuron degradation), from the beginning when practically only

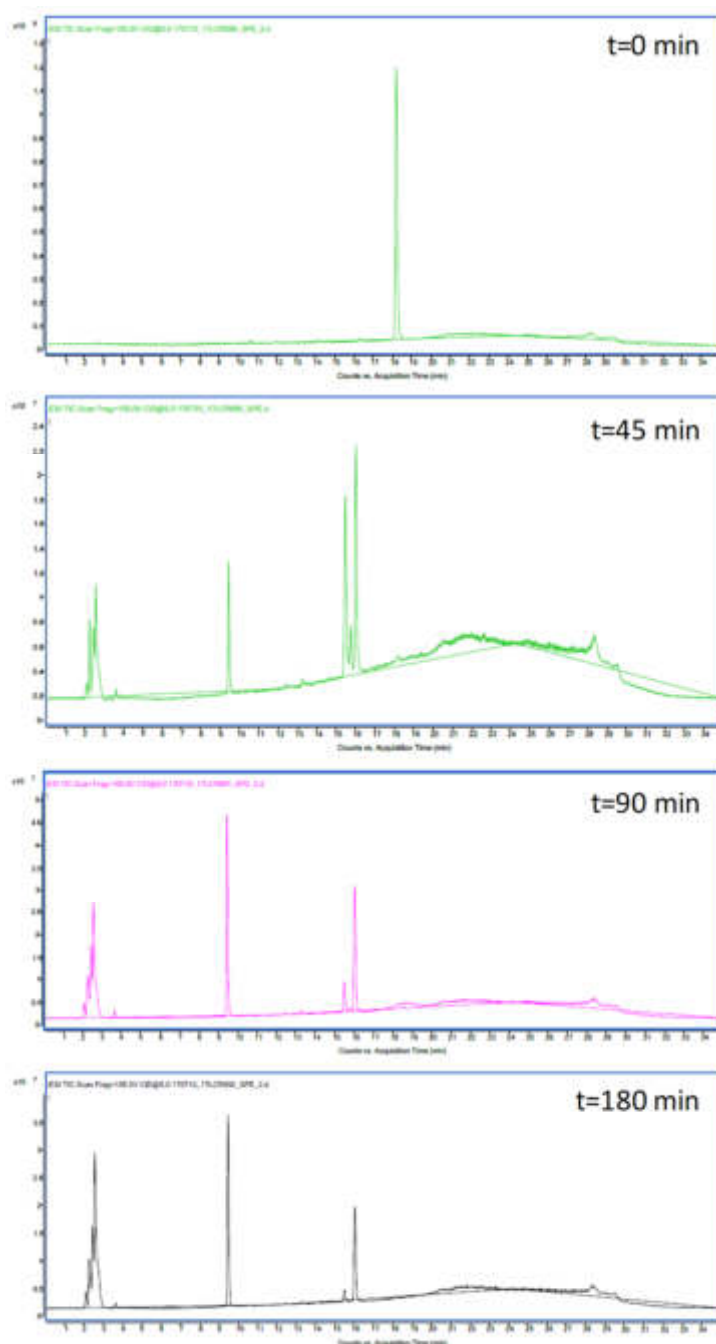tritosulfuron is detected to elevated reaction times when the parent compound has disappeared.

Figure 9. Total Ion Chromatograms (TICs) from tritosulfuron oxidation by the PMS/Cl⁻ system at different tritosulfuron oxidation stages. From top to bottom: 0, 24.7, 54.9 & 96.7% of tritosulfuron degradation. Reaction conditions: T=298 K, C_{Cl^-}=6·10⁻⁴ M, Q_{PMS}=0.7 mL min⁻¹, V_0=1 L, $C_{TtS,0}$=10 mg L⁻¹, C_{PMS_inlet}=0.2 M.

The analysis of detected peaks led to the proposal of a total of eight intermediates, whose chemical formulas are shown in Table 1. Main peaks appear at retention times in the range 15-16 min, as the parent compound (tritosulfuron), that reduce as the reaction progresses to smaller compounds. From the intermediates detected, tritosulfuron structure is broken by the carboxylic bond with central nitrogen atom, leading to an aromatic ring which maintains the sulfate group, and a triazine derivative. A proposed mechanism based in hydroxyl attack and chlorine addition is proposed in Figure 10.
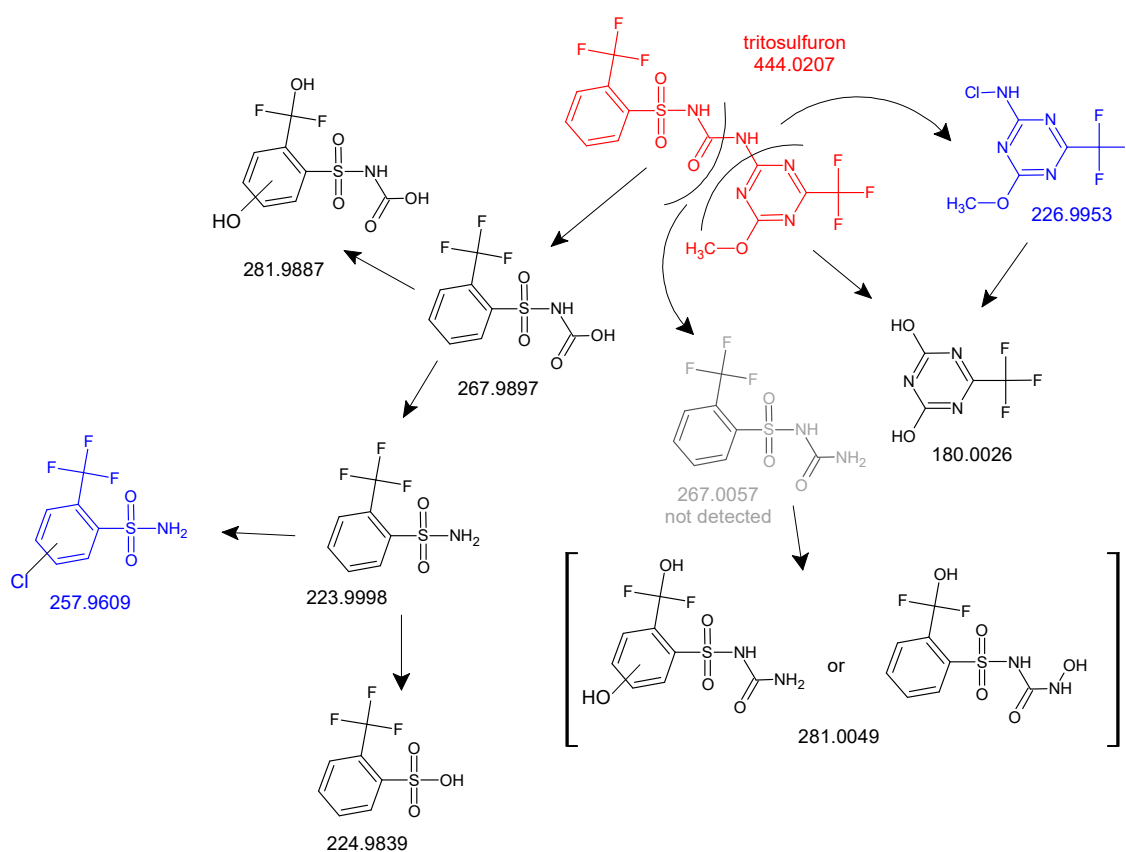
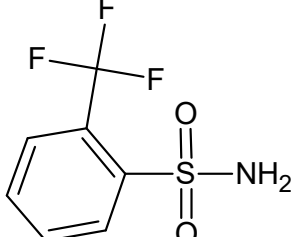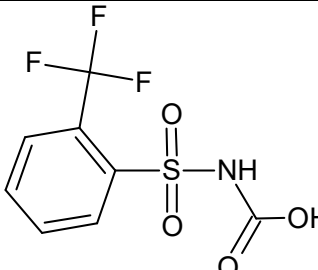**Figure 10.** Proposed mechanism of tritosulfuron oxidation by means of PMS/Cl⁻ combination.
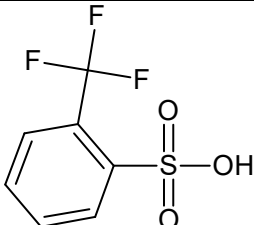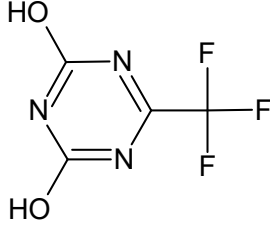
On one hand, the scission of tritosulfuron gives to the formation of an aromatic ring maintaining the sulfate group, producing the product of m/z=267.9897 which is further oxidized to give the production of m/z=223.9998 in which the carboxylic group is lost. The amine group of this compound is hydroxylated, leading to the final product of m/z=224.9839. Alternatively, a hydroxylation of the aromatic ring of compound 267.9897 joint to a fluorine substitution is observed, generating the product m/z=281.9887. Related to the chlorinated compounds of this first route, only the chlorination of the amine 223.9998 into his aromatic ring is appreciated, leading to the product m/z=257.9609.
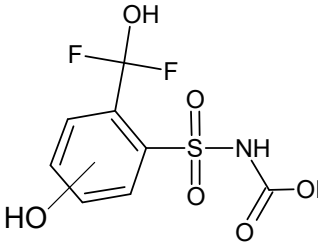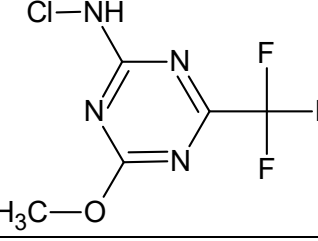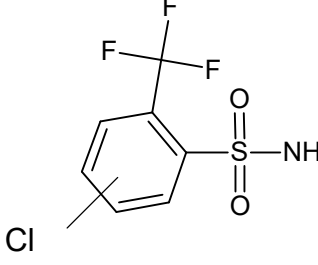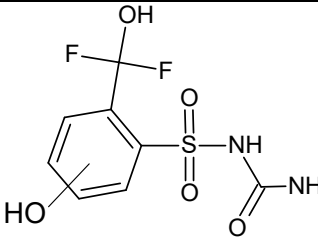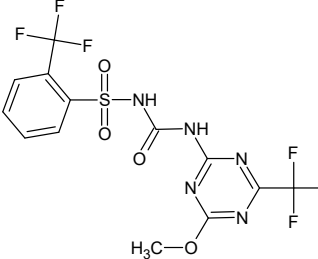
On the other hand, in a second route of degradation, the atrazine group has been appreciated to be chlorinated in the amine group, leading to the compound m/z=226.9953 in which the –O-CH_3 group is conserved. The other byproduct appreciated in this route maintaining the triazine ring is m/z=180.0026, in which all groups, with the exception of –CF_3, have been hydroxylated.

The evolution of these detected intermediates can be elucidated by analyzing the peaks' areas in the Extracted Ion Chromatogram (EIC) through reaction time. The intensity detected in EIC for each compound depends on the facility to be ionized and other operational measurements conditions, but since all compounds are derived from the same parent compound, i.e. tritosulfuron, this magnitude could be used as proportional to concentration in the same extension for all compounds. Figure 11 depicts the evolution of the EIC's peak areas with the oxidation time of the system PMS/Cl^-. Firstly, three intermediates (m/z: 224.9839, 257.9653 and 226.9953) appears in a higher intensity if compared to the rest, indicating that they are the main transformation products of the oxidation of tritosufuron. Two of these compounds are chlorinated; however, their concentrations decrease with time. Only m/z=224.9839 (retention time of 9.45 min),

which corresponds to the aromatic ring maintaining –CF_3 and –SO_3H groups, seems to be recalcitrant, as it can be appreciated in the TICs. The rest of compounds appears in one magnitude inferior of intensity, and all of them are almost completely oxidized with the exception of mass 281.0049 and 267.9897. The hidroxylated triazine ring (m/z=180.0026) is not detected after 90 min of reaction. The same happens with the compound m/z=281.9887.

Table 1. Detected intermediates and proposed structures of tritosulfuron oxidation by the PMS/Cl⁻ system

Estructure	Molecular Formula	Retention time (min)	Ring Double Bond Equivalent (RDBE)	m/z	Error (ppm)
	$C_7H_5F_3O_3S$	9.45	4	224.9839	-5.01
	$C_4H_2F_3N_3O_2$	12.01	4	180.0026	15.7
	$C_7H_6F_3NO_2S$	13.21	6	223.9998	-10.0
	$C_8H_6F_3NO_4S$	13.44	7	267.9897	7.78

	$C_8H_7F_2NO_6S$	14.66	7	281.9889	-39.5
	$C_5H_4ClF_3N_4O$	15.49	4	226.9953	8.81
	$C_7H_5ClF_3NO_2S$	16.03	6	257.9609	7.0
	$C_8H_8F_2N_2O_5S$	16.09	7	281.0049	13.2
	$C_{13}H_9F_6N_5O_4S$	18.19	11	444.0207	-0.07

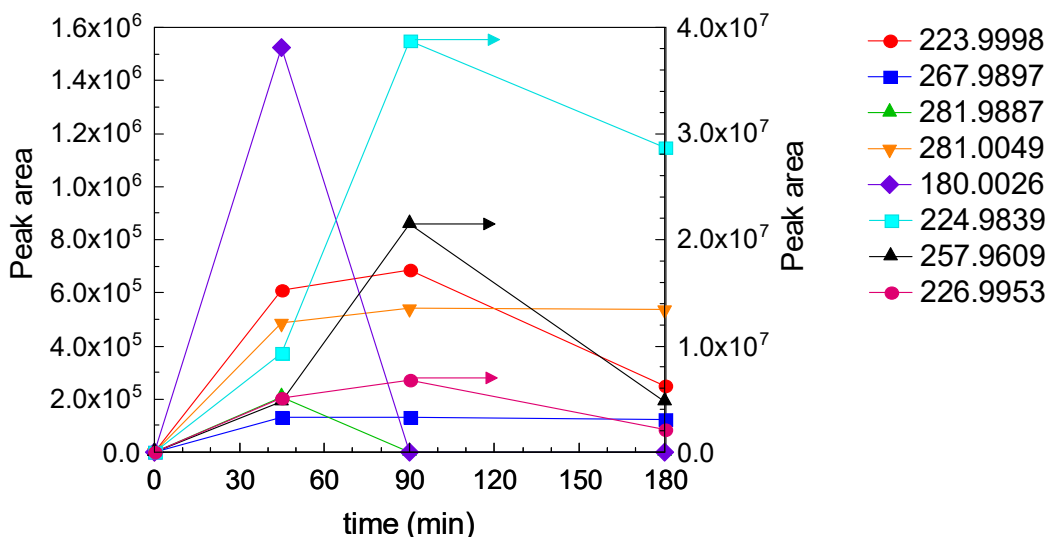**Figure 11.** Evolution of detected peak areas of the identified intermediates in PMS/Cl⁻ system. Reaction conditions: $T=298$ K, $C_{Cl^-}=6 \cdot 10^{-4}$ M, $Q_{PMS}=0.7$ mL min^{-1}, $V_0=1$ L, $C_{TtS,0}=10$ mg L^{-1}, $C_{PMS\_inlet}=0.2$ M.

4. Conclusions

Peroxymonosulfate activation can be carried out by chloride, leading to the generation of HClO/Cl$_2$ species. The capacity of peroxymonosulfate to directly oxidize TtS in presence of Cl⁻ has been proved to be accelerated if compared to absence of Cl⁻. The main variables affecting the process have been tested. A mechanism is capable of simulation the influence of oxidation species. Initial peroxymonosulfate and Cl⁻ concentration exert a positive effect, with differences less pronounced in the first case. This latter aspect has been confirmed by a sensitivity analysis of the rate constant modelling the process. A presence of optimal conditions has been appreciated. Moreover, no importance of direct TtS oxidation through peroxymonosulfate has been observed. Intermediates have been identified, appreciating the hydroxylation as the main route of oxidation and chlorine addition as secondary. A mechanism has been proposed, indicating the scission places of tritosulfuron and modification of its intermediates. The evolution of the peaks areas of

these intermediates demonstrates the preference to the formation of some of them, and their possible recalcitrance.

Acknowledgements

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