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HAL Id: hal-01712279
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Submitted on 2 Mar 2018

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An unprecedented route of 'OH radical reactivity evidenced by an
electrocatalytical process: ipso-substitution with
perhalogenocarbon compounds

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Paper submitted to \textit{Applied Catalysis B - Environment}

for consideration

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ABSTRACT

Hydroxyl radical (•OH) is ubiquitous in the environment and in metabolism. It is one of the most powerful oxidants and can react instantaneously with surrounding chemicals. Currently, three attack modes of •OH have been identified: hydrogen atom abstraction, addition to unsaturated bond and electron transfer. Perhalogenocarbon compounds such as CCl₄ are therefore supposed to be recalcitrant to •OH as suggested by numerous authors due to the absence of both hydrogen atom(s) and unsaturated bond(s). Here, we report for the first time a fourth attack mode of •OH through ipso-substitution of the halogen atom. This breakthrough offers new scientific insight for understanding the mechanisms of •OH oxidation in the related research areas of research. It is especially a great progress in organic contaminants removal from water. In this study, CCl₄ is successfully degraded and mineralized in aqueous media using a green and efficient electrocatalytical production of homogeneous and heterogeneous •OH. Maximum degradation rate of 0.298 min⁻¹ and mineralization yield of 82% were reached. This opens up new possibilities of emerging water pollutants elimination such as fluorosurfactants.

Keywords: carbon tetrachloride; anodic oxidation; electrocatalysis; electro-Fenton; oxidation pathway.
1. INTRODUCTION

The omnipresence of hydroxyl radical ('OH) is now well established in various types of environments including natural waters, atmosphere in which it plays a role of “detergent”, interstellar space as well as biological systems where 'OH has an important role in immunity metabolism [1–4]. It makes 'OH as the most important free radical in chemistry and biology because of its multiple implications and applications [5,6].

In water media, 'OH is the second strongest oxidizing agent after fluorine with a standard redox potential of 2.8 V/SHE [7]. The presence of unpaired electron on oxygen atom makes 'OH a very reactive species with a mean lifetime estimated as only a few nanoseconds in water [8]. It destroys most of organic and organometallic pollutants until total mineralization, i.e. conversion into CO₂, H₂O, and inorganic ions; hence the interest of its use in water treatment area. Indeed, the occurrence of hazardous and toxic pollutants into the water compartments led the water and wastewater regulatory requirements to become more stringent regarding the release of such compounds. Being xenobiotic, these contaminants cannot be removed by conventional wastewater treatment plant and therefore an advanced physicochemical treatment is required. Thus, since more than 30 years the outstanding properties of 'OH have been tested for water purification in the so-called advanced oxidation processes (AOPs) [9]. AOPs have gained increasing interests as they constitute promising, efficient and environmental-friendly methods to remove persistent organic pollutants (POPs) from waters [10,11]. Several types of AOPs have been developed based on the in situ formation of 'OH by means of various chemical, photochemical, sonochemical, or electrochemical reactions. Then, the 'OH formed can react according to three possible reaction modes proposed in literature: (i) hydrogen atom abstraction (dehydrogenation), (ii) electrophilic addition to an unsaturated bond (hydroxylation) and (iii) electron transfer (redox) reactions [6,10]. The first mode is typical for alkanes and alcohols (Eq. 1) with rate
constants in the range $10^6$-10$^8$ M$^{-1}$ s$^{-1}$ [12], whereas the second mode occurs especially with aromatics (ArH) (Eqs. 2a-2b) with rate constants as high as 10$^8$-10$^{10}$ M$^{-1}$ s$^{-1}$ [12] while the third mode is generally given with oxidizable inorganics such as cation (Fe$^{2+}$ (Eq. 3a)) as well as anions (Eq. 3b) (Cl$^-$, NO$_2^-$, HCO$_3^-$) and organics (Eq. 4) [1]:

$$\text{RH} + ^{\cdot}\text{OH} \rightarrow \text{R}^\cdot + \text{H}_2\text{O}$$  \hspace{1cm} (1)

$$\text{ArH} + ^{\cdot}\text{OH} \rightarrow \text{ArHOH}^\cdot$$  \hspace{1cm} (2a)

$$\text{ArHOH}^\cdot + \text{O}_2 \rightarrow \text{ArOH} + \text{HO}_2^*$$  \hspace{1cm} (2b)

$$\text{Fe}^{2+} + ^{\cdot}\text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^-$$  \hspace{1cm} (3a)

$$\text{Anion}^{n-} + ^{\cdot}\text{OH} \rightarrow \text{Anion}^{(n-1)-} + \text{OH}^-$$  \hspace{1cm} (3b)

$$\text{RH} + ^{\cdot}\text{OH} \rightarrow \text{RH}^{+} + \text{OH}^-$$  \hspace{1cm} (4)

Therefore, $^{\cdot}\text{OHs}$ are very active species that can oxidize even the most recalcitrant chemicals. However, $^{\cdot}\text{OH}$ have been considered in several studies as unreactive with perhalogenated alkanes (C$_x$X$_y$) water contaminants that contain only carbon and halogen atoms such as carbon tetrafluoride (CF$_4$), carbon tetrachloride (CCl$_4$), hexafluoroethane (C$_2$F$_6$) and hexachloroethane (C$_2$Cl$_6$) that are widely used as etchant in semiconductor manufacturing and as refrigerants. Indeed, these pollutants do not have any hydrogen atom as well as no unsaturated bond. Thus, no one of the three above-mentioned modes of $^{\cdot}\text{OH}$ actions can occur.

Interestingly, several authors intended to be able to degrade perhalogenocarbon compounds by applying some AOPs but in the presence of an organic precursor. Cho et al. [13,14] succeeded to degrade CCl$_4$ with a heterogeneous photocatalysis (UV/TiO$_2$) process in the presence of surfactant as organic precursor. It was proposed as a hypothesis that a complex formation between the surfactant functional groups and TiO$_2$ surface was responsible for the
weak visible light absorption and the subsequent photo-induced electron transfer to CCl$_4$

\[ \text{CCl}_4 + e^- \quad \text{(from a visible light activated reaction center)} \rightarrow \text{''CCl}_3 + \text{Cl}^- \quad (5a) \]

\[ \text{''CCl}_3 + \text{O}_2 \rightarrow \text{''OOCCl}_3 \rightarrow \rightarrow \rightarrow \text{CO}_2 + 3\text{Cl}^- \quad (5b) \]

Gonzalez et al. [15] employed methanol as precursor to mineralize CCl$_4$ by H$_2$O$_2$ photolysis according to the following reactions sequence (Eqs. (6a)-(6c)):

\[ \text{H}_2\text{O}_2 + h\nu \quad (254 \text{ nm}) \rightarrow 2 \text{ 'OH} \quad (6a) \]

\[ \text{'OH} + \text{CH}_3\text{OH} \rightarrow \text{''CH}_2\text{OH} + \text{H}_2\text{O} \quad (6b) \]

\[ \text{''CH}_2\text{OH} + \text{CCl}_4 \rightarrow \text{''CCl}_3 + \text{CH}_2\text{O} + \text{Cl}^- + \text{H}^+ \quad (6c) \]

In addition, some authors applying other AOPs also demonstrated the degradation of CCl$_4$ by suggesting the formation of additional inorganic species that were responsible for its decomposition. Thus, it was considered that sonication decomposes water molecules into hydrogen radical ('H) and 'OH and then CCl$_4$ reacts with 'H [16,17]:

\[ \text{H}_2\text{O} + )\) ) \rightarrow 'H + 'OH \quad (7a) \]

\[ \text{CCl}_4 + 'H \rightarrow \text{HCl} + '\text{CCl}_3 \quad (7b) \]

In a modified chemical Fenton’s treatment it was suggested that the superoxide ion (O$_2$') was responsible for the decomposition of CCl$_4$ [18–20]. O$_2$' is a weak nucleophile and reductant that was suggested to be able to degrade CCl$_4$ in aprotic media such as dimethyl sulfoxide and dimethylformamide as organic precursor [21,22] and more recently in aqueous media by using high concentration of H$_2$O$_2$ (>0.1 M) in a Fenton-like process.
However, an important feature is that at the operated Fenton pH (pH 3 initially), hydroperoxyl ion (HO$_2^\cdot$), a weak oxidant ($E^\circ = 1.65$ V/SHE), predominate in such acidic conditions ($pK_a = 4.8$) instead of O$_2^\cdot$ [23]. Therefore, the role of O$_2^\cdot$ has to be reconsidered.

Recently, electrochemical advanced oxidation processes (EAOPs) for generating 'OH in a catalytic and continuous mode have gained increasing interests [23–27]. They are not only more environmentally friendly as electron is a clean reagent but also more efficient as they can even degrade the most recalcitrant compounds [28–34] such as cyanuric acid known to be resistant to 'OH oxidation in more conventional AOPs [35]. Another advantage is that EAOPs are modular process according to the electrodes materials to be used which lead to different oxidizing/reducing species formed [23,36–40]. In other words, the nature of the electrogenerated species can be controlled by the adequate electrode materials and operating conditions. Therefore, the oxidative degradation of perhalogenated compounds such as CCl$_4$ has never been studied by EAOPs, it appears important to carry out it as it can bring novel tremendous scientific insights on the mechanism of degradation of such molecules according to the electrode material employed.

2. EXPERIMENTAL

2.1. Chemicals

All the chemicals were of analytical grade, and were used without any further purification. Carbon tetrachloride (CCl$_4$), titanium tetrachloride (TiCl$_4$), potassium hydrogen phthalate, hydrogen peroxide (H$_2$O$_2$) (30% w/w) and sodium sulfate (Na$_2$SO$_4$) were purchased from Sigma-Aldrich. Heptahydrated ferrous sulfate (FeSO$_4$.7H$_2$O), sulfuric acid (H$_2$SO$_4$) and phosphoric acid (H$_3$PO$_4$) (85% w/w) were supplied by Acros Organics. In all experiments, the
solutions were prepared with ultrapure water from a Millipore Simplicity 185 (resistivity > 18 MΩ cm at room temperature).

2.2. Electrochemical reactor set-up

Electrolysis experiments with CCl₄ aqueous solutions (0.2 mM) were run at controlled temperature (22.0 ± 0.1 °C), in a 0.20 L closed-undivided glass electrochemical reactor under current-controlled conditions. The cathode was either a 150 cm² carbon felt (CF) piece (Carbone-Lorraine, France) or a 28 cm² plate of stainless steel (SS) (GoodFellow, France). Either a Pt grid (5 cm height cylindrical (i.d. = 3 cm)) or boron-doped diamond (BDD) coated on a Niobium (Nb) plate (28 cm²) (Condias, Germany) was employed as an anode material with an electrode distance of 3.5 cm. The electrochemical cell was monitored by a power supply HAMEG 7042-5 (Germany) and the applied current was set to 1000 mA. An inert supporting electrolyte (Na₂SO₄ at 0.050 M) was added to the medium to ensure a constant ionic strength (0.15 M). The pH of the initial solution was adjusted to a pH of 3 [41]. The solutions were continuously stirred to assure homogeneous mixing. FeSO₄·7H₂O was added (0.05 mM) as a source of catalyst (Fe²⁺) to implement Fenton’s reaction in EF process. Compressed air was bubbled initially before starting the experiment and before adding CCl₄ compound [42]. This was to saturate the aqueous solution in O₂ as a source of H₂O₂ production (Eq. 9) while avoiding the volatilization of CCl₄. The reactor set-up for electrolysis experiments is illustrated in Fig. 1. The same reactor was employed to perform H₂O₂ oxidation experiments, except that the electrodes were absent.

2.3. Analytical methods

2.3.1. Cyclic voltammetry (CV)
CV experiments were performed to evaluate the electroactivity of CCl₄ in aqueous media with a potentiostat/galvanostat PGP201 VoltaLab (Radiometer Analytical S.A.) in a three-electrode system. Either Pt (1 mm diameter) or glassy carbon (3 mm diameter) was employed as working electrode while a Pt wire was used as counter electrode. A saturated calomel electrode (SCE) was employed as reference electrode; therefore, all the voltage values given in the text are expressed in V/SCE, unless stated otherwise. Sodium sulfate (0.050 M) was used as electrolyte and the solutions were acidified to pH 3.0, the optimal EAOPs conditions. The CV experiments were performed in a voltage range of -3.0 V to +3.0 V and at a scan rate of 10 mV s⁻¹.

2.3.2. Hydrogen peroxide experiments and analysis

The oxidation power of H₂O₂ onto CCl₄ was evaluated by adding initially H₂O₂ in excess (100 mM) into CCl₄ (0.2 mM) aqueous solution before starting the experiments. The amount of H₂O₂ accumulated in bulk solution was determined by performing electrolysis experiments in the same conditions than EAOPs treatments, except that no Fe²⁺ was added to avoid Fenton’s reaction to occur [37]. H₂O₂ was quantified by colorimetry using TiCl₄ [43]. The absorbance of the pertitanic acid complex formed was measured with a Perkin Elmer (USA) Lambda 10 UV-VIS spectrophotometer at a wavelength of 410 nm. An external calibration curve was obtained with standards of H₂O₂, giving a molar extinction coefficient of around 935 ± 2 L mol⁻¹ cm⁻¹. The H₂O₂ concentrations were then calculated according to the Beer-Lambert law.

2.3.3. Total organic carbon (TOC) measurements

TOC analyses were performed to quantify the mineralization degree during the different kind of treatments. The solution TOC values were determined by thermal catalytic oxidation (680
°C in presence of Pt catalyst) using a Shimadzu (Japan) V\textsubscript{CSH} TOC analyzer. All samples were acidified to pH 2 with H\textsubscript{3}PO\textsubscript{4} (25% w/w) to remove inorganic carbon. The injection volumes were 50 µL. Calibrations were performed by using potassium hydrogen phthalate solutions (50 mg C L\textsuperscript{-1}) as standard. All measured TOC values were given with a coefficient of variance below to 2%.

Mineralization yields (\(r_{\text{min}}\)) were considered equivalent to TOC removal percentage and can be determined according to the following Eq. 8:

\[
r_{\text{min}}(\%) = \frac{(\Delta\text{TOC})}{\text{TOC}_0} \times 100
\]

where (\(\Delta\text{TOC}\))\textsubscript{t} is the difference between the initial TOC (TOC\textsubscript{0}) and TOC at time t.

### 2.3.4. Ionic chromatography analysis

The inorganic ions released in the treated solutions were determined by ion chromatography using a Dionex ICS-1000 basic ion chromatography system (USA). The analysis of anions was monitored using an IonPac AS4A-SC (25 cm × 4 mm) anion-exchange column linked to an IonPac AG4A-SC (5 cm × 4 mm) column guard. The system was equipped with a DS6 conductivity detector containing a cell heated at 35 °C. The mobile phase contained 1.8 mM Na\textsubscript{2}CO\textsubscript{3} and 1.7 mM NaHCO\textsubscript{3}. The flow rate was set to 2 mL min\textsuperscript{-1}. The suppressor SRS (Self Regenerating Suppressor) needed to prevent the influence of the eluent ions in the detector signal was at a current of 30 mA.

### 2.3.5. Kinetic model for CCl\textsubscript{4} degradation

The decay rate of CCl\textsubscript{4} can be written as follow (Eq. 9):

\[
\frac{d[CCl_4]}{dt} = -k_{CCl_4}[\cdot OH][CCl_4]
\]
where $[\text{CCl}_4]$ is the concentration of CCl$_4$, $k_{\text{CCl}_4}$ is the decay rate constant of CCl$_4$ and $[^\cdot\text{OH}]$ is the concentration of $^\cdot\text{OH}$ radical.

Considering that the degradation of one mole of CCl$_4$ produce four moles of Cl$^-$, the following equivalence of chemical rate can be obtained (Eq. 10):

$$-\frac{d[\text{CCl}_4]}{dt} = \frac{1}{4} \frac{d[\text{Cl}^-]}{dt}$$  \hspace{1cm} (10)

By inserting Eq. 10 into Eq. 9, the Eq. 11 is given:

$$\frac{d[\text{Cl}^-]}{dt} = 4k_{\text{CCl}_4}[^\cdot\text{OH}][\text{CCl}_4]$$  \hspace{1cm} (11)

By considering that $[\text{Cl}^-]= [\text{CCl}_4]_0 - [\text{CCl}_4]$, that $[\text{CCl}_4] = [\text{CCl}_4]_0 - [\text{Cl}^-]_{\text{meas}}$ and that $[\text{Cl}^-] = 4[\text{Cl}^-]_{\text{meas}}$, the following Eq. 12 is retrieved from Eq. 11:

$$\frac{d[\text{Cl}^-]_{\text{meas}}}{dt} = k_{\text{CCl}_4}[^\cdot\text{OH}][\text{CCl}_4]_0 - [\text{Cl}^-]_{\text{meas}}$$  \hspace{1cm} (12)

where $[\text{CCl}_4]_0$ is the initial concentration of CCl$_4$ and $[\text{Cl}^-]_{\text{meas}}$ is the measured concentration of Cl$^-$ released into the solution.

By considering the quasi-steady state approximation towards the $^\cdot\text{OH}$ concentration evolution, a pseudo-first order kinetic model can be assumed [23]:

$$\frac{d[\text{Cl}^-]_{\text{meas}}}{dt} = k_{\text{app}}([\text{CCl}_4]_0 - [\text{Cl}^-]_{\text{meas}})$$  \hspace{1cm} (13)

where $k_{\text{app}} = k_{\text{CCl}_4}[^\cdot\text{OH}]$ is the apparent decay rate constant of CCl$_4$ oxidation by $^\cdot\text{OH}$.

After integration of Eq. 13, the semi-logarithmic Eq. 14 is obtained:

$$\ln\left(\frac{[\text{CCl}_4]_0}{[\text{CCl}_4]_0 - [\text{Cl}^-]_{\text{meas}}}\right) = \ln\left(\frac{[\text{CCl}_4]_0}{[\text{CCl}_4]_t}\right) = k_{\text{app}}t$$  \hspace{1cm} (14)

where $[\text{CCl}_4]_t$ is the concentration of CCl$_4$ at time $t$. 

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3. RESULTS AND DISCUSSION

3.1. Evaluation of electroactivity of CCl₄

Before studying the possibility of CCl₄ degradation by *OH produced by EAOPs, it appeared important to preliminary verify the electroactivity of CCl₄ to check if it can be degraded by direct electron transfer at anode or cathode surface. Cyclic voltammetry (CV) have been therefore performed in voltage window ranging from -3 V to +3 V in Na₂SO₄ (0.050 M) solution at pH 3. Either platinum (Pt) or glassy carbon was used as working electrode, since both electrode materials were later employed in the EAOPs. As anticipated, neither electro-oxidation nor electro-reduction of CCl₄ occurred by using Pt as working electrode (Fig. 2A).

Whatever the presence or not of CCl₄, no peak of current was observed except the oxidation of H₂O into O₂ (anode) and its reduction into H₂ (cathode). Employing vitreous carbon as working electrode further demonstrated the non-electroactivity of CCl₄ at the potential range studied (Fig. 2B). A difference was noticed between Pt and carbon electrode, since a cathodic peak, attributed to the formation of H₂O₂ (Eq. 15), was noticed at -0.6 V with the latter. This peak is expected because carbonaceous cathodes are well-known to promote the formation of H₂O₂ from 2-electron reduction of O₂ [44]:

\[
O₂ + 2H^+ + 2e^- \rightarrow H₂O₂ \quad (15)
\]

To further investigate the oxidative inaction of H₂O₂ towards CCl₄, experiments were performed by initially spiking H₂O₂ in excess (100 mM) in a 0.2 mM CCl₄ aqueous solution in a hermetic seal batch reactor (Fig. 2C and Fig. 1). As expected H₂O₂ was not able to degrade CCl₄ as no Cl⁻ were released in solution while the total organic carbon (TOC) values remained unchanged along the experiment. The H₂O₂ concentration measurements depicted in Fig. 3 highlights the absence of H₂O₂ consumption during oxidation experiments with CCl₄, as it remained constant (around 100 ± 0.1 mM) all along the experiment. H₂O₂ is known to be
a relatively weak oxidant ($E^{\circ}(H_2O_2/H_2O) = 1.8$ V/SHE) [45] that has relatively poor redox abilities which explain its unreliability to oxidize CCl₄.

3.2. Degradation of CCl₄ by EAOPs

3.2.1. Role of BDD anode: production of heterogeneous $\cdot$OH

The performance of EAOPs to degrade CCl₄ (0.2 mM) has been tested. Guided by the hypothesis described in section 3.1 regarding the role of $\cdot$OH in the CCl₄ degradation, an anodic oxidation (AO) experiment was first performed with a SS cathode and a BDD anode (AO-SS/BDD cell) in order to check this assumption (Fig. 4A). The experiments were performed in aqueous media, in absence of any other organic compound that could play a role of precursor for $\cdot$CCl₃ formation. Moreover, the electrolysis was carried out in dark conditions to avoid any photo-activity. To check whether H₂O₂ formation occurred at SS cathode, the accumulation of H₂O₂ in bulk solution during electrolysis using SS cathode and Pt anode has been performed and the results are represented in Fig. 5. It is shown that the H₂O₂ concentration could not reach higher value than 0.041 mM, which is very low. This is attributed to the SS material that do not favor the two electrons-oxygen reduction reaction (ORR) pathway to form H₂O₂ and will rather promote the four electron-ORR pathway that produce H₂O (Eq. 16) as previously stated [23,43]:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$  \hspace{1cm} (16)

Therefore, the use of SS cathode limited the formation of H₂O₂ through O₂ reduction (Eq. 15) (Fig. 5) while the BDD anode ensured the heterogeneous generation of BDD($\cdot$OH) thanks to its high O₂ evolution overvoltage (2.3 V/SHE) [46,47].

Excitingly, Fig. 4A highlights the release of Cl⁻ ions into the solution by performing an AO-SS/BDD experiment. Upon control experiments results showing, as expected, the absence of
Cl\(^{-}\) ions in solution when no current intensity was applied, CCl\(_4\) was successfully degraded by BDD(\(\cdot\)OH) generated in AO process. It can further be noticed that the amount of Cl\(^{-}\) formed could not reach the maximal Cl\(^{-}\) theoretical concentration ([Cl\(^{-}\)]\(_{\text{max,th}}\)) that could be released. In fact, the rate of chloride formation was in competition with the rate of its oxidation into Cl\(_2\) as highlighted by the decrease of [Cl\(^{-}\)] after 40 min of treatment (Fig. 4A). Indeed, Cl\(_2\) reacts quickly with H\(_2\)O to form HOCl [48] that undergoes further oxidation reactions to be converted into chlorate (ClO\(_3\)\(^{-}\)) and perchlorate (ClO\(_4\)\(^{-}\)) at BDD surface as shown by ionic chromatograms in Fig. 6. Thus, the chromatograms of anions evolution during EF treatment with BDD anode at different treatment time (0 min, 20 min, 40 min, 60 min, 120 min, and 240 min) display Cl\(^{-}\) peaks at retention time around 1.3 min and major peaks of SO\(_4\)\(^{2-}\) at retention time of 3.1 min. Interestingly, two more peaks could be distinguished at retention times of 2.2 min and 7.4 min, respectively. These peaks are ascribed to chlorine oxyanions such as ClO\(_3\)\(^{-}\) and ClO\(_4\)\(^{-}\), respectively. These anions can be formed by Cl\(^{-}\) oxidation into Cl\(_2\) gas at BDD anode due to its high oxidation ability with physisorbed \(\cdot\)OH formed at its surface (BDD(\(\cdot\)OH)) (Eqs. 17-18a). Cl\(_2\) reacts quickly with H\(_2\)O to form the hypochlorous acid (HClO) (Eq. 8b) in the bulk. Since the pH remained between 2.4 and 3.0 during the whole electrolysis, HClO is the predominant species as compared to ClO\(^{-}\) knowing the acid dissociation constant value of HClO; \(pKa = 7.54\) (at 25 \(^\circ\)C). HClO is then oxidized into ClO\(_2\)\(^{-}\) (Eq. 18c) which is quickly oxidized into ClO\(_3\)\(^{-}\) (Eqs. 18d-18e) and then into ClO\(_4\)\(^{-}\) (Eq. 18f) as end-product having the maximal oxidation state [49,50]:

\[
\begin{align*}
\text{BDD} + \text{H}_2\text{O} & \rightarrow \text{BDD}(\cdot\text{OH}) + \text{H}^+ + \text{e}^- \\
2\text{Cl}^- & \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^- \\
\text{Cl}_2(\text{g}) + \text{H}_2\text{O} & \rightarrow \text{HClO} + \text{H}^+ + \text{Cl}^- \\
\text{HClO} + \text{BDD}(\cdot\text{OH}) & \rightarrow \text{BDD} + \text{ClO}_2^- + 2\text{H}^+ + \text{e}^- \\
\text{HClO} + \text{ClO}_2^- & \rightarrow \text{ClO}_3^- + \text{H}^+ + \text{Cl}^- \\
\end{align*}
\]
\[ \text{ClO}_2^- + \text{BDD('OH)} \rightarrow \text{BDD} + \text{ClO}_3^- + \text{H}^+ + e^- \] (18e)

\[ \text{ClO}_3^- + \text{BDD('OH)} \rightarrow \text{BDD} + \text{ClO}_4^- + \text{H}^+ + e^- \] (18f)

Chlorite ion was not observed in the electrolysis with BDD because the high applied current density (35.7 mA cm\(^{-2}\) as reported to the BDD anode surface area) favor the rapid oxidation of ClO\(_2^-\) into ClO\(_3^-\) as noticed previously \[51\], especially in BDD experiments performed at 30 mA cm\(^{-2}\) \[52\].

As it can be seen at the detailed view of Cl\(^-\) peak evolution (Fig. 6B), a maximal peak area could be noticed at 20 min of electrolysis, while it started decreasing after longer treatment. At this time the peaks area of ClO\(_3^-\) increase until 60 min of treatment and start decreasing after electrolysis time longer than 120 min. In the meanwhile, peaks area of ClO\(_4^-\) start rising from 120 min until 240 min of treatment. The subsequent increase/decrease trends observed from Cl\(^-\) evolution concentration to ClO\(_3^-\) and then to ClO\(_4^-\) corroborated the reactions sequence (Eqs. 18a-18e).

In addition, the chromatogram of SO\(_4^{2-}\) (Fig. 6C) highlights a slight decrease of SO\(_4^{2-}\) peak right after the starting of the EF-CF/BDD treatment, corresponding to a SO\(_4^{2-}\) concentration decrease from 50 mM to 47.1 ± 0.9 mM. This is attributed to the reaction of SO\(_4^{2-}\) with high reactive BDD surface producing sulfate radical (SO\(_4^\cdot\)) (Eq. 19a) and persulfate (S\(_2\)O\(_8^{2-}\)) (Eq. 19b) as previously stated \[53,54\].

\[ \text{SO}_4^{2-} \rightarrow \text{SO}_4^\cdot + e^- \] (19a)

\[ \text{SO}_4^\cdot + \text{SO}_4^\cdot \rightarrow \text{S}_2\text{O}_8^{2-} \] (19b)

The oxidation power of SO\(_4^\cdot\) and S\(_2\)O\(_8^{2-}\) are lower than that of the 'OH, with standard reduction potentials of 2.6 and 2.01 V/SHE, respectively \[23\]. It has been previously demonstrated that SO\(_4^\cdot\) radical could not react with CCl\(_4\), since it was found as one of the end-
product during oxidation of chlorinated phenol by SO₄• radical [55]. It means that ‘OH is the only species responsible for the oxidation of CCl₄.

It is important to note that the same trends were observed with all BDD experiments (AO-SS/BDD, AO-CF/BDD and EF-CF/BDD) as these phenomenon depends on the use of BDD anode material itself.

3.2.2. Influence of CF cathode: production of homogeneous ‘OH by peroxone reaction

Interestingly, when a CF cathode was employed (AO-CF/BDD cell), the concentration of Cl⁻ released could reach [Cl⁻]_{max,th} (0.8 mM), highlighting a better degradation of CCl₄ (Fig. 4A).

To better understand this behavior, the accumulation of H₂O₂ in bulk solution during electrolysis using CF cathode and Pt anode is represented in Fig. 7. It was first noticed a transient phase followed by a steady state. This phenomenon is typical in undivided cell study and is referred to the competition reactions between H₂O₂ electrogeneration and H₂O₂ decomposition at the anode (Eqs. 20a-20b), at the cathode (Eq. 21) and in a lesser extent decomposition in bulk solution (Eq. 22) as stated previously by numerous authors [23]:

\[
\begin{align*}
H₂O₂ & \rightarrow HO₂⁻ + H⁺ + e⁻ \quad (20a) \\
HO₂⁻ & \rightarrow O₂ + H⁺ + e⁻ \quad (20b) \\
H₂O₂ + 2H⁺ + 2e⁻ & \rightarrow 2H₂O \quad (21) \\
2H₂O₂ & \rightarrow O₂ + 2H₂O \quad (22)
\end{align*}
\]

It was further emphasized that in presence of CF cathode the maximal amount of H₂O₂ accumulated in bulk solution was 1 mM, which was 24 times higher than with SS cathode. It was attributed to the nature of cathode material itself and to its surface area. Indeed, carbon-based cathodes have high H₂ evolution overpotential and low catalytic activity for H₂O₂ decomposition. Moreover, CF has a 3D porous structure that dramatically increases its
specific surface area as compared to the SS material employed. This property makes increase
the number of active sites for O\textsubscript{2} adsorption before its subsequent reduction into H\textsubscript{2}O\textsubscript{2}.

Therefore, the enhancement obtained with AO-CF/BDD cell as compared to AO-SS/BDD cell
could be due to the additional source of •OH formed by peroxone reaction between H\textsubscript{2}O\textsubscript{2}
electrogenerated at CF cathode and O\textsubscript{3} produced at the anode surface (Eq. 23) [56], as
previously shown in several studies performed in similar electrolysis conditions [57–59], thus
confirming the role of •OH in the degradation process.

\begin{equation}
\text{H}_2\text{O}_2 + 2\text{O}_3 \rightarrow 2\cdot\text{OH} + 3\text{O}_2 \tag{23}
\end{equation}

Indeed the high oxidation power of BDD anode allows also generating O\textsubscript{3} from water
oxidation at its surface (Eq. 24) [49].

\begin{equation}
3\text{H}_2\text{O} \rightarrow \text{O}_3 + 6\text{H}^+ + 6\text{e}^- \tag{24}
\end{equation}

It is worthy to specify that O\textsubscript{3} itself is a moderately strong oxidant (\(E^{\circ}(\text{O}_3/\text{O}_2) = 2.1\) V/SHE)
[45] compared to •OH and has no direct oxidation effect on CCl\textsubscript{4} as stated by a previous study
[19].

3.2.3. Role of iron catalyst: production of homogeneous •OH by Fenton reaction

The addition of Fe\textsuperscript{2+} (0.1 mM) in order to produce •OH through Fenton’s reaction (Eq. 25)
[23] was further investigated by performing electro-Fenton (EF) treatment with CF cathode
and BDD anode (EF-CF/BDD cell).

\begin{equation}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^- \tag{25}
\end{equation}

The presence of ferrous ion could even enhance better the degradation of CCl\textsubscript{4} by reaching
faster [Cl\textsuperscript{-}]\textsubscript{max,th} value as seen in Fig. 4A.
This enhancement in CCl₄ degradation rate is due to the formation of homogeneous 'OH formed in bulk solution that react directly with CCl₄, in addition to BDD('OH) formed at anode surface. In this process, Fenton’s reaction (Eq. 25) is electrocatalyzed by continuous regeneration of Fe²⁺ (catalyst) from electro-reduction of Fe³⁺ ions (Eq. 26) formed by Fenton’s reaction [48]:

\[
\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}
\]  (26)

The difference of efficiency between AO-CF/BDD and EF-CF/BDD experiments was therefore mainly attributed to the action of supplementary 'OH generated in the bulk solution by Fenton reaction (Eq. 25).

Furthermore, when Pt was used as anode instead of BDD in EF process (EF-CF/Pt cell), the dechlorination rate and yield were higher compared with AO-SS/BDD cell (Fig. 4A). It was also noticed that a plateau of Cl⁻ concentration was observed in EF-CF/Pt cell experiment, highlighting the accumulation of Cl⁻ in the solution. In order to better understand this evolution, the chromatograms of anions evolution during EF treatment with Pt anode at different treatment time (0 min, 5 min, 10 min, 20 min, 40 min, 60 min, 120 min, 180 min, 240 min) have been recorded and are represented in Fig. 8. Fig. 8A displays Cl⁻ peaks at retention time around 1.3 min and major peaks of SO₄²⁻ from the supporting electrolyte (Na₂SO₄) at retention time of 3.1 min, as observed with BDD anode electrolysis. To have a better view of the Cl⁻ chromatograms, an enlarged picture allows observing the evolution of Cl⁻ peaks area and height in Fig. 8B. From 0 min to 40 min of EF treatment, it is clearly seen an increase of peak area, meaning that CCl₄ is progressively degraded into Cl⁻. After 40 min of treatment the peaks area barely change, because at this time, the concentration of Cl⁻ has reached its theoretical level value (0.8 mM). Moreover, no other peak could be observed on the chromatogram whatever the time of treatment, meaning that chloride ions could not be
further oxidized into Cl\textsubscript{2}, chlorate, perchlorate species on the contrary to BDD experiments. It is also interesting to note that the peaks area of SO\textsubscript{4}\textsuperscript{2-} remain the same (50 ± 0.1 mM) whatever the treatment time (Fig. 8C), which underlines that the electrolyte stayed unreactive during the treatment, unlike with BDD treatments. This is in accordance with the low oxidation power of Pt that has a low O\textsubscript{2} evolution overvoltage (1.6 V/SHE) \cite{60}. In this case, •OH at Pt surface (Pt(•OH)) is chemisorbed and O\textsubscript{2} evolution is the main reaction (Eqs. 27a-27b) \cite{47}:

\begin{align}
\text{Pt} + \text{H}_2\text{O} & \rightarrow \text{Pt(•OH)} + \text{H}^+ + \text{e}^- \\
\text{Pt(•OH)} + \text{H}_2\text{O} & \rightarrow \text{Pt} + \text{O}_2 + 3\text{H}^+ + 3\text{e}^-
\end{align}

In addition, [Cl\textsuperscript{-}]\textsubscript{max,th} (0.8 mM) was reached only after 120 min against around 20 min with AO-CF/BDD and EF-CF/BDD cells. The superiority of AO-CF/BDD cell over EF-CF/Pt cell was attributed to the higher oxidation power of BDD and to the second source of •OH from peroxone reaction as discussed in section 3.2.2. Thus, the only source of •OH was coming from the electro-Fenton process through Fenton’s reaction in EF-CF/Pt cell. It further emphasized the primary role of homogeneous •OH formed by Fenton’s reaction as compared to heterogeneous •OH formed at BDD surface in AO-SS/BDD cell, because in such diluted solution the electrolysis is controlled by mass transfer rate.

\subsection{3.2.4. Quantitative comparison between oxidation mechanisms with kinetic rate constants}

In order to compare quantitatively each applied condition, a kinetic model has been established (section 2.3.5). The kinetic rate constants of CCl\textsubscript{4} degradation (k\textsubscript{app}) have been
determined considering a pseudo-first order kinetics for the reaction between CCl₄ and •OH by assuming a quasi-stationary state for •OH concentration.

Based on Eq. 14, a linear regression allowed determining $k_{app}$ values from the slope of the straight lines (Fig. 4B) that were ranked as follow: AO-SS/BDD (0.004 ± 0.001 min⁻¹) < EF-CF/Pt (0.072 ± 0.003 min⁻¹) < AO-CF/BDD (0.171 ± 0.002 min⁻¹) < EF-CF/BDD (0.298 ± 0.001 min⁻¹). All correlation coefficient ($R^2$) were higher than 0.989, highlighting the good fitting between experimental data and the pseudo-first order kinetic model. This rank was corroborating the dechlorination results. It highlights again the primary role of BDD(•OH) / •OH while EF-CF/BDD depicted more than 4 times quicker degradation kinetics due to the three sources of hydroxyl radicals generation (e.g. Fenton, peroxone and anodic oxidation mechanisms co-contributions).

3.3. Mineralization of CCl₄ by EAOPs

The mineralization of CCl₄ was evaluated by monitoring the TOC in the same experimental conditions, e.g. AO-SS/BDD, AO-CF/BDD, EF-CF/BDD and EF-CF/Pt cells (Fig. 9). After 8 h of electrolysis, the following mineralization rank was obtained: AO-SS/BDD (24 ± 1.2 %) < EF-CF/Pt (55 ± 1.8 %) < AO-CF/BDD (74 ± 0.9 %) < EF-CF/BDD (82 ± 1.4 %) (Fig. 9A). In addition, by assuming a pseudo-first order kinetic model for TOC decay [61], the same rank was noticed: AO-SS/BDD (0.123 ± 0.011 h⁻¹) < EF-CF/Pt (0.220 ± 0.013 h⁻¹) < AO-CF/BDD (0.772 ± 0.012 h⁻¹) < EF-CF/BDD (0.806 ± 0.010 h⁻¹) (Fig. 9B). All correlation coefficient ($R^2$) values were higher than 0.989, highlighting again the good fitting between experimental data and the pseudo-first order kinetic model.

Knowing that the control experiment has shown negligible TOC removal (2% in 8 h-electrolysis), we could first conclude that CCl₄ was successfully mineralized even with AO-
SS/BDD giving the lower production of \textsuperscript{•}OH as mentioned previously. Moreover, these ranks of mineralization efficiency were corroborating the degradation kinetics results, demonstrating again the superiority of EF-CF/BDD.

3.4. Proposed reaction pathway

Based on the above finding a reaction pathway for \textsuperscript{•}OH action on CCl\textsubscript{4} is proposed (Fig. 10A). For the sake of simplicity, hydroxyl radicals were presented by \textsuperscript{•}OH without making explicit the O-H bond. First, the presence of Cl atom favors the formation of a dipole between C(δ+) and Cl(δ-), atoms due to the higher electronegativity of Cl (3.16) compared to C (2.55) according to Pauling scale. Being a strong electrophilic species, \textsuperscript{•}OH reacts by ipso-substitution on the C atom (Eq. 28a) leading to the subsequent formation of trichloromethanol (CCl\textsubscript{3}OH) (Eq. 28b). Trichloromethanol is then decomposed in water into phosgene (CCl\textsubscript{2}O) (Eq. 29) \cite{62}. Finally CCl\textsubscript{2}O is quickly hydrolyzed in water by forming CO\textsubscript{2}, Cl\textsuperscript{-} and H\textsuperscript{+} (Eq. 30) \cite{63}.

\begin{align*}
\text{CCl}_4 + \text{•OH} & \rightarrow \text{CCl}_4(\text{•OH}) \quad \text{(28a)} \\
\text{CCl}_4(\text{•OH}) & \rightarrow \text{CCl}_3\text{OH} + \text{Cl}^\cdot \quad \text{(28b)} \\
\text{CCl}_3\text{OH} & \rightarrow \text{CCl}_2\text{O} + \text{H}^\cdot + \text{Cl}^\cdot \quad \text{(29)} \\
\text{CCl}_2\text{O} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + 2\text{Cl}^\cdot + 2\text{H}^\cdot \quad \text{(30)}
\end{align*}

Taking into account these considerations, a reaction pathway was therefore proposed for complete degradation of CCl\textsubscript{4} until mineralization, leading to a new attack mode of \textsuperscript{•}OH (Fig. 10B). Over the existing attack \textsuperscript{•}OH modes, e.g. dehydrogenation, hydroxylation and electron transfer \cite{6,64}, a fourth mode, namely \textbf{“ipso-substitution”} is proposed. It generally consists of the oxidation of perhalogenocarbon compounds (C\textsubscript{x}X\textsubscript{y}) into trihalo-alcohol (C\textsubscript{x}X\textsubscript{y-1}OH) in
a first step. Furthermore, it has been observed a slight continuous decrease of pH during the EAOPs treatments from an initial pH of 3.0 to a final pH of around 2.4 ± 0.2 after 8 h electrolysis with a standard deviation of 0.2 which is due to the kind of applied treatment. This is an evidence of the accumulation of protons formed through the mechanism proposed.

4. CONCLUSIONS

In summary, the treatment of CCl₄ in aqueous solution with EAOPs has been investigated for the first time. Upon successful degradation and mineralization of CCl₄ with the unique presence of •OH produced by anodic oxidation a new attack mode of •OH was proposed on perhalogenocarbon compounds by ipso-substitution of halogen atom with •OH. The decrease of pH during the electrolysis corroborated the proposed mechanism. The use of electro-Fenton process enhanced significantly the removal efficiency due to generation of supplementary •OH in the bulk solution.

This fourth oxidation pathway of •OH should be considered in other areas of research such as in atmospheric studies as some of these perhalogenocarbons are known to be volatile and can be subjected to •OH reactions.

Furthermore, this new finding opens up many opportunities in environmental protection by offering possibilities of degrading and mineralizing such recalcitrant perhalogenocarbons compounds that are used as solvents, refrigerant, aerosol propellant and representing an environmental issue, such as carbon tetrafluoride, hexafluoroethane, carbon tetrachloride, hexachloroethane, perfluorohexane, and so on, but also cyclic perfluoroalkanes like perfluorooctane, perfluoro-1,3-dimethylcyclohexane and perfluorodecalin. More recently fluorosurfactants such as perfluorooctanesulfonic acid, perfluorononanoic acid and perfluoroctanoic acid have been found into the environment and especially into water.
bodies. They are employed by some textile companies in emulsion polymerization process to produce fluoropolymers but they have caught recently the attention of regulatory agencies has they are persistent in the environment, toxic and bioaccumulate in the food chain.

In short, this study highlights that perhalogenocarbons compounds should be considered to be eliminated by 'OH generated in EAOPs.
REFERENCES


G.P. Anipsitakis, M.A. Gonzalez, Cobalt-Mediated Activation of Peroxymonosulfate


FIGURE CAPTIONS

Fig. 1. Reactor set-up for H₂O₂ oxidation and electrolysis experiments.

Fig. 2. Evaluation of CCl₄ electroactivity and reactivity with H₂O₂. (A), cyclic voltamograms in absence or presence of CCl₄ with Pt working electrode (Pt counter electrode); (B), cyclic voltamograms in absence or presence of CCl₄ with glassy carbon working electrode (Pt counter electrode), (C), oxidative treatment of CCl₄ with hydrogen peroxide.

Fig. 3. Hydrogen peroxide concentration evolution during spiking experiment.

Fig. 4. Degradation of CCl₄ by AO and EF treatments using different cathodes and anodes. (A), chloride concentration ([Cl⁻]) evolution normalized by the maximal theoretical Cl⁻ concentration ([Cl⁻]_{max,th}) and (B), determination of the apparent rate constants for CCl₄ decay assuming a pseudo-first order kinetic model (SI, Eq. 15). EF, electro-Fenton; AO, anodic oxidation; CF, carbon felt; SS, stainless steel; BDD, boron-doped diamond.

Fig. 5. Hydrogen peroxide accumulation using SS cathode and Pt anode. Conditions: I = 1000 mA, [Na₂SO₄] = 50 mM, V = 200 mL, pH 3.

Fig. 6. Chromatograms of anions evolution during EF treatments of CCl₄ with BDD anode (EF-CF-BDD) at different treatment time (0 min, 20 min, 40 min, 60 min, 120 min, 240 min). (A), ionic chromatograms. (B), Cl⁻ peaks evolution. (C), SO₄²⁻ peaks evolution. Conditions: I = 1000 mA, [Na₂SO₄] = 50 mM, [Fe²⁺] = 0.05 mM, V = 200 mL, pH 3.

Fig. 7. Hydrogen peroxide accumulation using CF cathode and Pt anode. Conditions: I = 1000 mA, [Na₂SO₄] = 50 mM, V = 200 mL, pH 3.
Fig. 8. Chromatograms of anions evolution during electro-Fenton treatments of CCl₄ with Pt anode (EF-CF/Pt) at different treatment time (0 min, 5 min, 10 min, 20 min, 40 min, 60 min, 120 min, 180 min, 240 min). (A), ionic chromatograms. (B), Cl⁻ peaks evolution. (C), SO₄²⁻ peaks evolution. Conditions: I = 1000 mA, [Na₂SO₄] = 50 mM, [Fe²⁺] = 0.05 mM, V = 200 mL, pH 3.

Fig. 9. Mineralization of CCl₄ by anodic oxidation and electro-Fenton treatments using different cathodes and anodes. (A), normalized TOC evolution by the initial TOC. (B), determination of the TOC decay rate constants assuming a pseudo-first order kinetic model. EF, electro-Fenton; AO, anodic oxidation; CF, carbon felt; SS, stainless steel; BDD, boron-doped diamond.

Fig. 10. Pathways of organic compounds oxidation by •OH. (A), CCl₄ oxidation by ipso-substitution with •OH. (B), schematic description of the four attack modes of •OH with organic compounds. RH, alkane; ArH, aromatic; CₓXᵧ, perhalogenocarbon compounds.
Fig. 1
Fig. 2
Fig. 3
Fig. 4
Fig. 5
Fig. 6
Fig. 7
Fig. 8
Fig. 9
Fig. 10