In situ UV-visible spectrum acquisition of Br$_3^-$ \textit{ Investigations of concentrated HBr aqueous solutions under 13-keV X-rays

D Saffrè$^1$, E Atinault$^{1,2}$, S Pin$^1$, JP Renault$^1$, JL Hazemann$^3$ and G Baldacchino$^1$

$^1$CEA Saclay, IRAMIS, UMR3299 CEA/CNRS SIS2M, Laboratoire de Radiolyse, 91191 Gif-sur-Yvette Cedex, France - $^2$CEA Saclay, IRAMIS, SPAM, Physique des Hautes Intensités, 91191 Gif-sur-Yvette Cedex, France - $^3$Institut Néel, Dept MCMF, 38042 Grenoble, France.

E-mail: gerard.baldacchino@cea.fr

Abstract. Water radiolysis has been investigated by \textit{in situ} and direct detection by using the scavenging method and 13-keV X-rays from ESRF synchrotron. By using a famous chemical system, concentrated hydrobromic acidic solutions over a range of concentrations (from 0.1 to 0.6 mole\textperthousand dm$^{-3}$), and real time absorption spectroscopy of Br$_3^-$ around 266 nm, we aimed at evaluating the effect of 13-keV X-rays, below the ionization K-edge of Br, on the Br\textsuperscript{-} oxidation yield value. The HO• scavenging time ranging in the picosecond scale is also taken into consideration going to the earliest initial yields. We have also observed the limit of use of N\textsubscript{2}O and air as saturation gas. The oxidation limitation also comes from the presence of H\textsubscript{3}O\textsuperscript{+} in abundance giving birth of competitive reactions. The determination of the dose rate delivered to the solution has been performed by using the Fricke dosimeter system by following absorbance at 304 nm. The dose rate was 18.5 Gy\textperthousand s$^{-1}$.

1. Introduction

Energetic X-rays are usually employed in many domains of science, industry and health care and investigation. Over a few 10 eV of energy, X-rays are ionizing particles with a Linear Energy Transfer (LET) similar to $\gamma$-rays (0.3 eV\textperthousand nm$^{-1}$) [1]. The radiation chemistry in water generated by these rays are known and detailed in the literature [1,2]. In some cases such as dynamic structure of molecule under short time excitation [3], the effect of X-rays must not be neglected because the radicals produced have their own chemistry. In this way it becomes crucial to rationally study the effect of X-rays on the production of the most known oxidizing radical, namely the hydroxyl radical, HO•. This species is largely involved in the oxidation of biological material like DNA, protein, membranes, etc and appears as the main species to investigate [4]. On the other hand, new system for the dosimetry is constantly required and a possibility recently investigated is the chemical system where hydrobromic acid (HBr) is involved at high concentration [5]. Bromine solutions have also been recently used to study the production of H\textsubscript{2} in water radiolysis [6]. Nevertheless this chemical system has never been studied under X-rays. Moreover Br\textsuperscript{-} is known for a long time as a good scavenger of hydroxyl radical[7] and its transient spectra and mechanism are known [7-11].

As an introduction to the radiolyis of HBr chemical system, we present in the table 1 the main reactions involved in the oxidation mechanism of Br\textsuperscript{-} by HO• in acidic conditions. In this article, the presented preliminary results concern a new study of HBr in high concentration conditions allowing the formation of the stable species Br$_3^-$ and by using various gas saturations. The aim is first to determine the oxidation yield of Br\textsuperscript{-} by HO• with X-rays having an energy of 13 keV, below the Br
ionization threshold [3,12]. In these conditions we have performed an optical setup as convenient as possible to detect the stable species formed: Br\(^{-}\). It is then expected to obtain real-time and in situ spectra under X-rays irradiation. We also aim at introducing high-temperature experiments with HBr. Indeed, it is known that salts are precipitating more efficiently at temperatures above 300°C. It is also obvious that the use of HBr solutions permit to avoid the cation effect (Na\(^{+}\), K\(^{+}\), Ga\(^{3+}\)) that can be seen in X-rays spectroscopies [13].

Table 1: Main reactions of the oxidation mechanism of bromide ions in acidic solutions

| N° | Reactions                  | Rate constants\(^{[5]}\) |
|----|---------------------------|--------------------------|
| 1  | Br\(^{-}\) + HO\(^{-}\) ↦ BrOH\(^{-}\)          | \(k_1 = 1.1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\) |
| 2  | BrOH\(^{-}\) + H\(_3\)O\(^{+}\) ↦ Br\(^{-}\) + 2H\(_2\)O | \(k_2 = 4.4 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\) |
| 3  | Br\(^{-}\) + Br\(^{-}\) ↦ Br\(_2\)\(^{-}\)          | \(k_3 = 1.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\) |
| 4  | Br\(_2\)\(^{-}\) + Br\(_2\)\(^{-}\) ↦ Br\(_3\)\(^{-}\) + Br\(^{-}\) | \(k_4 = 1.9 \times 10^{9} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\) |
| 5  | Br\(_2\) + Br\(^{-}\) ⇔ Br\(_3\)\(^{-}\)          | \(K = 16.1 \text{ dm}^3 \text{ mol}^{-1}\) |

X-rays absorption spectroscopies at high temperature are also considered in a furtherer global study. That is the reason why a reference study of the oxidation yield of bromide ions under X-ray irradiation at room temperature is necessary.

2. Methods

2.1 Setup

The solutions were stable at room temperature under room light. All solutions were irradiated at room temperature (21 - 23°C) with X-rays from the synchrotron source of the European Synchrotron Radiation Facility (ESRF) at Grenoble (France). The ESRF synchrotron is an intense source with a large spectrum of photon emission. Inside the synchrotron ring, the beam mode chosen was 4 bunches. The time between 2 bunches is roughly 700 ns. The study presented here has been carried out with a synchrotron ring loaded with 4 bunches of electrons. The energy of the electron beamline is 6 GeV. A large range of photons energy is obtained when the 6 GeV-accelerated electrons go through a binding magnet in the beamline BM31 [14]. A monochromator selected an energy of 13 keV with a great accuracy. At this energy, the LET is 0.3 eV nm\(^{-1}\). The beam size is 200 × 300 \(\mu\)m\(^{2}\).

Figure 1. Commercial optical flow cell (Hellma ref. 176.000-QS) used in the irradiation setup with 13-keV X-rays. This cell is made of fused silica and the penetration of 13-keV photon was possible only by reducing the thickness of the window to 1 mm perpendicularly to the analysis optical axis. In the picture the machined window is located on the left side in the middle of the dark part. The size of the X-ray beam determined the optical path length to 300 \(\mu\)m.

A 13-keV X-ray beam crosses an optical flow cell (figure 1). Steady-state irradiations have been carried out by analyzing the temporal evolution of the absorption spectrum during short-time irradiations (a few tens of seconds at maximum).
The absorption spectra were recorded with a fiber-coupled CCD detector (Avantes, AVS-SD 2000 with Avasoft 5.1 software) operating without any synchronization but with the following parameters: 90 ms of integration time and 10 averaged scans. The spectra were periodically saved with 1 second between each spectrum. A reference spectrum before irradiation and a spectrum without light were performed in order to obtain directly the real time absorption spectrum. The light from a deuterium lamp (Avantes dual light source) is used to record the spectra in the UV domain (240 – 400 nm). This kind of setup has not really been developed by the radiation chemistry laboratories in the past (except some attempts such as the transient spectrum direct acquisition [15]). The advance in easy to use convenient CCD matrix, in sensitivities in the UV-range allows now to perform this detection without trouble and adjustment.

2.2 Chemicals
The aqueous solutions were prepared using ultra pure water from a Millipore system. The chemicals were received without further purification: HBr (purity of 62%) from Sigma-Aldrich. The pH of the HBr aqueous solutions was measured by using an Orion 9107WMMD electrode. The pH was acidic (pH = 0.4 - 1.0). The uncertainty on the measurement of the pH value was 0.1 unit of pH. The solutions were saturated with nitrous oxide (N2O, purity > 99.98%) from Messer, by bubbling 30 minutes before irradiation.

2.3 Dosimetry
The dose rate used in the experiments was precisely determined by means of the Fricke method [16]. The chemical system is well described in the literature [1, 16]. The Fricke dosimeter ([Fe^{2+}] = 10^{-3} M, [H2SO4] = 0.4 M and [NaCl] = 10^{-3} M) solution was prepared with Fe(NH4)2(SO4)2(H2O)6 from Merck, H2SO4 (purity > 99.999%) from Sigma-Aldrich and NaCl (purity > 99.8 %) from Labosi. Figure 2 shows the spectrum of the oxidized Fricke solution (Fe^{3+} spectrum) after 20 s of exposure.

![Absorption spectrum of the Fricke solution (1 mM of Fe^{2+}) after 20 s of 13-keV X-rays exposure. \( \varepsilon_{304\text{nm}}(\text{Fe}^{3+}) = 2160 \text{ M}^{-1}\text{cm}^{-1} \). In this condition the dose at 20 s was 370 Gy falling in the known linearity domain of the Fricke dosimeter. At this stage dose rate was about 18.5 Gy\( \cdot \text{s}^{-1} \).](image)

The evolution of the absorbance at 304 nm is linear during at least 30 s as it can be noticed in the figure 3. The slope is determined with a good accuracy. Many Fricke dosimeter yields exist in the literature, especially for this range of X-ray energy [17, 18]. The recommended value for 13-keV X-rays can be deduced from the article of J. Law *et al.*: 13.4 ions/100 eV (13.9 × 10^{-7} moleJ^{-1}). The doses have been determined by using this value.

The challenge of knowing the dose rate with accuracy is linked to the knowledge of the intensity of the electrons which are in the storage ring. There is a tight correlation between the value of the dose rate and the intensity of the electrons which are accelerated in the ring.
Figure 3. Absorbance evolution at 304 nm of a Fricke solution (1 mM of Fe\(^{2+}\)) during 13-keV X-rays irradiation. The slope of the linear adjustment corresponds to the dose rate. In these conditions the dose rate was 18.5 Gy·s\(^{-1}\).

The dose rate is calculated thanks to the slope of the linear domain of the Fricke dosimeter. This domain is limited to the primary phenomena. Thus, the dose rate is sensitive to the stability of the X-ray beam as soon as the exposure has begun. But during short-time irradiations (30 seconds), the monitored intensity of the X-ray beam gave relative variations which were inferior to the absorbance measurement accuracy. Therefore the dose rate can be determined and its value is 18.5 Gy·s\(^{-1}\).

3. Results and discussion
Several types of HBr aqueous solutions were irradiated with X-rays at similar dose rates. Solutions were aerated or saturated with N\(_2\)O gas. The concentrations of HBr were 0.1, 0.3 and 0.6 M. Results of a N\(_2\)O-saturated solution of HBr 0.1 M are presented in figure 4.

Figure 4. Absorption spectrum of a hydrobromic acid solution (0.1 M) after 10 s of 13-keV X-rays exposure. The solution was bubbled with N\(_2\)O and was not flushed into the cell during the irradiation.

Under X-rays exposure of a few seconds, an intense absorption band around 266 nm appeared. This absorption band corresponds to the formation of the stable tribromine ion, which is known to have a great molar extinction coefficient at this wavelength (\(\varepsilon_{266nm}(\text{Br}_3^-) = 40900 \pm 400 \text{ M}^{-1}\cdot\text{cm}^{-1}\)). This intensity of the band at 266 nm is increasing with the irradiation time.
Considering the equilibrium between Br$_2$ and Br$_3^-$ (reaction 5 in table 1), both species Br$_2$ and Br$_3^-$ are present in solution. The proportions of each species with the initial concentration of bromide ions are gathered in table 2.

**Table 2:** Proportions of the oxidized forms of Br$^-$ at three different pH values

| HBr concentration (M) | pH | [Br$^-$] (M) | %Br$_3^-$ | %Br$_2$ |
|-----------------------|----|--------------|----------|---------|
| 0.1                   | 1.0| 0.1          | 61.7     | 38.3    |
| 0.3                   | 0.7| 0.2          | 76.3     | 23.7    |
| 0.6                   | 0.4| 0.4          | 86.6     | 13.4    |

Knowing that the molar extinction coefficient of Br$_2$ (47 M$^{-1}$ cm$^{-1}$ at 266 nm [19]) is very low at this range of wavelength, we can conclude that the absorption which is visible at 266 nm, is mainly due to Br$_3^-$. The spectrum corresponds to the Br$_3^-$ species which is stable enough and is accumulated in the cell. The optical pathlength was 300 μm.

The initial slope of the Br$_3^-$ formation shown in figure 5 gives a value of the yield G(Br$_3^-$) equal to $(0.9 \pm 0.1) \times 10^{-7}$ mol·J$^{-1}$.

At this low pH (pH = 1.0), there is a tight competition between two fast reactions [20] which occur at different time scales:

\[
e^{-}_{aq} + N_2O \rightarrow N_2 + O^- \quad k_6 = 9.1 \times 10^9 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1} \quad (6)
\]

\[
e^{-}_{aq} + H_3O^+ \rightarrow H^+ + 2 H_2O \quad k_7 = 2.3 \times 10^{10} \text{ dm}^3\text{mol}^{-1}\text{s}^{-1} \quad (7)
\]

The scavenging time of the reaction 6, if we consider the concentration of N$_2$O in our solution equal to CN$_{2O} = 2.5 \times 10^{-2}$ M at atmospheric pressure is $t_6 = 1/k_6C_{N2O} = 1/(9.1 \times 10^9 \times 2.5 \times 10^{-2}) = 4.4$ ns.

For a 0.1 M HBr solution, the scavenging time of the reaction 7 is $t_7 = 1/k_7C_{H3O+} = 1/(2.3 \times 10^{10} \times 0.1)$ = 0.4 ns.

Considering the scavenging times of the reactions 6 and 7, roughly 10% of the produced hydrated electrons are converted into HO$. The largest part is converted into H$. Nevertheless, H$ produced by reaction 7 also contributes to the formation of HO$ according to reaction 8:

\[
H^+ + N_2O \rightarrow N_2 + HO^- \quad k_8 = 7 \times 10^6 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1} \quad [20] \quad (8)
\]

This contribution plays an important role in the increase of the formation yield of the tribromine ion in the case of N$_2$O-saturated solutions of 0.1M HBr.

According to reaction 1 in table 1, in the presence of 0.1 M HBr, the HO$ scavenging time is 0.9 ns. Thus, the HO$ scavenging by bromide ions is favored over the recombination reaction:

\[
HO^+ + HO^- \rightarrow H_2O_2 \quad k_9 = 4.2 \times 10^9 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1} \quad [20] \quad (9)
\]

Both reactions 2 and 3 happening quickly, BrOH$\textsuperscript{-}$ mainly reacts first with H$_3$O$^+$, which is abundant in the solution, to lead to the species Br$. This species reacts quickly with a bromide ion to give Br$_2$$^\text{+}$. The disproportionation reaction of Br$_2$$^\text{+}$ leads to the formation of the tribromine ion (reaction 4). However,
this last reaction is in competition with another fast one which corresponds to the destruction of the precursor species \( \text{Br}_2^- \) by hydrogen atoms (reaction 10) produced by the water radiolysis and mainly thanks to the reaction 7:

\[
\text{Br}_2^- + \text{H}^+ \rightarrow 2 \text{Br}^- + \text{H}^+ \quad k_{10} = 1.4 \times 10^{10} \text{dm}^3\text{mol}^{-1}\text{s}^{-1}
\]  

(10)

The formed tribromine ion is also consumed by H• following a fast reaction:

\[
\text{Br}_3^- + \text{H}^+ \rightarrow \text{Br}_2^- + \text{Br}^- + \text{H}^+ \quad k_{11} = 1.2 \times 10^{10} \text{dm}^3\text{mol}^{-1}\text{s}^{-1}
\]  

(11)

These reactions 10 and 11 are a reason to explain why the formation yield of \( \text{Br}_3^- \) is slightly reduced after an exposure time superior to 10 seconds.

Figure 5. Absorbance at 266 nm of a hydrobromic acid solution (0.1 M) under 13-keV X-rays. The solution was aerated or bubbled with N\(_2\)O and was not flushed into the cell during the irradiation.

On the figure 5, we observe that there is an increase of the absorbance at 266 nm with the exposure time for both considered gas saturations. We notice that the variation is no more linear, the formation yield of \( \text{Br}_3^- \) decreasing with the exposure time.

Under N\(_2\)O, the increase of the absorbance due to \( \text{Br}_3^- \) is slightly more important than for the aerated solution. It seems that the impact of H• on the destruction of \( \text{Br}_2^- \) and \( \text{Br}_3^- \) is limited in the case of N\(_2\)O. As previously seen, for N\(_2\)O-saturated solutions, a small part of the hydrated electrons are converted into HO• (reaction 8). These hydroxyl radicals participate to the oxidation mechanism by scavenging bromide ions and then contribute to increase the formation yield of \( \text{Br}_3^- \).

In an aerated medium and at this pH value (pH = 1.0), the formation yield of \( \text{Br}_3^- \) is found to be lower than the yield determined for the N\(_2\)O-saturated solution. The hydrated electrons are totally converted into H•. The generated hydrogen atoms react with O\(_2\) present in the solution (2.5 \( \times \) 10\(^{-4}\) M at atmospheric pressure):

\[
\text{H}^+ + \text{O}_2 \rightarrow \text{HO}_2^\cdot \quad k_{12} = 1.3 \times 10^{10} \text{dm}^3\text{mol}^{-1}\text{s}^{-1}
\]  

(12)

This production of HO\(_2^\cdot\) leads to a decrease of the \( \text{Br}_3^- \) formation yield because HO\(_2^\cdot\) reduces all Br\(^-\) oxidized forms. The rate constant of these reactions is quite important (1.0 \( \times \) 10\(^8\) dm\(^3\)mol\(^{-1}\)s\(^{-1}\)).

Table 3 gathers values of the \( \text{Br}_3^- \) formation yield for different HBr concentrations of aerated and N\(_2\)O-saturated solutions. In the first column, the yield values have been obtained thanks to the slopes of the figure 5. In order to observe the influence of the initial concentration of bromide ions, we have worked at higher concentrations: 0.2 M and 0.4 M. A few experimental and simulation values of the HO\(^-\) yield can be found in the literature [3, 21].
In this study, a relation between \( G(\text{Br}_3^-) \) and \( G(\text{HO}^\cdot) \) cannot be anticipated because the scavenging time is short and several reactions of formation and destruction can occur in a complex mechanism. The best way could be simulation calculations including short-time and long-time scale.

| Table 3: Effect of the HBr initial concentration on the Br\(_3^-\) formation yield under 13-keV X-rays |
|-----------------------------------------------|
| HBr concentration (mole dm\(^{-3}\)) | 0.1 | 0.3 | 0.6 |
| Scavenging time of Br\(^{-}\) (ns) | 0.9 | 0.5 | 0.2 |
| \( G(\text{Br}_3^-) \) for aerated solutions (10\(^{-7}\) mol J\(^{-1}\)) | 0.6 ± 0.1 | 1.6 ± 0.2 | 2.6 ± 0.3 |
| \( G(\text{Br}_3^-) \) for N\(_2\)O-saturated solutions (10\(^{-7}\) mol J\(^{-1}\)) | 0.9 ± 0.1 | 1.0 ± 0.2 | 2.1 ± 0.3 |
| Absorbance due to Br\(_3^-\) after 30 seconds of exposure for aerated solutions | 0.03 | 0.08 | 0.105 |
| Absorbance due to Br\(_3^-\) after 30 seconds of exposure for N\(_2\)O-saturated solutions | 0.045 | 0.055 | 0.075 |

First, in the case of Br\(^{-}\) aerated solutions, the formation yield of the tribromine ion increases constantly with the Br\(^{-}\) concentration to reach \((2.6 ± 0.3) \times 10^{-7} \text{ mol J}^{-1}\) which corresponds to the expected effect widely described in the literature [3,19]. The formation of Br\(_3^-\) is also favored at high concentrations in bromide ions if we consider the equilibrium between Br\(_3^-\) and Br\(_2^-\) (reaction 5). An increase of the initial Br\(^{-}\) concentration leads to an increase of the ratio between Br\(_3^-\) and Br\(_2^-\) (table 2). Thus, the absorbance at 266 nm due to Br\(_3^-\) is higher. In presence of N\(_2\)O, the effect is similar and the Br\(_3^-\) formation yield reaches \((2.1 ± 0.3) \times 10^{-7} \text{ mol J}^{-1}\). Whereas \( G(\text{Br}_3^-) \) for N\(_2\)O-saturated 0.1 M HBr solutions is higher than \( G(\text{Br}_3^-) \) for aerated 0.1 M HBr solutions (first column in table 3), we notice that in case of 0.6 M HBr, the Br\(_3^-\) formation yield found under N\(_2\)O is slightly inferior to the value found for the aerated system (third column in table 3).

The concentration of H\(_3\)O\(^+\) increases with the concentration of bromide ions, so the hydrated electrons are scavenged much rapidly by H\(_3\)O\(^+\) to lead to H-atoms. For example, the scavenging time of e\(_{aq}\) by H\(_3\)O\(^+\) (reaction 7) is 110 ps for 0.6 M HBr whereas it is 430 ps for 0.1 M HBr. It means that the proportion of hydrated electrons which are converted into HO\(^\cdot\) radicals by N\(_2\)O (reaction 6) is only 3%. In other terms, the effect of N\(_2\)O in the medium becomes negligible.

In order to describe the pH effect on the oxidation mechanism of bromide ions and to understand why the Br\(_3^-\) formation is not linear with the 13-keV X-rays exposure time, it is crucial to highlight the main reactions involved in both gas saturation conditions: N\(_2\)O-saturated and aerated aqueous solutions. In the case of a N\(_2\)O-saturated 0.6 M HBr solution ([Br\(^{-}\)] = 0.4 M, pH = 0.4), we have to consider the reactions in which H\(^+\) are involved because these radicals are present in a large amount in our acidic conditions. As previously seen, H\(^+\) can react with N\(_2\)O (reaction 8), with Br\(_3^-\) (reaction 11) and also with Br\(^{-}\) (reaction 13):

\[
H^+ + Br^- \rightarrow HBr^\cdot \\
k_{13} = 1.7 \times 10^6 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}
\]
At 0.4 M of Br\textsuperscript{-}, 97% of the hydrated electrons are converted into H\textsuperscript{•}. The scavenging time of the reaction 13 is the shortest one (t\textsubscript{13} = 1.8 \mu s). The reaction 11, which consumes Br\textsubscript{3}\textsuperscript{-}, is in competition with reaction 13 as soon as the Br\textsubscript{3}\textsuperscript{-} concentration reaches a concentration of \(5 \times 10^{-5}\) mol dm\textsuperscript{-3}. It corresponds to an absorbance of 0.06. According to table 3, the absorbance of the N\textsubscript{2}O-saturated 0.6 M HBr solution at the end of the exposure was 0.075. This value reveals that the reactions 11 and 13 are in a tight competition after about 10 seconds of irradiation.

In the case of an aerated 0.6 M HBr solution, the reactions 11 and 13 are also highlighted as in the case of a N\textsubscript{2}O-saturated solution. In addition, we have to take into account the reaction between H\textsuperscript{•} and O\textsubscript{2}, which is present in the atmosphere (reaction 12). The scavenging time of this reaction 12 is the shortest one (t\textsubscript{12} = 0.3 \mu s). The competition between the reactions 12 and 13 happens then when the concentration of the formed tribromine ion reaches \(3.0 \times 10^{-4}\) mol dm\textsuperscript{-3}, which corresponds to an absorbance of 0.3. According to table 3, the absorbance of the aerated 0.6 M HBr solution at the end of the irradiation was 0.105. This low value shows that the competition does not play an important role within the 30 seconds of exposure. The competition should be more significant after 60 seconds of irradiation. However, the decrease of the Br\textsubscript{3}\textsuperscript{-} formation yield is visible. It could be partially due to HO\textsubscript{2}\textsuperscript{•}. Indeed, this radical is produced by the reaction 12 and reacts quickly with Br\textsubscript{2}\textsuperscript{-} and Br\textsubscript{3}\textsuperscript{-} with similar rate constants, \(1.0 \times 10^{8}\) dm\textsuperscript{3} mol\textsuperscript{-1} s\textsuperscript{-1}.

In both cases, we observe that the diminution of the oxidation yield is limited. Despite the destruction of Br\textsubscript{2}\textsuperscript{-} by H\textsuperscript{•}, we notice, on the one hand, there is a non negligible production of oxidizing species (HO\textsuperscript{•}, HBr\textsuperscript{-}) which contributes to raise this yield in the case of N\textsubscript{2}O-saturated HBr solutions. On the other hand, there is the presence of the molecular oxygen which scavenges a part of H\textsuperscript{•} and limits their impact in the case of aerated HBr solutions.

4. Conclusion
Those preliminary results obtained on the ESRF synchrotron are a great opportunity to understand better the oxidation mechanism of bromide ions under X-rays irradiation. The analysis of the in situ formation of the tribromine ion could give information about the radiolytic yield of HO\textsuperscript{•}.

Unfortunately, HO\textsuperscript{•} radical yield is not easily accessible from the Br\textsubscript{3}\textsuperscript{-} formation resulting from the scavenging of HO\textsuperscript{•} by Br\textsuperscript{-}. As the complexity of the chemical system does not allow us to determine the HO\textsuperscript{•} yield, it should be interesting to carry out simulation in a large time scale (from ps to \mu s) in order to take into account the scavenging processes in the spurs and the homogeneous chemistry for the reactions of secondary products (Br\textsubscript{2}\textsuperscript{-}, Br\textsuperscript{•}…). Actually, the use of HBr system, initially motivated by the absence of the counter-ion unlike in the use of salts NaBr or KBr, implies a strong effect of the pH. This paper was thus an opportunity to detail the chemical mechanism of Br\textsuperscript{-} action in presence of H\textsubscript{2}O\textsuperscript{•}.

The concentrations of hydrobromic acid were 0.1, 0.3 and 0.6 M, corresponding to three scavenging times. The effect of two saturation gas was also used: aerated and N\textsubscript{2}O saturation. The presence of N\textsubscript{2}O in the aqueous bromide solutions has shown an increase in the value radiolytic yield of Br\textsubscript{3}\textsuperscript{-} comparing to the yield determined for the aerated solution but only for the lowest concentration of HBr, 0.1 M. This increase is due to the part of the hydrated electrons which is converted into HO\textsuperscript{•} and thus, which contributes to the oxidation of the bromide ions.

At higher concentrations of HBr (0.3 and 0.6 M), as expected, the oxidation yield of Br\textsuperscript{-} aims at increasing. It was explained by two main reasons. First, by increasing the concentration of Br\textsuperscript{-}, the HO\textsuperscript{•} scavenging power is enhanced. So, the oxidation yield of Br\textsuperscript{-} is raised following the higher and higher HO\textsuperscript{•} yield. Then, considering the equilibrium which is present in the oxidation mechanism, by raising the initial concentration of Br\textsuperscript{-}, the ratio between Br\textsubscript{3}\textsuperscript{-} and Br\textsubscript{2}\textsuperscript{-} is greater and the absorbance at 266 nm due to Br\textsubscript{3}\textsuperscript{-} is higher. Nevertheless, the presence of N\textsubscript{2}O, unlike O\textsubscript{2} in aerated solutions, complicates the system. N\textsubscript{2}O should normally aims at increasing the tribromine ion yield but the competition between reactions existing in the case of the presence of O\textsubscript{2}, does not exist at all in N\textsubscript{2}O saturation. H-atoms which are involved in the mechanism are then available to react with Br\textsubscript{2}\textsuperscript{-} and influence the decrease way of the observed yield of Br\textsubscript{3}\textsuperscript{-}. Therefore the initial pH value plays an important role in
the understanding of the mechanism too. At acidic pH, hydrated electrons are rapidly converted into H⁺. This study has then exhausted a system of several reactions in competition involving H⁺ which is less pronounced in the case of neutral NaBr and KBr solutions.

This work has been carried out with a 13-keV X-rays beam which corresponds to energy below the Br atom ionization threshold. It could be interesting to work at higher X-rays energies in order to observe the effect of the direct ionization of Br atom on the oxidizing mechanism.

Finally this study stresses the importance of the liquid state radiolysis under X-rays. Several spectroscopic techniques using X-rays do not take into account the effect of this ionizing ray on the degradation of the samples. It clearly shows that the radiolysis is a phenomenon which cannot be neglected.

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