# Radiation chemical behavior of aqueous butanal oxime solutions irradiated with helium ion beams

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## HIGHLIGHTS

- The butanal oxime consumption yield has been determined by GC–MS in aqueous media.
- Enhancement of the hydrogen production is observed in the presence of butanal oxime.
- Diminution of the $H_2O_2$ production is observed in the presence of butanal oxime.
- Butanal oxime reaction with $H^{\bullet}/HO^{\bullet}$ by hydrogen abstraction mechanism is discussed.

## ARTICLE INFO

## ABSTRACT

Samples of butanal oxime in aqueous solution have been irradiated with the helion ($^4He^{2+}$) beam of the ARRONAX (Nantes) and the CEMHTI (Orléans) cyclotrons. The consumption yield of butanal oxime has been measured by gas-chromatography coupled with mass spectrometry. Yields of gaseous products (mainly $H_2$) have also been measured by micro-gas-chromatography. Butanal oxime can react with $H^{\bullet}$ radicals by abstraction mechanism to enhance $H_2$ production. Yields of liquid phase products (hydrogen peroxide and nitrite ion) have been measured by colorimetric methods. Butanal oxime acts as a scavenger of $OH^{\bullet}$ radical to inhibit the production of $H_2O_2$. The observation of the radiolytic products allows then to discuss a degradation mechanism of butanal oxime in aqueous solutions.

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## 1. Introduction

The process used in industry to separate uranium and plutonium for nuclear fuel reprocessing (Choppin et al., 2002) consists in a liquid–liquid extraction using an organic species, tributyl-phosphate (TBP), which shows a specific affinity with the valence states +IV of plutonium (Best et al., 1957) and +VI of uranium (Alcock et al., 1958) whereas trivalent plutonium (+III) is hardly extracted ($D < 0.3$) by TBP (Best et al., 1959). In order to stabilize Pu(+III) in the aqueous phase, hydrazinium nitrate, is added at different stages of the process to avoid nitrous acid accumulation in this medium (Biddle and Miles, 1968; Browne and Overman,
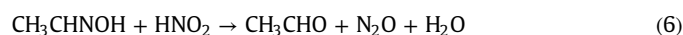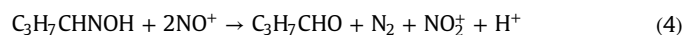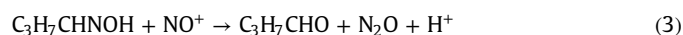
1916; Doherty et al., 1995; Koltunov and Marchenko, 1967; Perron et al., 1976; Perrott and Stedman, 1977). Nevertheless, with an aqueous-based anti-nitrous reactant such as hydrazine, a Pu(+III) re-oxidation can still occur in the organic phase (Sze et al., 1982). Then, it is difficult to keep $Pu^{+III}$ in solution under this oxidation state for a long time. Nitrous acid is indeed well extracted in the organic phase by TBP (Gourisse and Gautier, 1969).

Numerous substitutes to hydrazinium nitrate have then been reviewed to find a compound which quickly reacts with $HNO_2$ and which can be partly extracted by TBP (Marchenko et al., 2009). In this way, butanal oxime show interesting properties (Dinh et al., 2008). This species can react with nitrous acid (Kliegman and Barnes, 1972) under $NO^+$ form (Eqs. (1) and (2)) to form nitrous oxide ($N_2O$) (Eq. (3)), and nitrogen gas ($N_2$) (Eq. (4)). The $NO_{2+}$ formed can be eliminated by reaction with nitrous acid to
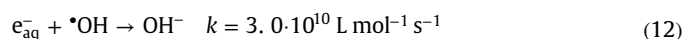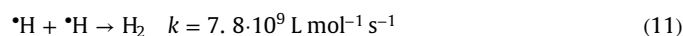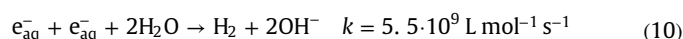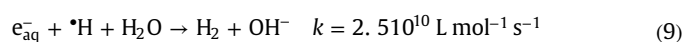
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give $N_2O_4$, a precursor of nitric and nitrous acids (Eq. (5)). The acetaldoxime–nitrous acid reaction has been studied previously (Koltunov et al., 2000a, 2000b). In the case of butyraldoxime the balance of the reaction is written on Eq. (6).

$$H^+ + HNO_2 \leftrightarrow H_2NO_2^+ \tag{1}$$

$$H_2NO_2^+ \leftrightarrow H_2O + NO^+ \tag{2}$$

$$C_3H_7CHNOH + NO^+ \rightarrow C_3H_7CHO + N_2O + H^+ \tag{3}$$

$$C_3H_7CHNOH + 2NO^+ \rightarrow C_3H_7CHO + N_2 + NO_2^+ + H^+ \tag{4}$$

$$NO_2^+ + HNO_2 \leftrightarrow N_2O_4 + H^+ \tag{5}$$

$$CH_3CHNOH + HNO_2 \rightarrow CH_3CHO + N_2O + H_2O \tag{6}$$

Butanal oxime has been thoroughly studied towards its reactivity with actinide ions (Koltunov et al., 2001a, 2001b, 2001c). In fact butanal oxime has proven that it can stabilize Pu($+$III) in extraction systems (Sze and Gosselin, 1983).

The presence of actinides in the medium induces radiolytic phenomena resulting from the alpha radioactivity of such radionuclides. First of all, water undergoes ionization/excitation phenomena, which further leads to the generation of free radicals and molecular species by a series of recombination reactions (Allen, 1961; Spinks and Woods, 1990) (Eq. (7)). Besides all the different reactions that can lead to the main stable products, molecular hydrogen and hydrogen peroxide, the most significant ones are displayed thereafter (Eqs. (8) and 12)) (Buxton et al., 1988; Le Caër, 2011).

$$H_2O \overset{\text{Ionizing radiation}}{\Longrightarrow} e_{aq}^-, \ ^\bullet OH, \ ^\bullet H, \ H_3O^+, \ H_2O_2, \ H_2 \tag{7}$$

$$^\bullet OH + {}^\bullet OH \rightarrow H_2O_2 \quad k = 5.5 \cdot 10^9 \ \text{L mol}^{-1} \text{s}^{-1} \tag{8}$$

$$e_{aq}^- + {}^\bullet H + H_2O \rightarrow H_2 + OH^- \quad k = 2.5 10^{10} \ \text{L mol}^{-1} \text{s}^{-1} \tag{9}$$

$$e_{aq}^- + e_{aq}^- + 2H_2O \rightarrow H_2 + 2OH^- \quad k = 5.5 \cdot 10^9 \ \text{L mol}^{-1} \text{s}^{-1} \tag{10}$$

$$^\bullet H + {}^\bullet H \rightarrow H_2 \quad k = 7.8 \cdot 10^9 \ \text{L mol}^{-1} \text{s}^{-1} \tag{11}$$

$$e_{aq}^- + {}^\bullet OH \rightarrow OH^- \quad k = 3.0 \cdot 10^{10} \ \text{L mol}^{-1} \text{s}^{-1} \tag{12}$$
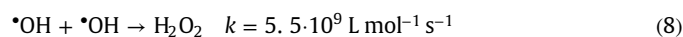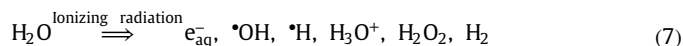
Organic solutes in aqueous solutions can react with the radicals produced by water radiolysis (Spinks and Woods, 1990). Even though there is no information available on the radiolysis of butanal oxime or any other oxime, some data can be found about the reactivity of these radicals towards compounds with chemical functions related to the oxime. Alcohols, for instance, are known to react rapidly with $^\bullet OH$ radical ($k = 9.7 \cdot 10^8$ L mol$^{-1}$ s$^{-1}$ for methanol) and $^\bullet H$ radicals ($k = 2.6 \cdot 10^6$ L mol$^{-1}$ s$^{-1}$ for methanol) (Alam et al., 2003; Asmus et al., 1973; Riesz and Burr, 1962).

The aim of this work is to investigate the radiolytic stability of aqueous solutions of butanal oxime under alpha irradiation. Helium ion beams are indeed used in this study to mimic the alpha radiolysis without using actinide ions in solution. The first part of this work is focused on the measurement of butanal oxime consumption yield in binary (water–butanal oxime) solutions. Then, the impact of the irradiation on the formation yields of some gaseous products ($H_2$, $N_2O$) and liquid phase products ($H_2O_2$) is discussed.

## 2. Experimental section

### 2.1. Irradiation equipment

The irradiation cell is the same as previously described (Garaix et al., 2015). The radiolysis cell contained 20 mL of a stirred solution under 21 mL air atmosphere. The cell is gas-tightened using a screwed joint.

The beams of helium ions ($^4He^{2+}$) provided by the CEMHTI (Orléans, France) and the ARRONAX (Nantes, France) cyclotron facilities, with an initial energy of respectively 28 and 68 MeV, have been used as an irradiation source. The simulation code SRIM2008 (Ziegler et al., 2010) demonstrated that the initial energy of particles in solution was actually $9.4 \pm 1.3$ MeV for the CEMHTI cyclotron and $60.7 \pm 0.3$ MeV for the ARRONAX cyclotron. The helium ions are totally stopped in the solutions and the values of the linear energy transfer (LET) are respectively $95 \pm 9$ and $23.3 \pm 0.3$ keV μm$^{-1}$. During all the experiments, the current value of $^4He^{2+}$ flux, monitored by an internal Faraday cup, is calibrated in order to maintain 70 nA in the radiolysis cell. For lower intensities, the helium ion beams used become less stable.

### 2.2. Dose rate and radiolytic yields determination

The dose rate absorbed by the irradiated solution is determined by Fricke dosimetry (Fricke and Hart, 1966). This method is based on the oxidation of $Fe^{2+}$ to $Fe^{3+}$ by the species produced by the water radiolysis reactions. The concentration of ferric ions is monitored by ex situ (CEMHTI) or in situ (ARRONAX) (Costa et al., 2012) UV-vis spectrophotometry ($\lambda = 304$ nm, $\varepsilon = 2197$ L mol$^{-1}$) with a CARY-60 (CEMHTI) or CARY-4000 (ARRONAX) spectrophotometer. The ex-situ measurements are performed a few minutes after the irradiation of the sample. The in-situ measurements are carried out during the irradiation via two 20 m long fiber optics and a probe (HELLMA, optical path 10 mm). The ferric ion radiolytic yields for the CEMHTI and the ARRONAX beam are respectively $G(Fe^{3+}) = 5.9$ mol J$^{-1}$ and 11.7 mol J$^{-1}$ (Costa et al., 2012).

In each case, the dosimeter solution is actually a Super-Fricke solution and is prepared by dissolving Mohr's salt ($[Fe^{3+}] = 10$ mmol L$^{-1}$) and NaCl (1 mmol L$^{-1}$) in aerated aqueous 0.4 mol L$^{-1}$ $H_2SO_4$ solutions. Sodium chloride is added to avoid any organic impurities. The dose rate received by the Fricke dosimeter is then calculated by (Eq. (13)).

$$\dot{D}_{\text{Fricke}} = \frac{1}{G(Fe^{3+}) \cdot \rho_{\text{Fricke}}} \cdot \frac{d[Fe^{3+}]}{dt} \tag{13}$$

$\dot{D}_{\text{Fricke}}$ (J kg$^{-1}$ min$^{-1}$) is the dose rate in the Fricke dosimeter, $G(Fe^{3+})$ (mol J$^{-1}$) is the radiolytic yield of ferric ions, $\rho_{\text{Fricke}}$ (kg L$^{-1}$) is the density of the Fricke solution, $[Fe^{3+}]$ (mol L$^{-1}$) is the ferric ion concentration and $t$ (min) is the irradiation time.

However, it appears more convenient to express the absorbed dose in J L$^{-1}$ (Eq. (14)) in order to measure the radiolytic yields $G(X)$ (mol J$^{-1}$), which represent the amount of species $X$ formed by unit of energy absorbed by the solution.

$$\dot{D} = \rho \cdot \dot{D}_{\text{Fricke}} \tag{14}$$

$\dot{D}$ (J L$^{-1}$) is the dose rate in the solution, $\rho$ (kg L$^{-1}$) is the density of the solution.

$G(X)$ is indeed obtained from the slope at the origin of the curve representing the variation of the concentration of $X$ (mol L$^{-1}$) in solution versus the deposited dose (J L$^{-1}$). The consumption yield $G(-X)$ of species $X$ is also obtained by plotting the quantity of species consumed (mol L$^{-1}$) versus the deposited dose (J L$^{-1}$) (Fig. 1). These curves are built by irradiating samples at several doses. For each irradiation dose, the solution is renewed.