Radiation chemical behavior of aqueous butanal oxime solutions under alpha irradiation

A. Costagliola, L. Venault, G. Garaix, G. Blain, Johan Vandenborre, N. Vigier, S. de Sio, M. Fattahi-Vanani

Radiation chemical behavior of aqueous butanal oxime solutions under alpha irradiation

A. COSTAGLIOLA[a,b*], L. VENAULT[a], G. GARAIX[a], G. BLAIN[b], J. VANDENBORRE[b], N. VIGIER[c], S. DE SIO[c], M. FATTAHI-VANANI[b]

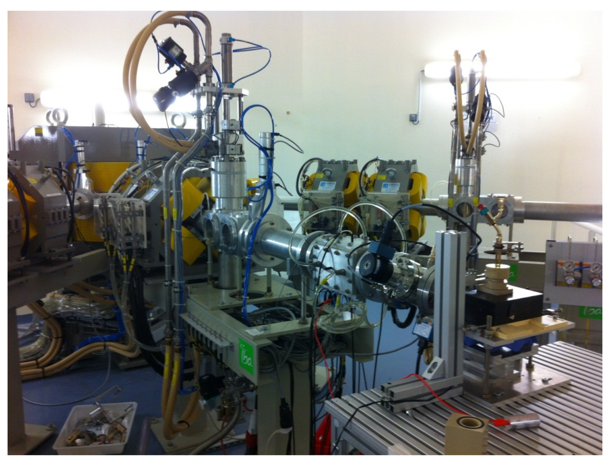
[a] CEA, DEN/DRCP/SERA/LCAR, F-30207 Bagnols-sur-Cèze, France
[b] SUBATECH – UMR 6457 – Ecole des mines de Nantes, 4 rue Alfred Kastler, BP 20722, 44307 Nantes Cedex 3, France
[c] AREVA NC, BUR/DIRP/RDP, 1 place Jean Millier, 92084 Paris La Défense, France
[*] A. COSTAGLIOLA Tel: +33 (0)4 66 39 79 63 E-mail: amaury.costagliola@cea.fr

Context

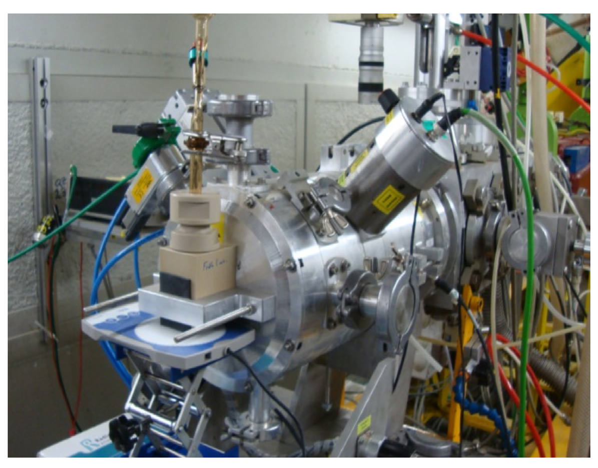
Hydrazinium nitrate is a compound used in industry to avoid nitrous acid accumulation during the liquid-liquid separation of uranium and plutonium (PUREX). Now, hydrazinium nitrate is a CMR (Carcinogenic, Mutagenic, or toxic to Reproduction) compound and its use has to be reduced according to the European REACH directive of 2007. Moreover, hydrazinium nitrate is not extracted in the organic phase. Then it induces an accumulation of nitrous acid in this medium due to its partition between the two phases. It leads to an over-consumption of the Pu reducer, U(IV), due to the reoxidation of plutonium (III) to plutonium (IV) by HNO_2 in the organic phase. Numerous substitutes to hydrazinium nitrate have then been considered to find a compound which quickly reacts with HNO_2 and which can be partly extracted by TBP. The aim of this study is actually to investigate the behavior of these potential substitutes under irradiation. As a result of previous investigations [1-2], butanal oxime has been selected as potential substitute to hydrazinium nitrate in the PUREX process.

Butanal oxime radiolytic degradation in water

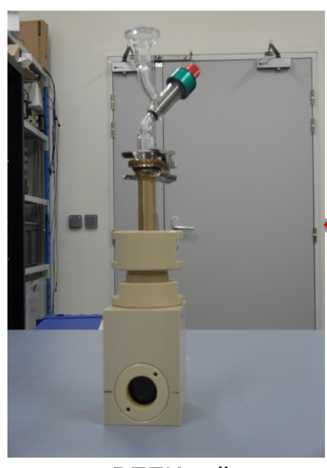
Irradiation of fresh butanal oxime solutions in water
➔ External irradiation: α cyclotron beam
➔ 1 Irradiation = 1 precise dose
➔ Dose monitored by Fricke dosimetry



AX line of the ARRONAX cyclotron (68 MeV)

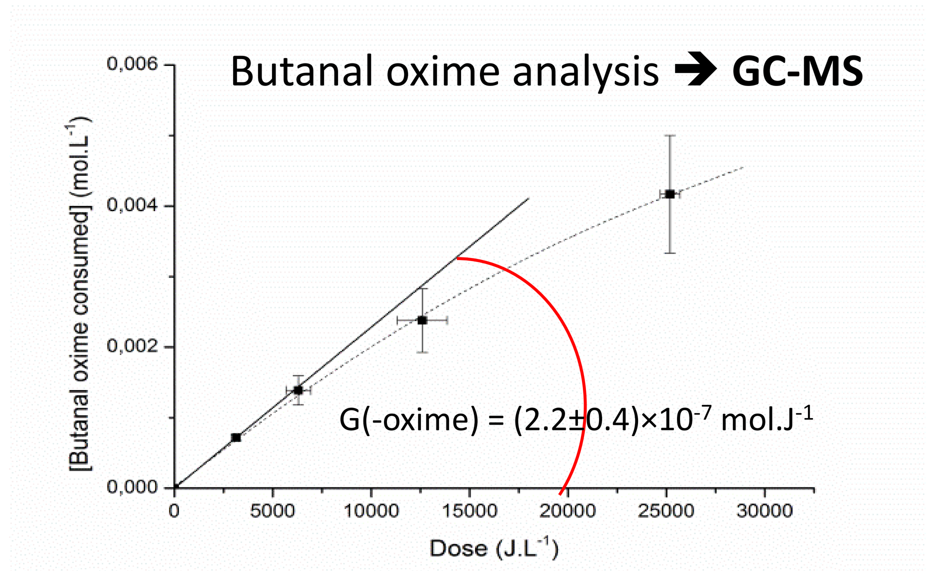


End of the CEMHTI line (28 MeV)



α PEEK cell containing the samples

Butanal oxime analysis ➔ **GC-MS**



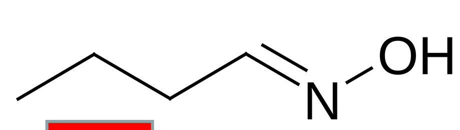
Measurement of the butanal oxime consumption yield by irradiation of aqueous solution of 10^{-2} mol.L^{-1} butanal oxime.

[Butanal oxime] (M)	Butanal oxime consumption yield (10^{-7} mol.J^{-1})	
	CEMHTI	ARRONAX
1.04×10^{-3}	2.6 ± 0.4	1.9 ± 0.2
1.04×10^{-2}	3.9 ± 0.5	2.2 ± 0.4
1.04×10^{-1}	18 ± 2	12 ± 2

Evolution of the butanal oxime consumption yield according to the butanal oxime concentration in aqueous solutions.

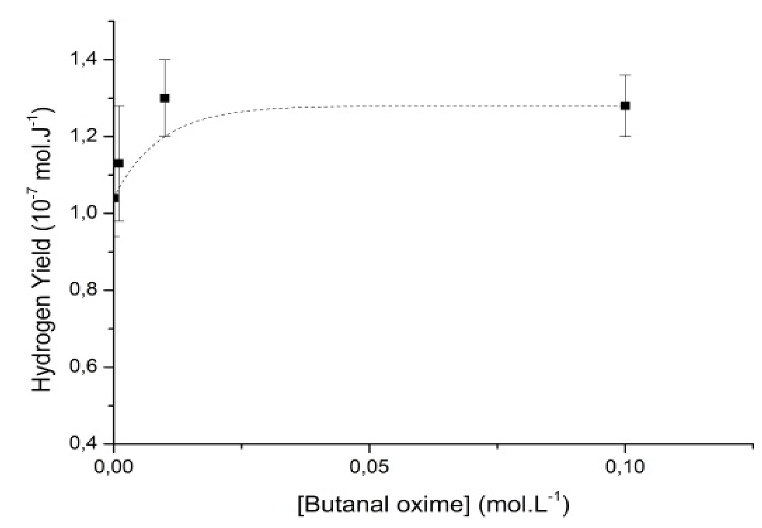
Radiolytic degradation mechanism

Butanal oxime



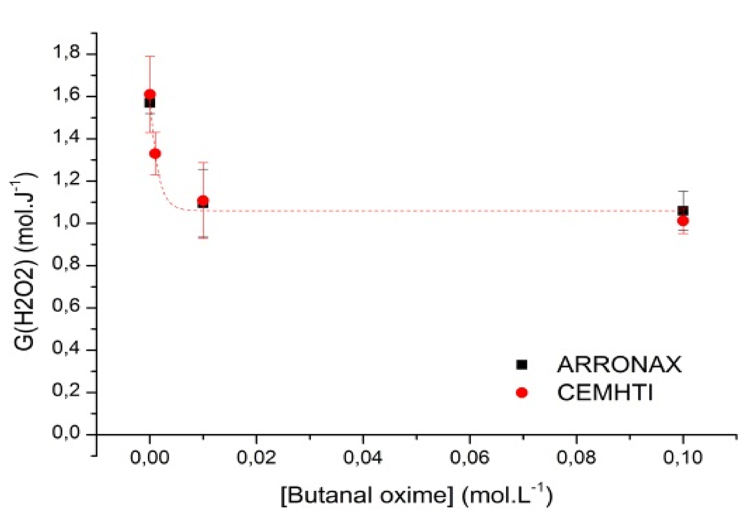
H_2 analysis by µGC
Butanal oxime enhances H_2 production
➔ **Hydrogen abstraction mechanism**

$$C_3H_7CH{=}NOH + {}^{\bullet}H \rightarrow \begin{cases} {}^{\bullet}CH_2-CH_2-CH_2-CH{=}NOH + H_2 \\ CH_3-{}^{\bullet}CH-CH_2-CH{=}NOH + H_2 \\ CH_3-CH_2-{}^{\bullet}CH-CH{=}NOH + H_2 \\ CH_3-CH_2-CH_2-{}^{\bullet}C{=}NOH + H_2 \\ CH_3-CH_2-CH_2-CH{=}NO^{\bullet} + H_2 \end{cases}$$



Influence of butanal oxime concentration on the hydrogen yield in aqueous butanal oxime solutions.

H_2O_2 analysis by Ti^{+IV} colorimetry



Influence of butanal oxime concentration on the Hydrogen peroxide yield in aqueous butanal oxime solutions.

Butanal oxime inhibits H_2O_2 production
➔ Scavenging of °OH
➔ **Hydrogen abstraction mechanism**

$$C_3H_7CH{=}NOH + {}^{\bullet}OH \rightarrow \begin{cases} {}^{\bullet}CH_2-CH_2-CH_2-CH{=}NOH + H_2O \\ CH_3-{}^{\bullet}CH-CH_2-CH{=}NOH + H_2O \\ CH_3-CH_2-{}^{\bullet}CH-CH{=}NOH + H_2O \\ CH_3-CH_2-CH_2-{}^{\bullet}C{=}NOH + H_2O \\ CH_3-CH_2-CH_2-CH{=}NO^{\bullet} + H_2O \end{cases}$$

➔ Reaction blocked by this mechanism:

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2$$

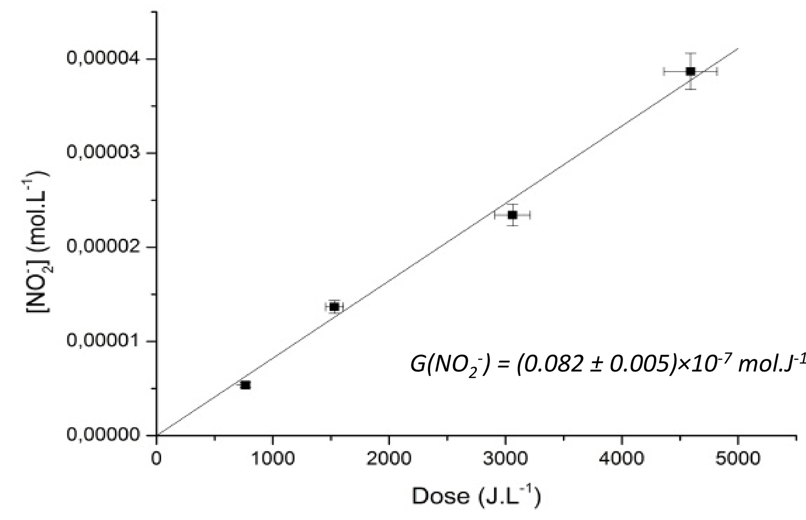
➔ Most stable radicals

$$CH_3-CH_2-{}^{\bullet}CH-CH{=}NOH \leftrightarrow CH_3-CH_2-CH{=}CH-{}^{\bullet}NOH$$
$$CH_3-CH_2-CH_2-CH{=}NO^{\bullet} \leftrightarrow CH_3-CH_2-CH_2-{}^{\bullet}CH-N{=}O$$

Evolution of these radicals ?

Nitrite ion formation

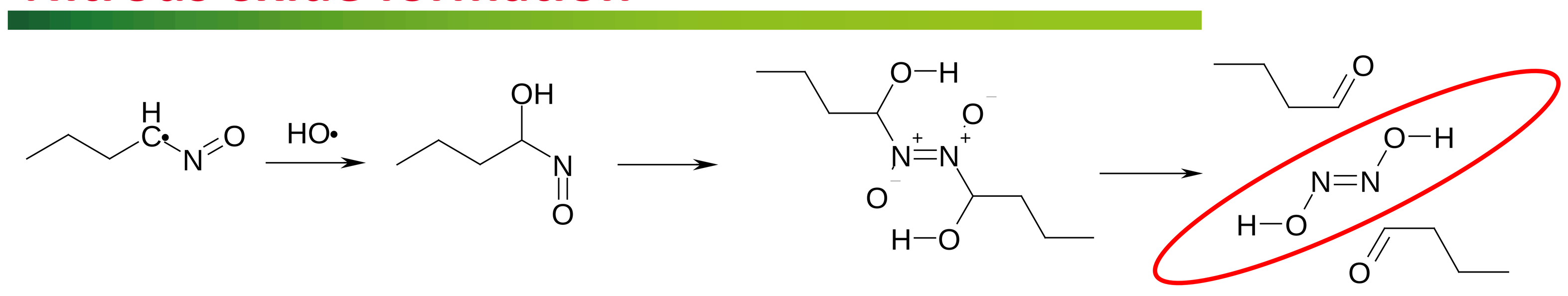
$$CH_3-CH_2-CH{=}CH-{}^{\bullet}N-OH + {}^{\bullet}OH \rightarrow CH_3-CH_2-CH{=}CH_2 + H^+ + NO_2^-$$



NO_2^- analysis by Griess reagent colorimetry

Nitrite ion radiolytic yield after irradiation of 10^{-3} mol.L^{-1} butanal oxime solutions at several doses in CEMHTI facility.

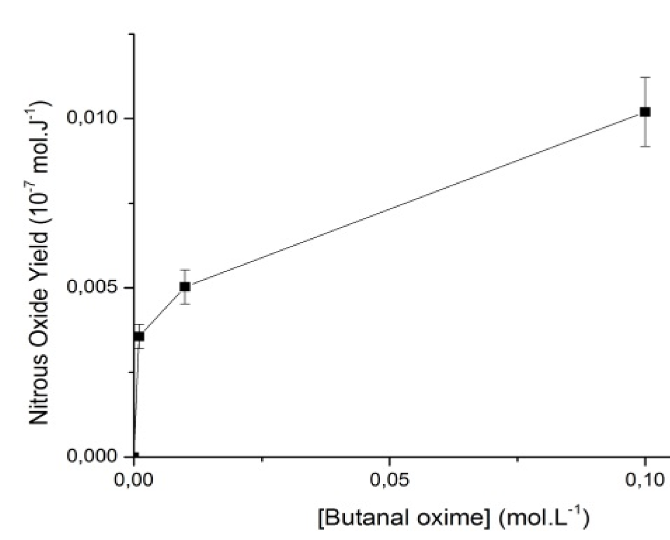
Nitrous oxide formation



Formation of hyponitrous acid [3]
➔ Decomposes itself [4]

$$N_2O_2H_2 \rightarrow N_2 + 2\,{}^{\bullet}OH$$
$$N_2O_2H_2 \rightarrow N_2O + H_2O$$

N_2O analysis by µGC



Influence of butanal oxime concentration on the Nitrous oxide yield in aqueous butanal oxime solutions.

Conclusion and perspectives

- **First objective:** quantification of the butanal oxime degradation yield in aqueous phase
  - Slow evolution at low concentration ➔ indirect effects
  - At high concentration ➔ Direct effects
- **Description of a probable radiolytic mechanism**
  - Enhancement of the H_2 production
  - Inhibition of H_2O_2 production
  - Observation of nitrite ion and nitrous oxide (quantified)
  - Observation of butanal, butene, propene (not quantified)
- **Perspectives**
  - Quantitative analysis of liquid phase products (butanal, butyronitrile…)
  - Atmosphere controlled irradiation ➔ N_2, CO_2 analysis
  - Development of a method to follow NO_X

References

[1] V. Marchenko, K. Dvoeglazov, V. Volk, *Radiochemistry*, **2009**, *51*, 329
[2] Dinh, B., Baron, P., Moisy, P., Venault, L., Bernier, G., Pochon, P., **2008**. FR 2 917 227 A1
[3] Bird, J.W., Diaper, D.G.M., Can. J. Chem. **1969**, *47*, 145.
[4] Buchholz, J.R., Powell, R.E., J. Am. Chem. Soc. **1963**, *85*, 509.

The authors would like to express their gratitude for the ARRONAX and CEMHTI facility teams for their technical support in this study.

DIRECTION DE L'ÉNERGIE NUCLÉAIRE
Département RadioChimie et Procédés
Service d'Études du Recyclage des combustibles et d'Analyses

Commissariat à l'énergie atomique et aux énergies alternatives
Centre de Marcoule | BP17171 | 30207 Bagnols-sur-Cèze Cedex
T. +33 (0)4 66 79 66 48 | F. +33 (0)4 66 79 60 27
Établissement public à caractère industriel et commercial | RCS Paris B 775 685 019