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Radiation chemical behavior of aqueous butanal oxime solutions under alpha irradiation

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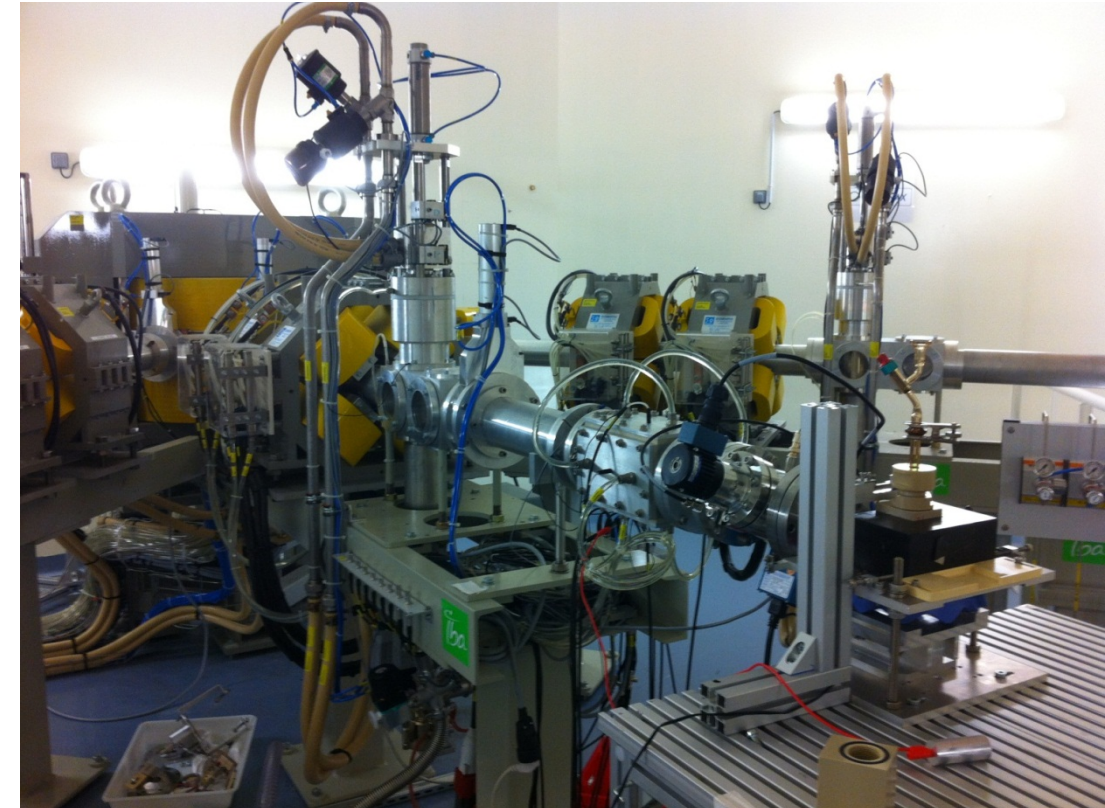
Context

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 HNO₂ in the organic phase. Numerous substitutes to hydrazinium nitrate have then been considered to find a compound which quickly reacts with HNO₂ 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.

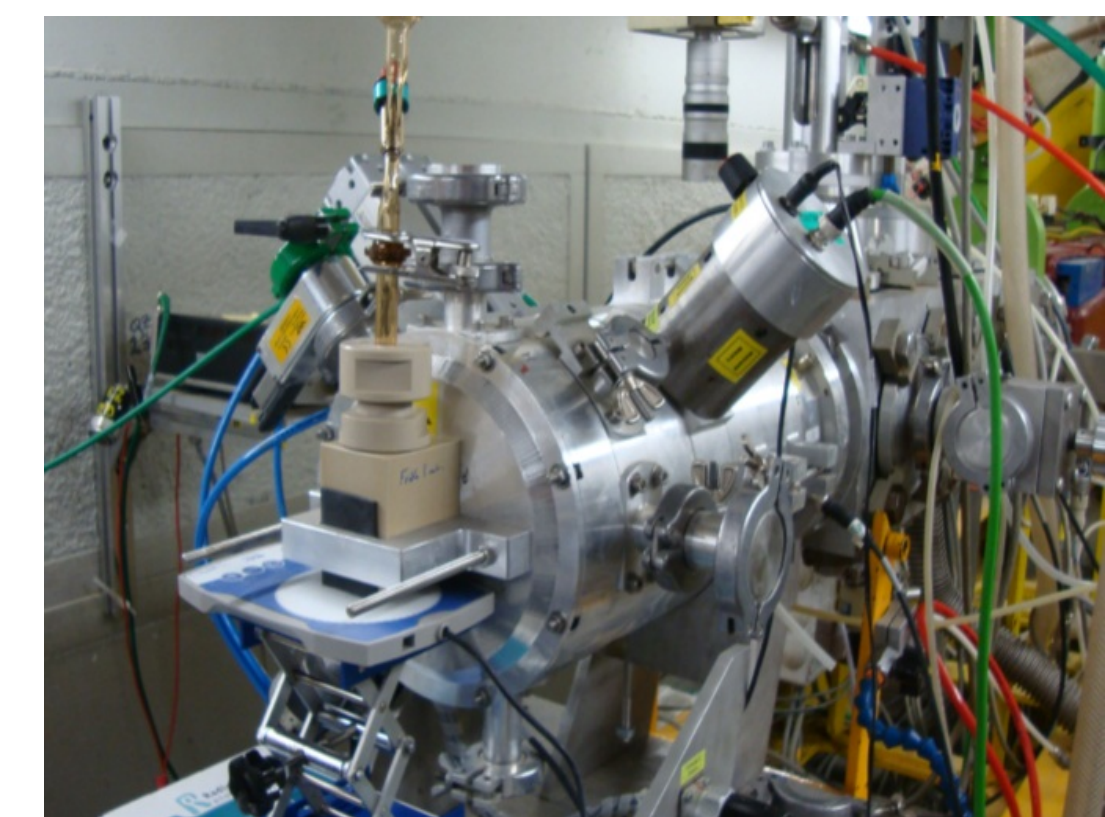
Butanal oxime radiolytic degradation in water

Irradiation of fresh butanal oxime solutions in water

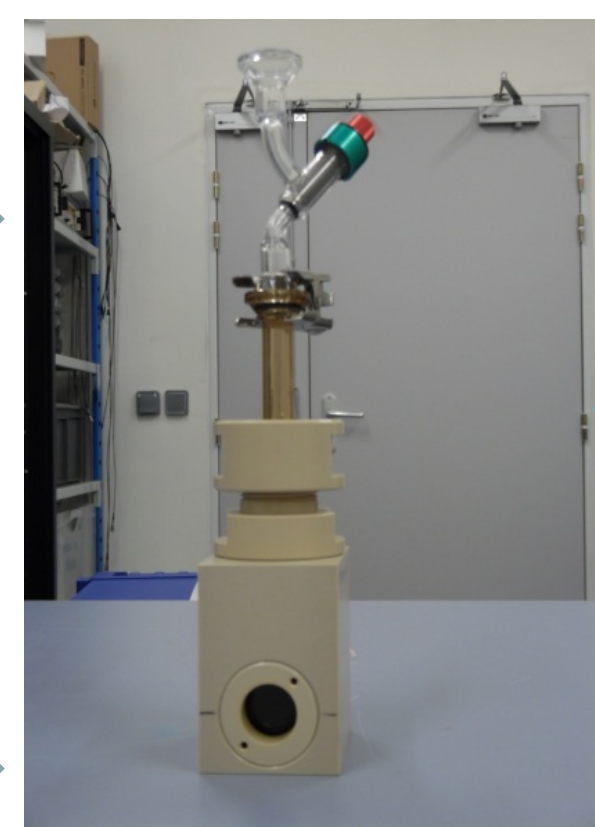
- External irradiation: α cyclotron beam
- 1 Irradiation = 1 precise dose
- Dose monitored by Fricke dosimetry



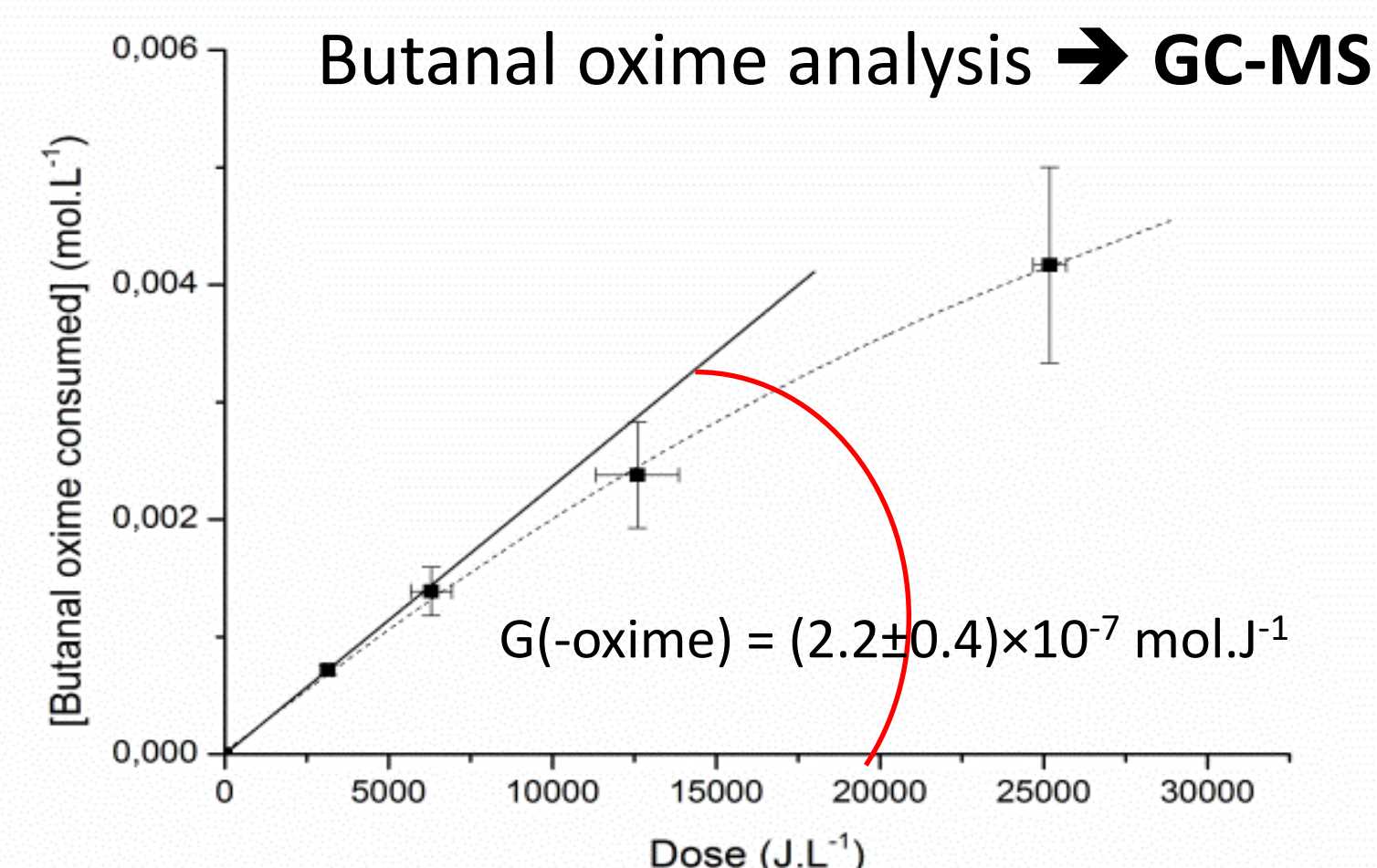
AX line of the ARRONAX cyclotron (68 MeV)



End of the CEMHTI line (28 MeV)



α PEEK cell containing the samples

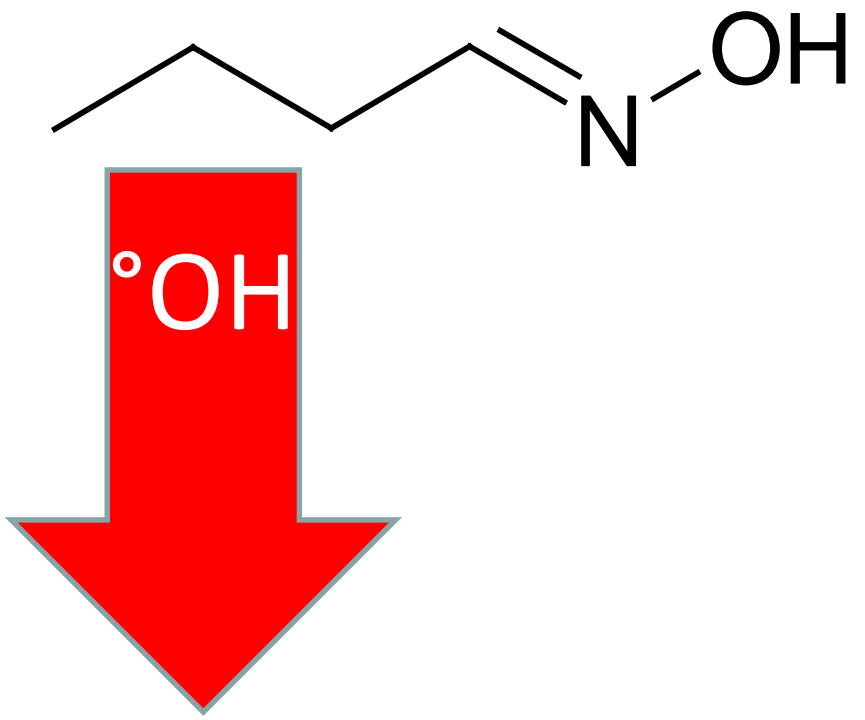
Measurement of the butanal oxime consumption yield by irradiation of aqueous solution of 10⁻² mol.L⁻¹ butanal oxime.

[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

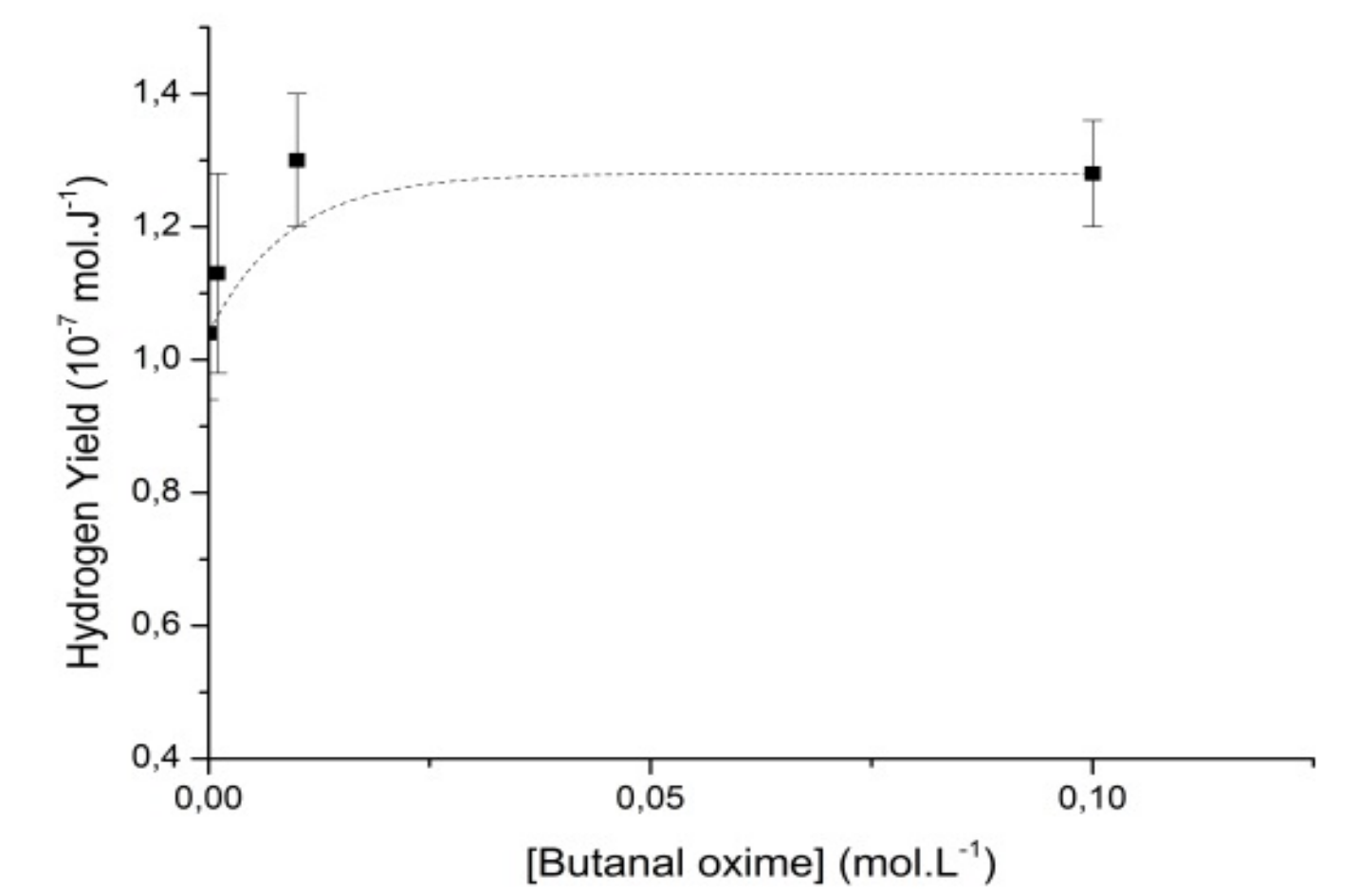
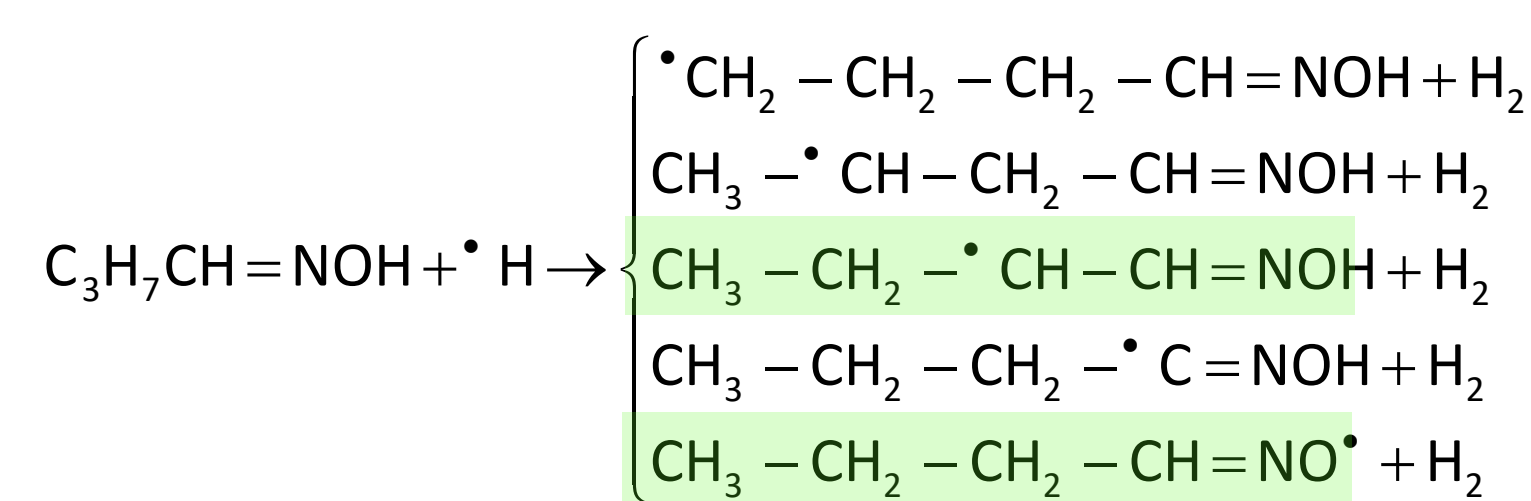
Evolution of the butanal oxime consumption yield according to the butanal oxime concentration in aqueous solutions.

Radiolytic degradation mechanism

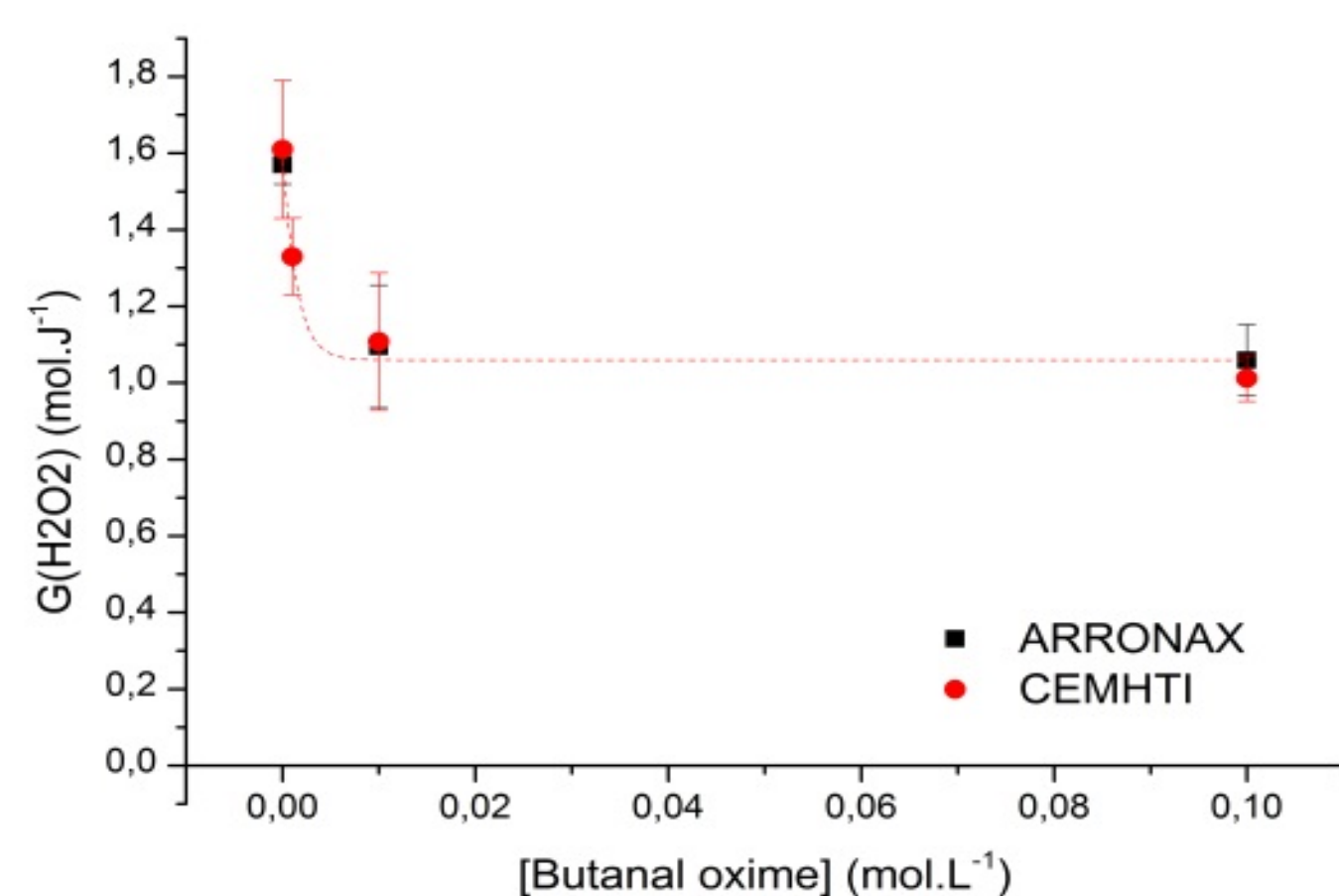
Butanal oxime



H₂ analysis by μGC
Butanal oxime enhances H₂ production
→ Hydrogen abstraction mechanism



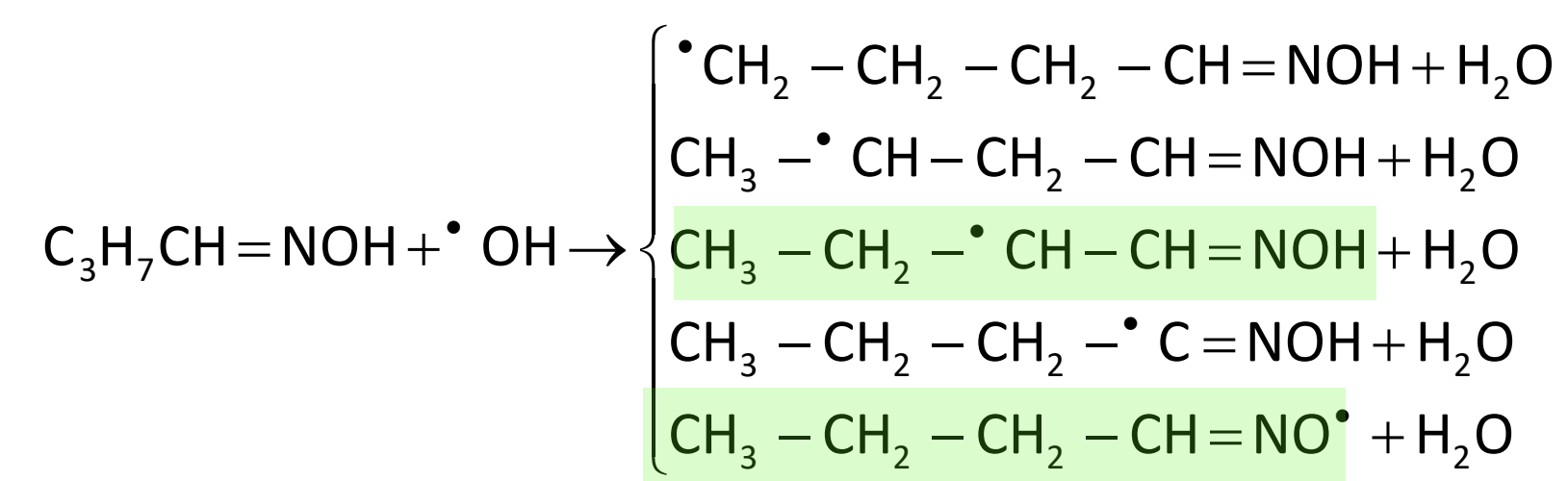
Influence of butanal oxime concentration on the hydrogen yield in aqueous butanal oxime solutions.

H₂O₂ analysis by Ti^{IV} colorimetry

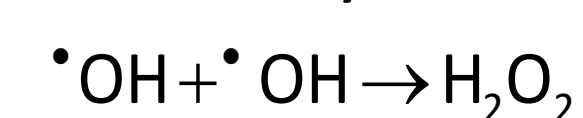
Influence of butanal oxime concentration on the Hydrogen peroxide yield in aqueous butanal oxime solutions.

Butanal oxime inhibits H₂O₂ production

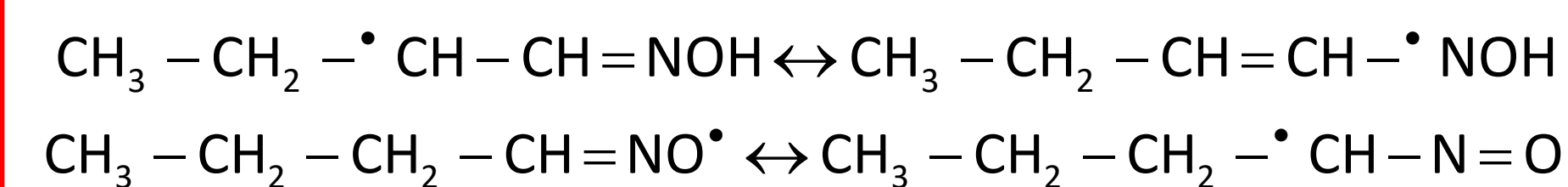
- Scavenging of °OH
- Hydrogen abstraction mechanism



→ Reaction blocked by this mechanism:

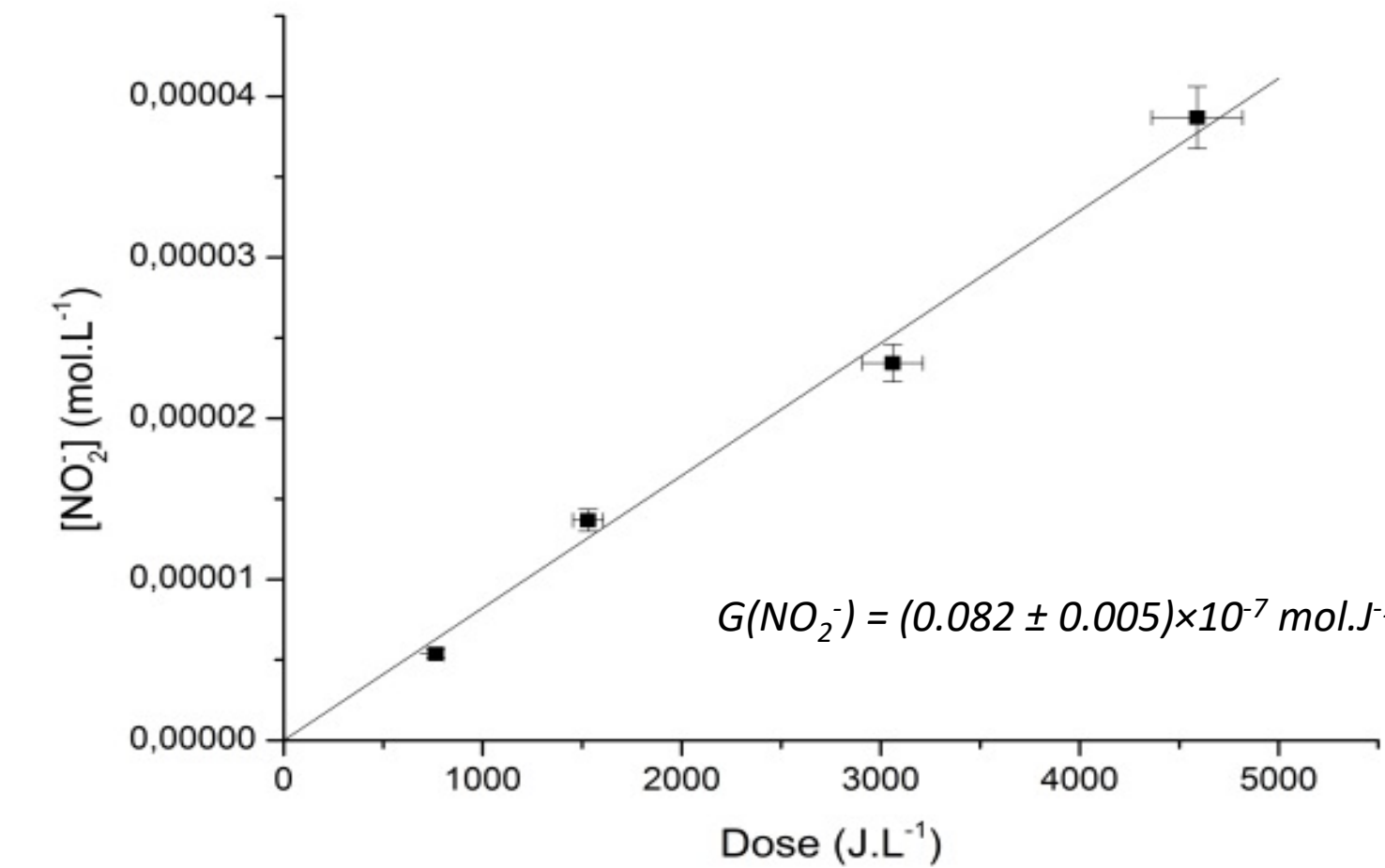
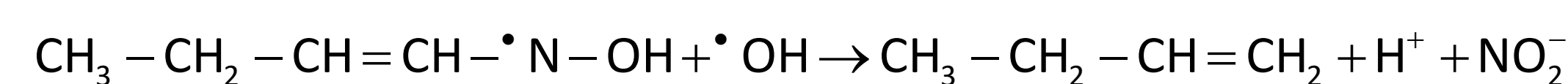


→ Most stable radicals

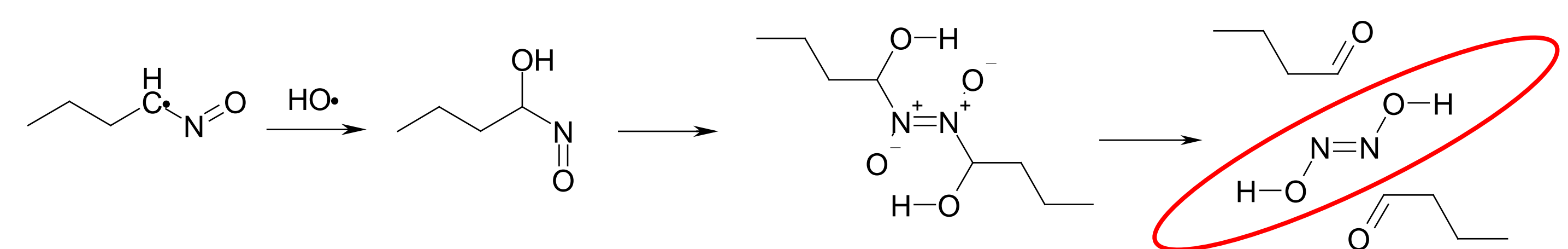


Evolution of these radicals ?

Nitrite ion formation

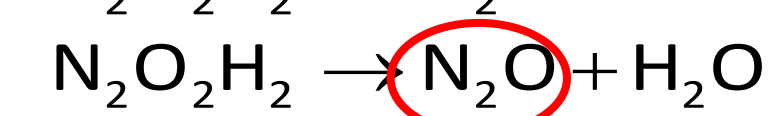
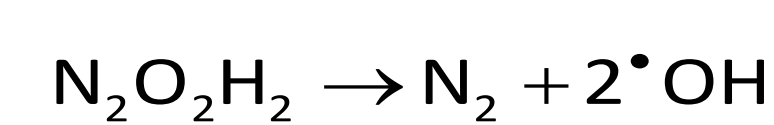
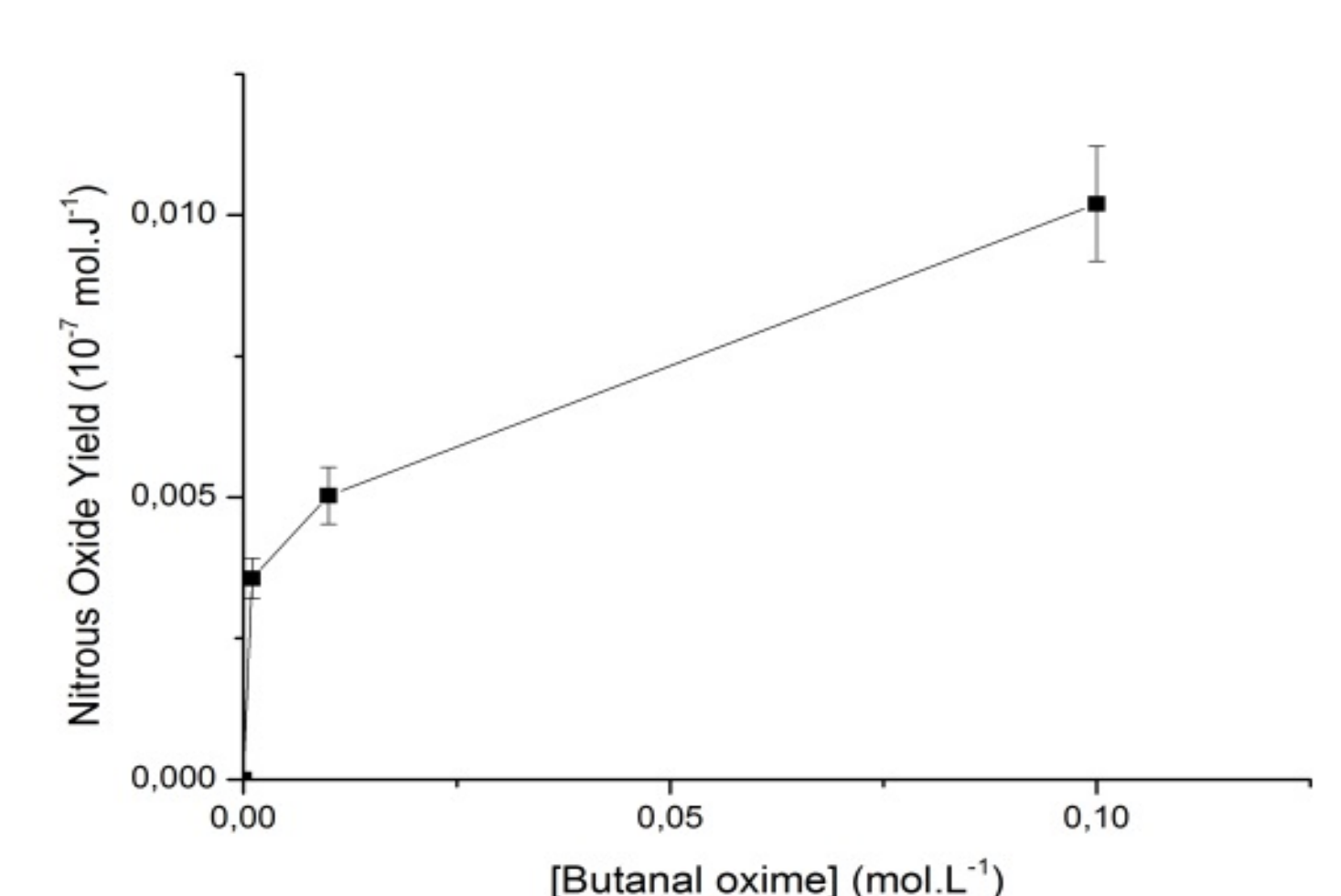
Nitrite ion radiolytic yield after irradiation of 10⁻³ mol.L⁻¹ butanal oxime solutions at several doses in CEMHTI facility.NO₂⁻ analysis by Griess reagent colorimetry

Nitrous oxide formation



Formation of hyponitrous acid [3]

→ Decomposes itself [4]

N₂O 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 H₂ production
 - Inhibition of H₂O₂ 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 → N₂, CO₂ 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.

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