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Experimental study of interactions between uranium and n-alkanes in hydrothermal conditions (500 bar, 200°C)

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Abstract

Organic matter is commonly involved in uranium deposits by reducing and alteration processes. An experimental study of the pyrolysis of linear n-alkanes at 200°C, 500 bar for 2 months in presence of water and/or uranium were carried out. These experiments reveal that the initiation mechanism of the reaction pathway is the reduction of uranium and the oxidation of organic matter and that the oxidation of n-alkanes produces different compounds (aldehydes, alcohols, ketones, carboxylic acids, esters) in different configurations and proportions by auto-oxidation and free-radical reactions. Another parameter observed during the experiments is the increase of the oxidation process the longer the aliphatic chain is. The pyrolysis of n-octane particularly revealed the role of water as an oxidizing agent instead of auto-oxidation mechanisms.

Keywords:

n-alkane, uranium, oxidation, hydrothermal conditions, pyrolysis

1 INTRODUCTION

The affinity of uranium and other metals of economic interest for carbon compounds and organic materials especially is such that it has been proposed as a criterion for prospecting [1]. Carbonaceous material is frequently observed in uranium field, which raises the question of the role played by carbon compounds in the formation of some deposits.

Naturally occurring carbonaceous organic materials such as coals are known to have played important roles in controlling uranium concentrations within the different stages of the sedimentary cycle [2-4]. The relationship between organic compounds and uranium show that these interactions are various: transport, remobilization, reduction, concentration, and preservation [5].

Most uranium deposits associated with carbon compounds are generally formed at relatively low or moderate temperatures ($<350\text{ }^{\circ}\text{C}$). This is the case of roll-front type deposits of Dongsheng in China [3, 6], deposits of Oklo in Gabon [7-15] and Lodève in France [16-18].

The relationship between uranium and organic matter is observed both at deposits scale and at molecular scale where chemical bonds were established between certain functional groups of organic compounds and uranium atoms [5].

This work aims to better understand the intimate interaction reactions between uranium and organic compounds under conditions of temperature and pressure corresponding to the fields of organic diagenesis and low temperature hydrothermalism.

Several experiments have been performed with models compounds representing the mineral phase and the organic compounds. The use of such simplified systems allows good control of the experimental conditions and to propose reaction mechanisms.

A first set of experiments designated as reference that involves organic compounds alone was performed to evaluate their stability in the absence of uranium in the chosen

experimental conditions. Then, a second set were carried out in the same conditions but in the presence of uranium under solid form. Comparison of these two sets of experiments will allow a better understanding of:

- i) the role of the compounds resulting from the decomposition of the organic matter in the reduction of uranium;
- ii) the effect of uranium on the organic compounds;
- iii) Determining the dominating reactions between reduction of uranium, solubility and modification of the organic compounds.

2 MATERIAL AND METHOD

2.1 Confined pyrolysis

Experiments were performed at high pressures using confined pyrolysis. This technique first used in geochemistry for mineral syntheses and simulation of hydrothermal metamorphism [19-20] found applications in organic geochemistry [21-26]. Confined pyrolysis allows working in a range of pressure and temperature similar as those that can be found in sedimentary basins.

The loading of the gold cells (40 mm in length, 5 mm in diameter and 0.5 mm in thickness) was made under helium atmosphere (purity 99.9999%) The reactors were sealed by arc welding while the sample was refrigerated by a cold nitrogen flow. The gold cells were then loaded and heated under pressure in stainless steel autoclaves. Special care was taken to avoid oxygen concentration in the gold cells because oxygen speeds up the reactivity [27-29].

2.2 Choice of the organic compounds

The organic compounds used in these experiments are different n-alkane with different lengths (see table 1) in order to study the influence of this parameter on the different reactions. The individual pyrolysis of each of these compounds in different experimental conditions has been very widely studied [30-32].

2.3 Choice of the uranium carriers

Many authors have highlighted the role of reducing agent of the organic matter on uranium and on the hydrothermal deposition of deposits [33-36]. It has been shown that uranium is brought by the fluids under the state of oxidation VI in the form of uranyl complex. In contact with organic matter, uranium is reduced and mineralized.

In order to highlight the role of organic matter in the precipitation of uranium and particularly associated reactions uranium VI oxide UO_3 has been selected as reactants.

2.4 Experimental study of the four experimental series

Four experimental series were carried out in order to highlight the mechanisms of interaction between uranium and the organic compounds.

- The first serie of experiments corresponds to the pyrolysis of organic compound exclusively
- The second serie of experiments corresponds to the pyrolysis of organic compounds with deuterated water
- The third serie of experiments corresponds to the pyrolysis of organic compound with solid uranium under the state of oxidation UO_3
- The fourth serie of experiments corresponds to the pyrolysis of organic compound with solid uranium under the state of oxidation UO_3 and deuterated water

The experimental conditions of all the experiments were 473K (200°C), 50MPa (500 bar) for 2 months.

The first two series correspond to a frame of reference to control experiments with an organic compound exclusively (first serie) or with deuterated water (second serie). It was established in order to determine the stability and the behaviour of the organic compounds under our experimental conditions and to show experimentally the reactional complexity which can exist in the pyrolysis of certain organic molecules under the conditions close to the formation of a uranium deposit.


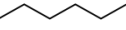
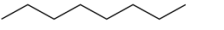
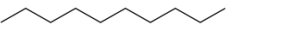

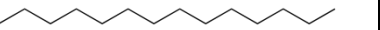
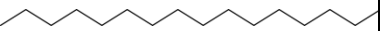
The third serie simulates the reaction between an organic compound and solid uranium. The uranium VI oxide UO_3 allows the study of the reactions of uranium at the solid state. These reactions using solid uranium are not the same as the reactions occurring during the formation of a uranium deposit where uranium is transported to the trap via an aqueous fluid. However, reactions of this type between a solid containing some uranium and the organic compound are taken into account when the latter remobilise uranium in order to transport it as it is considered by Capus (1979) [17] in the deposit of Lodève. The solubility of the uranium is also studied in the organic liquid phase of our experiments involving a series of possible reactions that it is also necessary to take into account. The comparison with the frame of reference allows the characterization of the reactions specific to the interactions between the organic compounds and uranium.


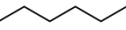
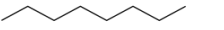
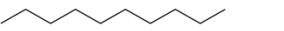
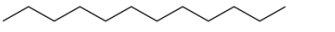
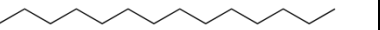
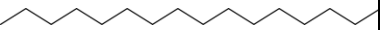
The fourth serie of experiments is a ternary system with organic compound, solid uranium (UO_3) and deuterated water to simulate the mechanism of interaction under the conditions close to the formation of a uranium deposit.

The reactants were composed of 1 cm³ of organic compound (99.5% purity obtained from Fluka and used as received) for reference without deuterated water and organic compound-

uranium experiments and 0,5 cm³ of organic compound and 0,5 cm³ of deuterated water (D2O, ultra-pure water) for reference experiments with water and ternary solution experiments. For the organic compound-uranium-(D2O) experiments, the gold cells were loaded with 0.6 g of UO₃ (table 1).

Table 1 Summary of experiments performed and reagents and quantities used

| Name of the compound | Formula | Chemical Formula | Molecular weight (g.mol ⁻¹) | SERIE 01 | SERIE 02 | |
|-----------------------|---------------------------------|---|---|---|---|------------------------------------|
| | | | | Reference experiments without water | Reference experiments with water | |
| | | | | Volume of organic compound (cm ³) | Volume of organic compound (cm ³) | Volume of water (cm ³) |
| <i>n</i> -pentane | C ₅ H ₁₂ |  | 72.15 | 1 | 0.5 | 0.5 |
| <i>n</i> -hexane | C ₆ H ₁₄ |  | 86.18 | 1 | 0.5 | 0.5 |
| <i>n</i> -octane | C ₈ H ₁₈ |  | 114.23 | 1 | 0.5 | 0.5 |
| <i>n</i> -decane | C ₁₀ H ₂₂ |  | 142.28 | 1 | 0.5 | 0.5 |
| <i>n</i> -dodecane | C ₁₂ H ₂₆ |  | 170.33 | 1 | 0.5 | 0.5 |
| <i>n</i> -tetradecane | C ₁₄ H ₃₀ |  | 198.39 | 1 | 0.5 | 0.5 |
| <i>n</i> -hexadecane | C ₁₆ H ₃₄ |  | 226.44 | 1 | 0.5 | 0.5 |

| Name of the compound | Formula | Chemical Formula | Molecular weight (g.mol ⁻¹) | SERIE 03 | | SERIE 04 | | |
|-----------------------|---------------------------------|---|---|--|---|--|---|------------------------------------|
| | | | | Binary system organic compound-uranium | | Ternary system organic compound-uranium-deuterated water | | |
| | | | | Weight of solid uranium (g) | Volume of organic compound (cm ³) | Weight of solid uranium (g) | Volume of organic compound (cm ³) | Volume of water (cm ³) |
| <i>n</i> -pentane | C ₅ H ₁₂ |  | 72.15 | 0.6 | 0.5 | 0.6 | 0.5 | 0.5 |
| <i>n</i> -hexane | C ₆ H ₁₄ |  | 86.18 | 0.6 | 0.5 | 0.6 | 0.5 | 0.5 |
| <i>n</i> -octane | C ₈ H ₁₈ |  | 114.23 | 0.6 | 0.5 | 0.6 | 0.5 | 0.5 |
| <i>n</i> -decane | C ₁₀ H ₂₂ |  | 142.28 | 0.6 | 0.5 | 0.6 | 0.5 | 0.5 |
| <i>n</i> -dodecane | C ₁₂ H ₂₆ |  | 170.33 | 0.6 | 0.5 | 0.6 | 0.5 | 0.5 |
| <i>n</i> -tetradecane | C ₁₄ H ₃₀ |  | 198.39 | 0.6 | 0.5 | 0.6 | 0.5 | 0.5 |
| <i>n</i> -hexadecane | C ₁₆ H ₃₄ |  | 226.44 | 0.6 | 0.5 | 0.6 | 0.5 | 0.5 |

3 ANALYTICAL

3.1 Extraction

3.1.1 Liquid phase

After pyrolysis, gold capsules were pinched at one end and placed in contact with a vial allowing the recovery of the liquid phase. A large part of the liquid phase is carried along by the gas flowing out of the capsule. This flow is directed towards the vial specified for the organic liquid phase. When the capsule is no longer in pressure it is completely opened in order to recover the remaining liquid phase. The aqueous phase is removed using a glass pipette and placed in the aqueous liquid vial. The two liquid phases are then centrifuged to remove suspended particles.

3.1.2 Solid phase

The recovering step of the solid phase is performed immediately after the liquid one. The second end of the capsule is open using a cutter and the solid is recovered.

3.2 Gaz chromatography – mass spectrometry

The samples were analyzed by a gas chromatograph (Hewlett-Packard HP 6890) coupled to a mass spectrometer (Hewlett-Packard HP 5972) using a split/splitless injector, a 60 m DB-5 J & W, 0.25 mm i.d., 0.1 mm film fused silica column. Two different temperature programs were used according to the injection mode:

Split injection mode : 70°C-130°C with 15°C/min, 130°C-300°C with 3°C/min followed by an isothermal stage at 300°C during 15 min with, constant flow of helium of 1 ml/min.

Splitless injection mode: 70°C-130°C with 15°C/min, 130°C-300°C with 3°C/min followed by an isothermal stage at 300°C during 15 min with, constant flow of helium of 1 ml/min.

The mass spectrometer was operated in the electron ionization (EI) mode at 70 eV ionization energy and mass spectra were scanned from 50 to 500 Da using a quadrupole detector. Data

were acquired and processed using the Agilent ChemStation software. Compounds were identified by comparison of their mass spectra with published spectra and those from the Wiley275 database, or by interpretation of MS fragmentation patterns.

3.3 Derivatization (silylation)

Because of the presence of alcohols and carboxylic acids in the extracts, a silylation step was carried out in order to improve the chromatographic resolution. The organic solutions were diluted in a flask at a concentration of 4mg/ml with a silylating reagent (BSTFA + TMCS 99.1, Supelco). To accelerate the reaction, the flasks were heated up to 50 ° C for 15 minutes. Then, 0.5 ml of the solution was introduced into the chromatograph injector in splitless mode. All the samples were run with and without silylation to identify hydrocarbons and oxygenated products separately.

4 RESULTS

4.1 Reference System (organic compounds pyrolysed alone or with water)

The 7 reference n-alkanes were pyrolyzed alone or with deuterated water. The products of reactions were analyzed by GC-MS. The chromatograms of these 2 series of experiments do not show the formation of pyrolysis products. One organic compound is shown for illustration (figure1).

This is consistent with previous studies indicating that the temperature of 200°C is too low to observe any advancement of the reaction [37, 38, 48, 49].

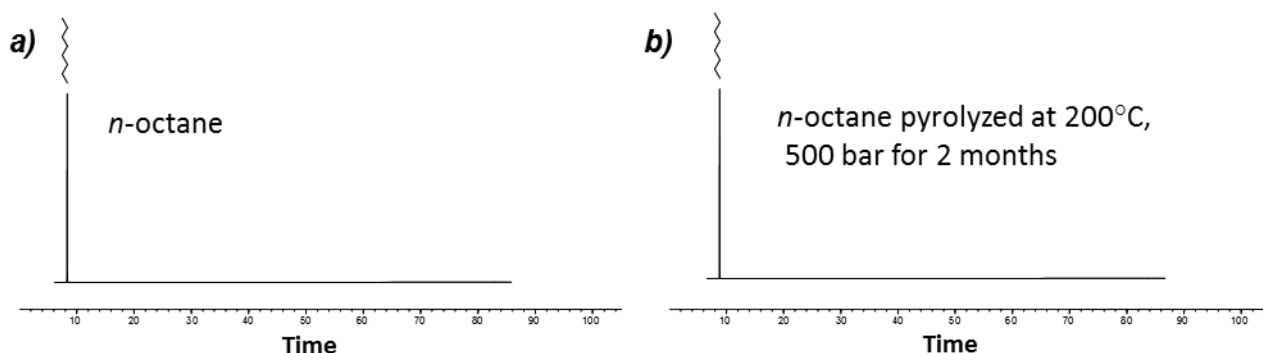


Figure 1 : Chromatograms (split mode) of pyrolysis's at 200°C, 500 bar for 2 months: a) pristine *n*-octane ; b) *n*-octane pyrolyzed.

4.2 Experiments with binary mixture: uranium UO_3 (solid) + *n*-alkane

4.2.1 Analyses of the liquid organic phase by GC-MS

These compounds were pyrolyzed for 2 months at 500 bar, 200°C in the presence of UO_3 and the results are summarized in table 2.

- *n*-pentane

The analysis of the products of reaction of *n*-pentane in the presence of UO_3 did not show any formation of organic compounds. Furthermore uranium still had a yellow color at the end of the experiment, corresponding to the form of uranium trioxide UO_3 .

- *n*-hexane

The experiments with *n*-hexane reveal the presence of a secondary alcohol (*n*-hexanol) having the same number of carbon as hexane. However the position of the hydroxyl group could not be specified (figure 2).

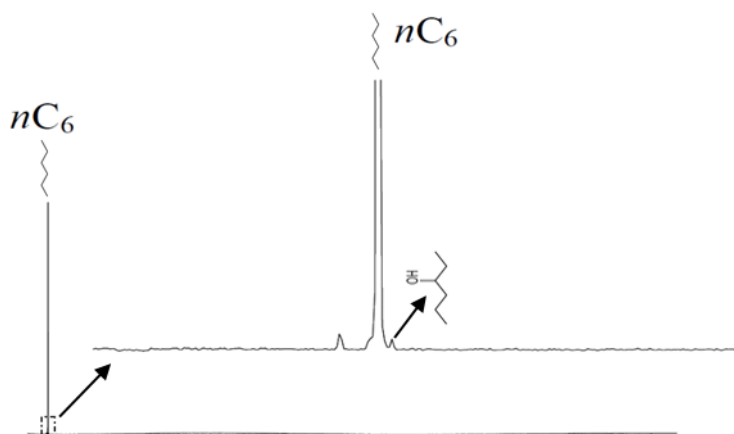


Figure 2: Chromatogram of the pyrolyzed *n*-hexane + UO_3 at 200°C, 500 bar for 2 months

- *n*-octane

Analysis of the reaction products by GC-MS in split mode resulting from the *n*-octane/ UO_3 solution enables to identify several types of compounds: ketones, alcohols and carboxylic acids (figure 3). The various compounds can be gathered in three families:

- Oxygenated compounds having preserved the chain length of the *n*-octane: *ketones* compounds corresponding to various isomers of position of *n*-octanone (2, 3 and 4-octanone), *n*-alcohols products corresponding to various isomers of position of secondary alcohols with 8 carbon atoms (2, 3 - and 4-octanol). These two sub-families of compounds imply an incorporation of oxygen in the *n*-octane chain without rupture of it.

- Oxygenated compounds with aliphatic chain shorter than the reactant:

Carboxylic acids show chain lengths ranging from 5 to 8 carbon atoms (from the pentanoic acid to the octanoic acid). The presence of carboxylic acids with shorter aliphatic chains (between C_1 and C_4) is possible but cannot be detected by the analysis technique (column not adapted for the light polar compounds).

- Oxygenated compounds with aliphatic chains longer than *n*-octane:

Analysis of the same organic solution resulting from *n*-octane pyrolysis but this time by GC-MS in “splitless” mode after silylation confirms the presence of carboxylic acids and

alkanols with a higher chromatographic resolution. In addition, another series of compounds in lower concentration is observed (figure 3). Because the initial reagent (*n*-octane) is not detected (solvent delay), it is then possible to inject it at higher concentration and thus to detect compounds in very low abundance. These compounds are gathered in isomer triplets with carbon number ranging from 12 to 16 with the following formulas: $C_{12}H_{24}O_2$, $C_{13}H_{22}O_2$, $C_{14}H_{28}O_2$, $C_{15}H_{30}O_2$, $C_{16}H_{32}O_2$.

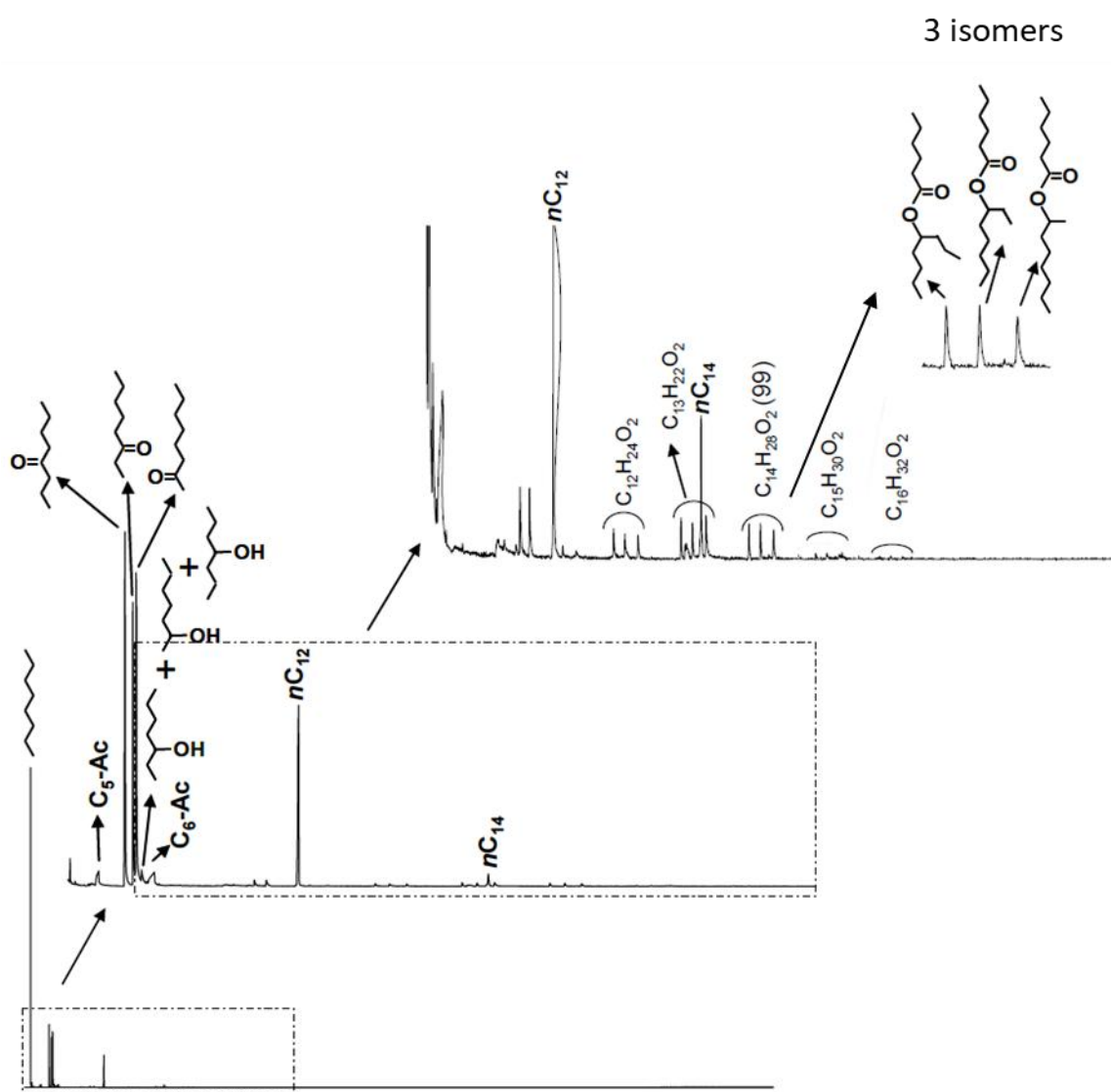


Figure 3: GC-MS Chromatogram (Split and splitless mode) of the pyrolysis of the mixture *n*-octane + UO_3 at 200°C, 500 bar for 2 months. C_n -CA: Carboxylic Acid with *n* carbons

- *n*-dodecane

For *n*-dodecane, the observations are very close to those made for *n*-octane with the occurrence of the same three products families (Figure 4):

- Oxygenated compounds having preserved the chain length of the reactant: various isomers of position of *n*-dodecanone (2, 3, 4, 5 and 6-dodecanone) and various isomers of position of dodecanol (2, 3, 4, 5 - and 6-dodecanol).
- Oxygenated compounds with aliphatic chain shorter than the reactant. These compounds correspond to carboxylic acids containing 5 to 12 carbon atoms. It has not been possible to detect acids with shorter chains in GC-MS with the analytical conditions used.
- Oxygenated compounds with aliphatic chains longer than the initial reactant. These compounds are combined into groups of 5 isomers, each of these groups containing the same number of carbon atoms (from 15 to 24 carbon atoms). These compounds were identified as esters with the following formulas: $C_{15}H_{30}O_2$, $C_{16}H_{32}O_2$, $C_{17}H_{34}O_2$, $C_{18}H_{36}O_2$, $C_{19}H_{38}O_2$, $C_{20}H_{40}O_2$, $C_{21}H_{42}O_2$, $C_{22}H_{44}O_2$, $C_{23}H_{46}O_2$, $C_{24}H_{48}O_2$. They were identified on the basis of their mass spectrum with the assistance of the Wiley data base. They present the same mass spectrum before and after silylation suggesting the absence of the hydroxyl function in their structure. The figure 4 proposes a structure for these various esters.

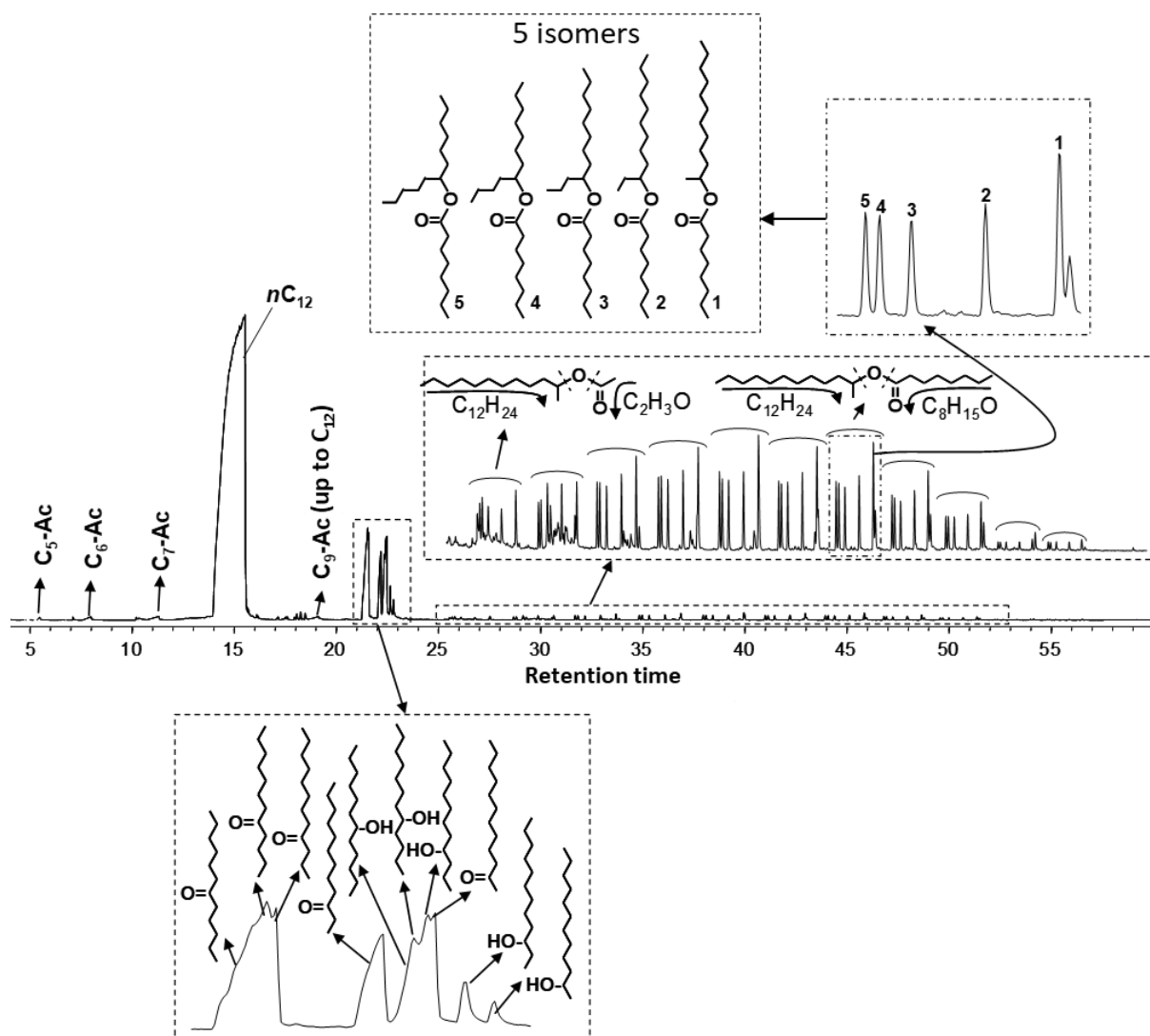


Figure 4: GC-MS Chromatogram (Split mode) of the pyrolysis of the solution *n*-dodecane + UO₃ at 200°C, 500 bar for 2 months. C_n-CA: Carboxylic Acid with *n* carbons

- - *n*- tetradecane and *n*-hexadecane

Analysis of the products of reaction of *n*-tetradecane (Figure 5a) and of *n*-hexadecane (Figure 5b) pyrolyzed at 200°C, 500 bar for 2 months also show the same 3 families:

- oxygenated compounds having preserved the length of chains of the initial product: various isomers of position *n*-tetradecanone (2, 3, 4, 5, 6 and 7-tetradecanone) and of *n*-hexadecanone (2, 3, 4, 5, 6 - 7 and 8-hexadecanone) as well as various isomers of position of secondary alcohols with 14 and 16 carbon atoms (2, 3, 4, 5, 6 and 7-tetradecanol/2, 3, 4, 5, 6, 7 - and 8-hexadecanol observed only in “splitless” injection mode).

- oxygenated compounds with aliphatic chains shorter than the initial product:

carboxylic acids containing 4 to 14 carbon atoms for *n*-tetradecane and 4 to 16 carbon atoms for *n*-hexadecane (observed in mode of injection “splitless”), *n*-alkanes with chains shorter than the initial product, corresponding to *n*-alkanes containing 8 to 13 carbon atoms for the tetradecane and 7 to 14 carbon atoms for hexadecane are also present.

- oxygenated compounds with aliphatic chains longer than the initial product. This time, these compounds combine in group of 6 isomers containing 15 to 27 atoms of carbon for the tetradecane and 7 isomers (6 and 7 being partially coeluted on the chromatograms) containing 20 to 32 carbon atoms for *n*-hexadecane. As for *n*-dodecane, these compounds were identified out of esters of empirical formulas ($C_{15}H_{30}O_2$, $C_{16}H_{32}O_2$, $C_{17}H_{34}O_2$, $C_{18}H_{36}O_2$, $C_{19}H_{38}O_2$, $C_{20}H_{40}O_2$, $C_{21}H_{42}O_2$, $C_{22}H_{44}O_2$, $C_{23}H_{46}O_2$, $C_{24}H_{48}O_2$, $C_{25}H_{50}O_2$, $C_{26}H_{52}O_2$, $C_{27}H_{54}O_2$ for *n*-tetradecane and $C_{20}H_{40}O_2$, $C_{21}H_{42}O_2$, $C_{22}H_{44}O_2$, $C_{23}H_{46}O_2$, $C_{24}H_{48}O_2$, $C_{25}H_{50}O_2$, $C_{26}H_{52}O_2$, $C_{27}H_{54}O_2$, $C_{28}H_{56}O_2$, $C_{29}H_{58}O_2$, $C_{30}H_{60}O_2$, $C_{31}H_{62}O_2$, $C_{32}H_{64}O_2$ for *n*-hexadecane).

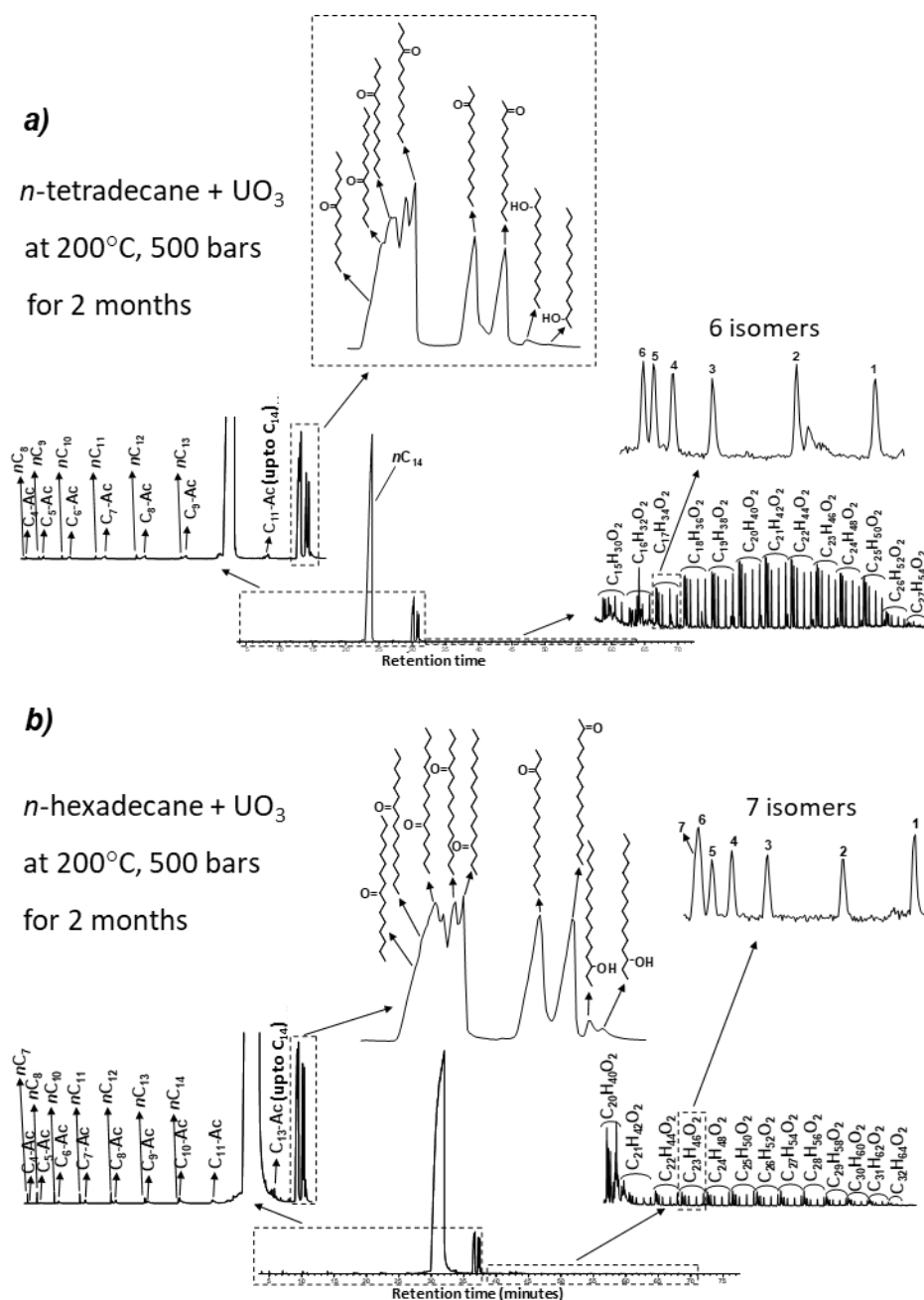


Figure 5: Chromatograms (Split mode), a) n -tetradecane and b) n -hexadecane pyrolyzed with UO_3 at 200°C, 500 bar for 2 months. C_n -CA: Carboxylic Acids with n carbons

4.3 Experiments with ternary solutions: uranium UO_3 (solid) + n -alkane + water

As for the experiments carried out with the binary mixture (organic compounds - UO_3), we carried out a characterization of the organic phases in the case of the ternary systems (organic compounds - UO_3 - D_2O) by GC-MS.

Organic compounds detected during the experiments of *n*-alkanes with UO_3 and D_2O are relatively close to those observed during the experiments without deuterated water. We observe three various families (example of *n*-tetradecane in Figure 6):

- Compounds having preserved the same number of carbon that the initial *n*-alkane.

These compounds correspond to secondary alkanols and ketones presenting their various isomers of positions. But if the *n*-alkanols are identical to the experiments without D_2O , the *ketones* presents shifts of molecular weight of 1 or 2 suggesting the replacement of one or two hydrogen by one or two deuterium during the formation of the ketones.

- Compounds of shorter aliphatic chains represented by carboxylic acids. The number of carbon in the aliphatic chains of these acids lies between 5 (the lighter compounds are not observable under the analytical conditions used) and numbers of carbon of *n*-initial alkane. Like *ketones*, the carboxylic acids show a shift of mass of 1 or 2 units revealing an exchange of 1 or 2 hydrogen by one or 2 deuterium.

- Compounds with longer aliphatic chains than starting products. Esters, highlighted during the experiments *n*-alkanes - UO_3 are also observed in the case of the ternary mixtures. Just like the ketones and the carboxylic acids, these esters present a shift of mass of one or two units. For a given ester, the abundance relating of isomer to a deuterium atom is lower than that with two deuterium atoms suggesting a preferential production of the configuration with two deuterium atoms.

Table 2 summarizes the products of the ternary experiment including various esters observed or deduced (due to limitations from our analytical conditions) for the different *n*- alkanes used.

Table 2: Summary table compiling the compounds detected in the experiments of series 03 and 04. For series 01 and 02, the reaction products were similar to reactants. Compounds in *italics** were not detected but deduced

| | | Reactants | <i>n</i> -pentane (C ₅ H ₁₂) | <i>n</i> -hexane (C ₆ H ₁₄) | <i>n</i> octane (C ₈ H ₁₈) | | <i>n</i> decane(C ₁₀ H ₂₂) | | <i>n</i> dodecane (C ₁₂ H ₂₆) | | <i>n</i> tetradecane (C ₁₄ H ₃₀) | | <i>n</i> hexadecane (C ₁₆ H ₃₄) | | | |
|----------|--|--|--|---|---|---|---|---|--|---|---|---|---|---|---|---|
| | | reaction products | | | | | | | | | | | | | | |
| SERIE 03 | Oxygenated compounds having preserved the chain length of the reactant | <i>n</i> -alkanes | | C ₅ H ₁₂ | C ₆ H ₁₄ | C ₈ H ₁₈ | | | | | | C ₁₄ H ₃₀ | | C ₁₆ H ₃₄ | | |
| | | <i>n</i> -alkanones | | | | C ₆ H ₁₂ O | | C ₁₀ H ₂₂ O | | C ₁₂ H ₂₄ O | | C ₁₄ H ₂₈ O | | C ₁₆ H ₃₂ O | | |
| | | <i>n</i> -alkanols | | | C ₆ H ₁₄ O | C ₈ H ₁₈ O | | C ₁₀ H ₂₂ O | | C ₁₂ H ₂₆ O | | C ₁₄ H ₃₀ O | | C ₁₆ H ₃₄ O | | |
| | Oxygenated compounds with aliphatic chain shorter than the reactant | <i>n</i> -alkanes | | | | | | C ₈ H ₁₈ | | C ₈ H ₁₈ | | C ₈ H ₁₈ | C ₁₂ H ₂₆ | C ₈ H ₁₈ | C ₁₃ H ₂₄ | |
| | | | | | | | | C ₈ H ₂₀ | | C ₈ H ₂₀ | | C ₈ H ₂₀ | C ₁₃ H ₂₈ | C ₈ H ₁₈ | C ₁₃ H ₂₈ | |
| | | | | | | | | | | C ₁₀ H ₂₂ | | C ₁₀ H ₂₂ | | C ₈ H ₂₀ | C ₁₃ H ₂₈ | |
| | | | | | | | | | C ₁₁ H ₂₄ | | C ₁₃ H ₂₄ | | C ₁₀ H ₂₂ | C ₁₄ H ₃₀ | | |
| | | Carboxylic acids | | | | C ₆ H ₁₀ O ₂ | C ₈ H ₁₆ O ₂ | | C ₈ H ₁₆ O ₂ | C ₁₂ H ₂₂ O ₂ | C ₈ H ₁₆ O ₂ | C ₁₁ H ₂₂ O ₂ | C ₈ H ₁₆ O ₂ | C ₁₁ H ₂₂ O ₂ | | |
| | | | | | | C ₆ H ₁₂ O ₂ | C ₈ H ₁₂ O ₂ | | C ₈ H ₁₂ O ₂ | C ₈ H ₁₂ O ₂ | C ₁₂ H ₂₄ O ₂ | C ₈ H ₁₆ O ₂ | C ₁₂ H ₂₄ O ₂ | | | |
| | | | | | | C ₇ H ₁₄ O ₂ | C ₉ H ₁₄ O ₂ | | C ₉ H ₁₄ O ₂ | C ₉ H ₁₄ O ₂ | C ₈ H ₁₂ O ₂ | C ₁₁ H ₂₀ O ₂ | C ₈ H ₁₂ O ₂ | C ₁₃ H ₂₆ O ₂ | | |
| | | | | | | C ₈ H ₁₆ O ₂ | C ₈ H ₁₆ O ₂ | | C ₈ H ₁₆ O ₂ | C ₈ H ₁₆ O ₂ | C ₉ H ₁₈ O ₂ | C ₁₃ H ₂₈ O ₂ | C ₉ H ₁₈ O ₂ | C ₁₄ H ₃₀ O ₂ | | |
| | | | | | | | | | C ₈ H ₁₈ O ₂ | C ₈ H ₁₈ O ₂ | C ₉ H ₂₀ O ₂ | C ₁₃ H ₃₀ O ₂ | C ₉ H ₁₈ O ₂ | C ₁₃ H ₂₈ O ₂ | | |
| | | | | | | | | | C ₁₀ H ₂₀ O ₂ | C ₁₀ H ₂₀ O ₂ | C ₈ H ₁₈ O ₂ | C ₉ H ₂₀ O ₂ | C ₁₃ H ₂₆ O ₂ | C ₁₆ H ₃₂ O ₂ | | |
| | | | | | | | | | | C ₁₁ H ₂₂ O ₂ | | C ₁₀ H ₂₀ O ₂ | | C ₁₀ H ₂₀ O ₂ | | |
| | Esters | | | | C ₁₂ H ₂₄ O ₂ | | C ₁₂ H ₂₄ O ₂ | C ₁₂ H ₂₄ O ₂ | C ₁₂ H ₂₄ O ₂ | C ₁₂ H ₂₄ O ₂ | C ₁₂ H ₂₄ O ₂ | C ₁₂ H ₂₄ O ₂ | C ₁₂ H ₂₄ O ₂ | C ₁₂ H ₂₄ O ₂ | | |
| | | | | | C ₁₃ H ₂₆ O ₂ | | C ₁₃ H ₂₆ O ₂ | C ₁₃ H ₂₆ O ₂ | C ₁₃ H ₂₆ O ₂ | C ₁₃ H ₂₆ O ₂ | C ₁₃ H ₂₆ O ₂ | C ₁₃ H ₂₆ O ₂ | C ₁₃ H ₂₆ O ₂ | C ₁₃ H ₂₆ O ₂ | | |
| | | | | | C ₁₄ H ₂₈ O ₂ | | C ₁₄ H ₂₈ O ₂ | C ₁₄ H ₂₈ O ₂ | C ₁₄ H ₂₈ O ₂ | C ₁₄ H ₂₈ O ₂ | C ₁₄ H ₂₈ O ₂ | C ₁₄ H ₂₈ O ₂ | C ₁₄ H ₂₈ O ₂ | C ₁₄ H ₂₈ O ₂ | | |
| | | | | | C ₁₅ H ₃₀ O ₂ | | C ₁₅ H ₃₀ O ₂ | C ₁₅ H ₃₀ O ₂ | C ₁₅ H ₃₀ O ₂ | C ₁₅ H ₃₀ O ₂ | C ₁₅ H ₃₀ O ₂ | C ₁₅ H ₃₀ O ₂ | C ₁₅ H ₃₀ O ₂ | C ₁₅ H ₃₀ O ₂ | | |
| | | | | | C ₁₆ H ₃₂ O ₂ | | C ₁₆ H ₃₂ O ₂ | C ₁₆ H ₃₂ O ₂ | | C ₁₆ H ₃₂ O ₂ | C ₁₆ H ₃₂ O ₂ | C ₁₆ H ₃₂ O ₂ | C ₁₆ H ₃₂ O ₂ | C ₁₆ H ₃₂ O ₂ | | |
| | | | | | | | | C ₁₇ H ₃₄ O ₂ | C ₁₇ H ₃₄ O ₂ | | C ₁₇ H ₃₄ O ₂ | C ₁₇ H ₃₄ O ₂ | C ₁₇ H ₃₄ O ₂ | C ₁₇ H ₃₄ O ₂ | | |
| | | | | | | | | C ₁₈ H ₃₆ O ₂ | C ₁₈ H ₃₆ O ₂ | | C ₁₈ H ₃₆ O ₂ | C ₁₈ H ₃₆ O ₂ | C ₁₈ H ₃₆ O ₂ | C ₁₈ H ₃₆ O ₂ | | |
| | SERIE 04 | Oxygenated compounds with aliphatic chains longer than the initial reactant. | Esters | | | | | C ₉ H ₁₇ DO ₂ * | C ₉ H ₁₅ D ₂ O ₂ * | C ₁₁ H ₂₁ DO ₂ * | C ₁₁ H ₁₉ D ₂ O ₂ * | C ₁₃ H ₂₅ DO ₂ * | C ₁₃ H ₂₃ D ₂ O ₂ * | C ₁₅ H ₂₉ DO ₂ * | C ₁₅ H ₂₇ D ₂ O ₂ * | C ₁₇ H ₃₃ DO ₂ * |
| | | | | | | | C ₁₀ H ₁₉ DO ₂ * | C ₁₀ H ₁₇ D ₂ O ₂ * | C ₁₂ H ₂₃ DO ₂ * | C ₁₂ H ₂₁ D ₂ O ₂ * | C ₁₄ H ₂₉ DO ₂ * | C ₁₄ H ₂₇ D ₂ O ₂ * | C ₁₆ H ₃₃ DO ₂ * | C ₁₆ H ₃₁ D ₂ O ₂ * | C ₁₈ H ₃₉ DO ₂ * | C ₁₈ H ₃₇ D ₂ O ₂ * |
| | | | | | | | C ₁₁ H ₂₁ DO ₂ * | C ₁₁ H ₁₉ D ₂ O ₂ * | C ₁₃ H ₂₅ DO ₂ * | C ₁₃ H ₂₃ D ₂ O ₂ * | C ₁₅ H ₃₁ DO ₂ * | C ₁₅ H ₂₉ D ₂ O ₂ * | C ₁₇ H ₃₅ DO ₂ * | C ₁₇ H ₃₃ D ₂ O ₂ * | C ₁₉ H ₄₁ DO ₂ * | C ₁₉ H ₃₉ D ₂ O ₂ * |
| | | | | | | | C ₁₂ H ₂₃ DO ₂ | C ₁₂ H ₂₁ D ₂ O ₂ | C ₁₄ H ₂₇ DO ₂ | C ₁₄ H ₂₅ D ₂ O ₂ | C ₁₆ H ₃₁ DO ₂ | C ₁₆ H ₂₉ D ₂ O ₂ | C ₁₈ H ₃₇ DO ₂ | C ₁₈ H ₃₅ D ₂ O ₂ | C ₂₀ H ₄₃ DO ₂ | C ₂₀ H ₄₁ D ₂ O ₂ |
| | | | | | | | C ₁₃ H ₂₅ DO ₂ | C ₁₃ H ₂₃ D ₂ O ₂ | C ₁₅ H ₂₉ DO ₂ | C ₁₅ H ₂₇ D ₂ O ₂ | C ₁₇ H ₃₃ DO ₂ | C ₁₇ H ₃₁ D ₂ O ₂ | C ₁₉ H ₃₉ DO ₂ | C ₁₉ H ₃₇ D ₂ O ₂ | C ₂₁ H ₄₅ DO ₂ | C ₂₁ H ₄₃ D ₂ O ₂ |
| | | | | | | | C ₁₄ H ₂₇ DO ₂ | C ₁₄ H ₂₅ D ₂ O ₂ | C ₁₆ H ₃₁ DO ₂ | C ₁₆ H ₂₉ D ₂ O ₂ | C ₁₈ H ₃₇ DO ₂ | C ₁₈ H ₃₅ D ₂ O ₂ | C ₂₀ H ₄₃ DO ₂ | C ₂₀ H ₄₁ D ₂ O ₂ | C ₂₂ H ₄₉ DO ₂ | C ₂₂ H ₄₇ D ₂ O ₂ |
| | | | | | | | C ₁₅ H ₂₉ DO ₂ | C ₁₅ H ₂₇ D ₂ O ₂ | C ₁₇ H ₃₃ DO ₂ | C ₁₇ H ₃₁ D ₂ O ₂ | C ₁₉ H ₃₉ DO ₂ | C ₁₉ H ₃₇ D ₂ O ₂ | C ₂₁ H ₄₅ DO ₂ | C ₂₁ H ₄₃ D ₂ O ₂ | C ₂₃ H ₅₁ DO ₂ | C ₂₃ H ₄₉ D ₂ O ₂ |
| | | | | | | | C ₁₆ H ₃₁ DO ₂ | C ₁₆ H ₂₉ D ₂ O ₂ | C ₁₈ H ₃₇ DO ₂ | C ₁₈ H ₃₅ D ₂ O ₂ | C ₂₀ H ₄₃ DO ₂ | C ₂₀ H ₄₁ D ₂ O ₂ | C ₂₂ H ₄₉ DO ₂ | C ₂₂ H ₄₇ D ₂ O ₂ | C ₂₄ H ₅₅ DO ₂ | C ₂₄ H ₅₃ D ₂ O ₂ |
| | | | | | | | | | C ₁₉ H ₃₉ DO ₂ | C ₁₉ H ₃₇ D ₂ O ₂ | C ₂₁ H ₄₅ DO ₂ | C ₂₁ H ₄₃ D ₂ O ₂ | C ₂₃ H ₅₁ DO ₂ | C ₂₃ H ₄₉ D ₂ O ₂ | C ₂₅ H ₅₇ DO ₂ | C ₂₅ H ₅₅ D ₂ O ₂ |
| | | | | | | | | | C ₂₀ H ₄₁ DO ₂ | C ₂₀ H ₃₉ D ₂ O ₂ | C ₂₂ H ₄₇ DO ₂ | C ₂₂ H ₄₅ D ₂ O ₂ | C ₂₄ H ₅₃ DO ₂ | C ₂₄ H ₅₁ D ₂ O ₂ | C ₂₆ H ₅₉ DO ₂ | C ₂₆ H ₅₇ D ₂ O ₂ |
| | | | | | | | | | | | C ₂₃ H ₄₇ DO ₂ | C ₂₃ H ₄₅ D ₂ O ₂ | C ₂₅ H ₅₃ DO ₂ | C ₂₅ H ₅₁ D ₂ O ₂ | C ₂₇ H ₅₉ DO ₂ | C ₂₇ H ₅₇ D ₂ O ₂ |
| | | | | | | | | | | | C ₂₄ H ₄₉ DO ₂ | C ₂₄ H ₄₇ D ₂ O ₂ | C ₂₆ H ₅₅ DO ₂ | C ₂₆ H ₅₃ D ₂ O ₂ | C ₂₈ H ₆₁ DO ₂ | C ₂₈ H ₅₉ D ₂ O ₂ |
| | | | | | | | | | | | | | C ₂₇ H ₅₇ DO ₂ | C ₂₇ H ₅₅ D ₂ O ₂ | C ₂₉ H ₆₃ DO ₂ | C ₂₉ H ₆₁ D ₂ O ₂ |
| | | | | | | | | | | | | | C ₂₈ H ₅₉ DO ₂ | C ₂₈ H ₅₇ D ₂ O ₂ | C ₃₀ H ₆₅ DO ₂ | C ₃₀ H ₆₃ D ₂ O ₂ |
| | | | | | | | | | | | | | | | C ₃₁ H ₆₇ DO ₂ | C ₃₁ H ₆₅ D ₂ O ₂ |
| | | | | | | | | | | | | | | | C ₃₂ H ₆₉ DO ₂ | C ₃₂ H ₆₇ D ₂ O ₂ |

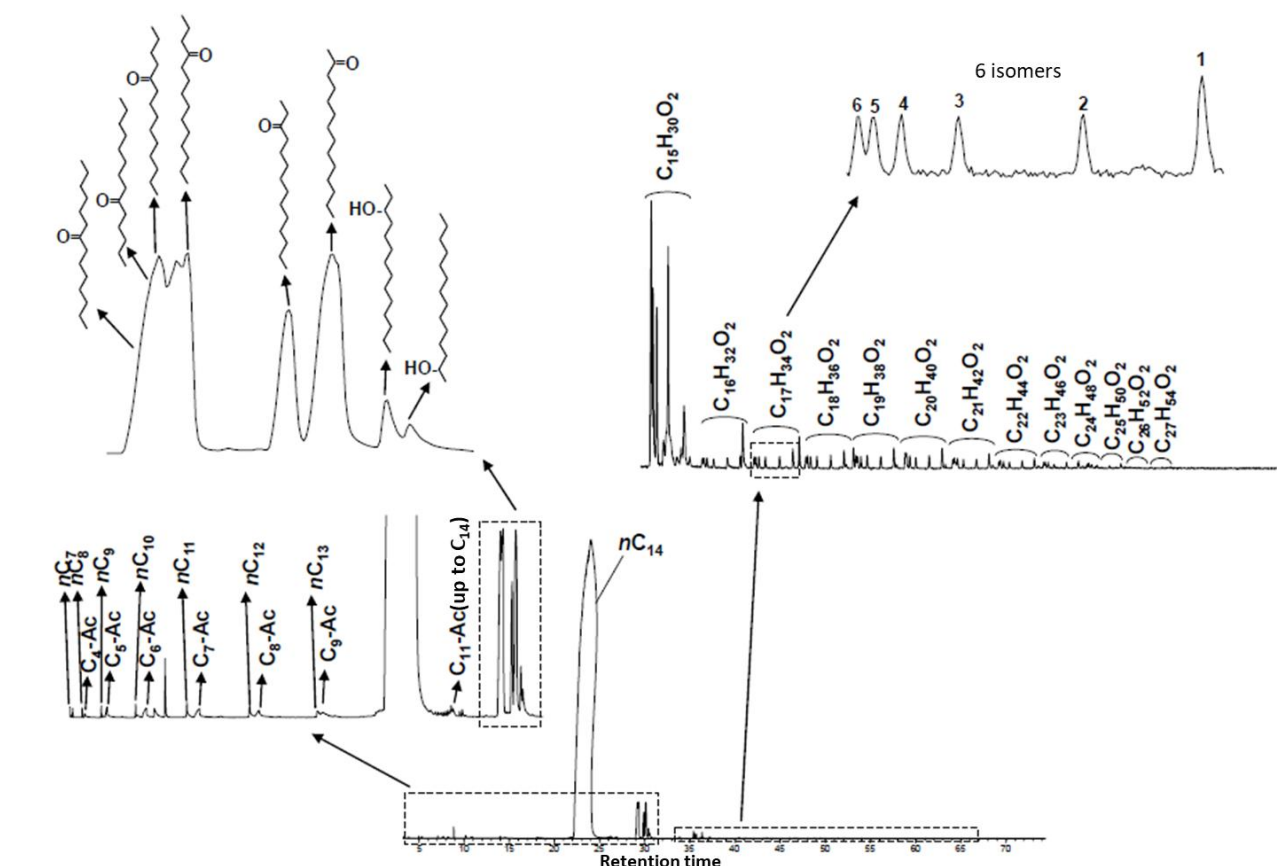


Figure 6: Chromatogram of the products after pyrolysis of the n-tetradecane in the presence of D_2O and uranium at 200°C, 500 bar (Split). Cn-CA: Carboxylic Acids with n carbons

All the reactions products for the four series of experiments are resumed in a master table proposed in an annex (Annex 1)

4.4 Dominant reactions

Analysis by GC-MS enables the percentage of product formed to be qualitatively determined by the ratio between the abundance of the initial reagent at the end of the experiment and the abundance of products. Table 3 shows that 85.07% of the reagent is still present at the end of the experiment in the presence of D_2O compared to 88.21% in the deuterated water-free experiment. However, there are only 0,14% esters formed in the presence of D_2O compared to 0,55% in waterless experiments.

Table 3: Percentage calculated by measuring by GC-MS the abundance of products formed at the end of the experiment at 200°C, 500 bar (ca: carboxylic acid, al: alcohol, ke: ketone).

| Experiment | Initial reactant (%) | Oxygenated products (%) | ca+al+ke (%) | Esters (%) |
|---|----------------------|-------------------------|--------------|------------|
| <i>n</i> -pentane + UO ₃ 2 months | 100,00 | 0,00 | 0,00 | 0,00 |
| <i>n</i> -pentane + UO ₃ + D ₂ O months | 100,00 | 0,00 | 0,00 | 0,00 |
| <i>n</i> -hexane + UO ₃ 2 months | 100,00 | 0,00 | 0,00 | 0,00 |
| <i>n</i> -hexane+ UO ₃ + D ₂ O 2 months | 87,45 | 12,55 | 12,55 | 0,00 |
| <i>n</i> -octane + UO ₃ 2 months | 88,21 | 11,79 | 11,24 | 0,55 |
| <i>n</i> -octane + UO ₃ + D ₂ O 2 months | 85,07 | 14,93 | 14,79 | 0,14 |
| <i>n</i> -decane+ UO ₃ 2 months | 99,82 | 0,18 | 0,18 | 0,00 |
| <i>n</i> -decane+ UO ₃ + D ₂ O months | 99,56 | 0,44 | 0,44 | 0,00 |
| <i>n</i> -dodecane + UO ₃ 2 months | 85,61 | 14,39 | 13,36 | 1,03 |
| <i>n</i> -dodecane + UO ₃ + D ₂ O 2 months | 84,83 | 15,17 | 14,61 | 0,56 |
| <i>n</i> -tetradecane + UO ₃ 2 months | 84,14 | 15,86 | 14,60 | 1,27 |
| <i>n</i> -tetradecane + UO ₃ + D ₂ O 2 months | 86,52 | 13,48 | 11,84 | 1,64 |
| <i>n</i> -hexadecane + UO ₃ 2 months | 90,95 | 9,05 | 8,31 | 0,74 |
| <i>n</i> -hexadecane + UO ₃ + D ₂ O 2 months | 84,95 | 15,05 | 14,17 | 0,88 |

5 DISCUSSION

No organic matter except the initial reagent (and contaminants) is observed in the reference experiments. The different *n*-alkanes are stable under these conditions or their conversion is too weak to be observed regardless their chain length.

For the experiments of *n*-alkane pyrolysis in the presence of uranium, the formation of oxygenated products with aliphatic chain length increase has been shown for all the *n*-alkanes studied. Moreover, the more the length of the *n*-alkane chain increases, the more we observe products of pyrolysis and the more the conversion is important.

We have chosen to focus the first part of our discussion on the *n*-octane because it is the first reagents showing the formation of oxygenated products and a chain length increase.

The conversion of *n*-octane becomes observable when it is pyrolyzed in the presence of uranium. The presence of deuterated water alone does not cause changes in the initial

reagent indicating that the presence of uranium speed-up existing reaction and/or induces new reactions.

5.1 Reactivity of the mixture *n*-octane – uranium

5.1.1 *Initiation of the mechanism*

The presence of uranium in the reaction medium is most likely the cause of the initiation of reactions leading to the high diversity of degradation products observed. The redox mechanism is the mechanism of initiation of the reaction process: the reduction of uranium releasing oxygen atoms on the one hand and the oxidation of organic compound generating free radicals on the other hand (figure 7 (1). The numbers in parentheses indicate the reaction in Figures 7 to 10.). Landais (1996) [39] summarizes the oxidation of organic matter during the reduction of uranium by the following chemical reaction: $2(\text{RH}) + \text{UO}_2^{2+} \rightarrow 2\text{R}^\bullet + 2\text{H}^+ + \text{UO}_2$

The release of oxygen atoms into the reaction medium makes the latter oxidizing. The contact between oxygen atoms and *n*-alkane boosts auto-oxidation processes and trigger oxidation of the *n*-alkane.

5.1.2 *Radical mechanism*

Mechanism involving free radicals generated from *n*-alkanes in auto-oxidation processes are well described in literature [40-42]. Especially, Faure et al. (2003) [42] have studied in detail the low temperature air oxidation of *n*-alkanes in the presence of Na-smectite. Their results achieved with a different substrate are very similar to those presented here.

In the case of *n*-octane, the free radicals can be generated during the oxidation reaction by metathesis and locate into four different positions (R^\bullet) (Figure 7 (1)).

Radicals (R^\bullet) then react with molecular oxygen and form peroxide radicals (ROO^\bullet) (Figure 7 (2)) inducing there after successive radical reactions. Then peroxide radicals stabilize into

hydroperoxide (Figure 7 (3)) by incorporation of a hydrogen atom and production of other free radicals. From this point three sets of reactions corresponding to the creation of the three different families of detected compounds can occur. The first set, preservation of the aliphatic chain (corresponding to compounds having preserved the same number of carbon that the initial *n*-alkane) is described in Faure et al. (2003) [42]. Formation of hydroperoxide and homolytic cleavage leads to the formation of alcohol then ketones with all the position isomers we observed in our chromatograms (figure 7 and 8).

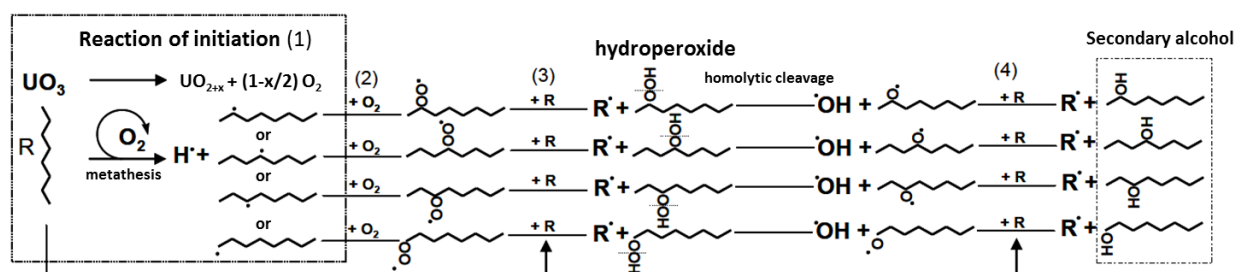


Figure 7: Reaction pathway showing the secondary alcohol formation

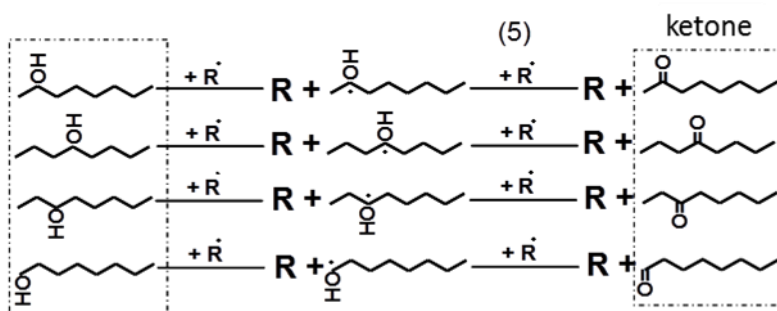


Figure 8: Reaction pathway showing the ketone formation

The second set of reactions corresponds to the reduction of the aliphatic chain length (figure 9). A β -cleavage can also occur on the peroxides radicals (ROO^\bullet) (figure 9 (6)) and leads to the production of aldehydes as well as an aliphatic fragment having a free radical located on the last carbon atom of the chain. The oxidation of the aldehyde can induce the production

of carboxylic acids (figure 9 (7)) with carbon chain shorter than initial *n*-alkane indicating that decompositions processes occur on the aliphatic chain.

A homolytic cleavage can occur once again inducing in a first step the production of a ketone radical (figure 9 (8)) and in a second stage the formation of a peroxide radical by oxidation (figure 9 (9)). By the same mechanisms, two peroxides radical can be obtained according to the side of the chain (short or long side) where β -cleavage occurred. In a third step of auto-oxidation, the different peroxides radicals will capture hydrogen of the initial reactant (in our case *n*-octane being the most abundant compound into the reaction medium). *N*-octane will be transformed by this reaction into radicals and will be able to react and follow the (1) - (9) reaction mechanism. The rupture of the weak oxygen-oxygen bond by homolytic cleavage (Figure 9 (10)) boosts a last auto-oxidation process with *n*-octane which will induce the formation of carboxylic acids.

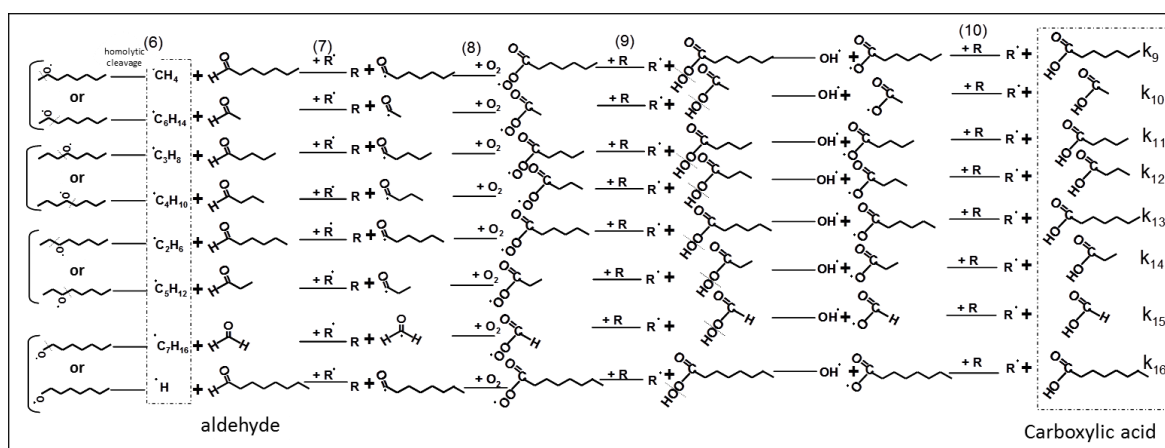


Figure 9: Reaction pathway showing the formation of the carboxylic acids

The third set of reactions corresponds to an increase of the length of the aliphatic chain and the production of esters (figure 10 (11)). Formation of esters with carbon chains longer than the initial *n*-alkanes indicates that addition processes occur on the aliphatic chains. Additions of a carboxylic acid and an alkanol will produce the formation of esters with water release. Triplets of isomers with molecular masses equivalent to CH_2 (14 g/mol) are detected. These

numbers of isomers per group are correlated with the numbers of ketones and alkanols and would correspond to the dominant positions of the functional groups on the aliphatic chain.

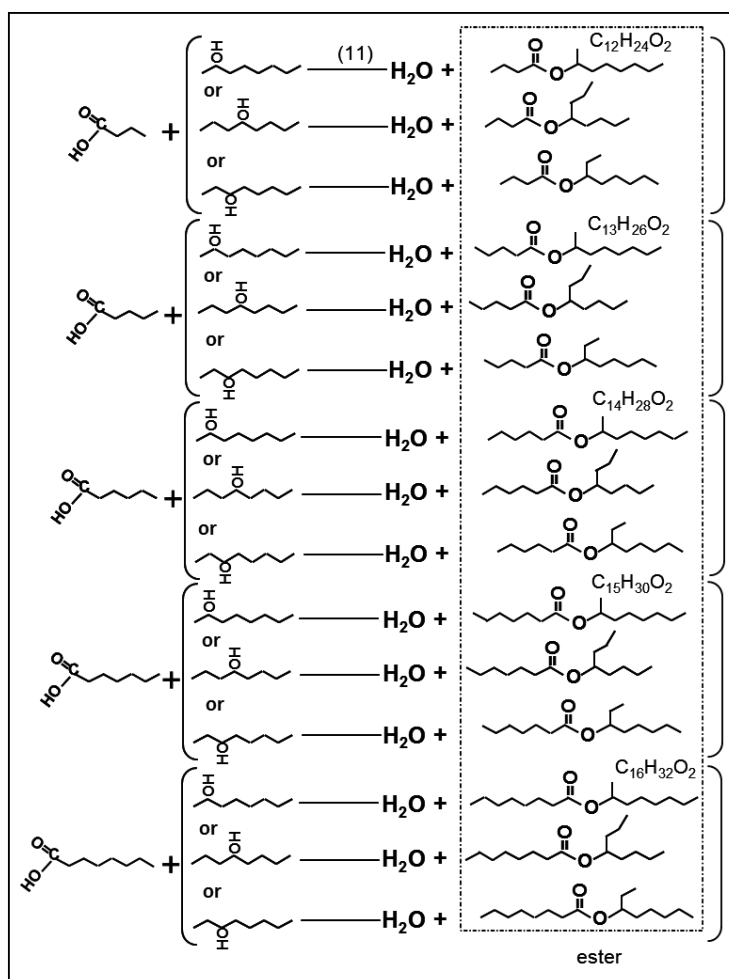


Figure 10: Reaction pathway showing the formation of esters

5.1.3 Reactivity of mixture *N*-octane – uranium- D_2O

In the experiment with deuterated water there is no shift of mass for the alkanols unlike for the esters, carboxylic acids and ketone where there is a shift of mass of one or two unit(s) which indicates an involvement of water as an oxidizing agent ((3), (4), (9) and (10)) replacing auto-oxidations of *n*-octane by an oxidation by deuterated water. The deuterated water being an abundant compound of the medium, the probability that one of the free radical compounds interacts with water is high, leading to incorporation of deuterium in organic compounds, in contrast with the experiments without water where the latter is only a

marginal product. Moreover, having deuterium atoms in the alkyl chain, due to an isomerization reaction in which a hydrogen atom of the chain is exchanged with the deuterium atom of a functional group, suggests the use of water as an oxidizing agent.

The assumption of a neutralization related to the presence of water as a reactive component of the ester-forming reaction can be considered due to the fact that the reaction with *n*-octane has a higher yield in the presence of water but a smaller quantity of products formed.

5.2 Extension of *n*-octane oxidation mechanisms in the presence of uranium to others organic compounds

Salze (2008) [43] obtained similar compounds after the pyrolysis of *n*-alkanes, *n*-dec-1-ene and butyl-cyclohexane. The hypothesis of a reaction pathway identical to that of *n*-octane can be proposed: i) Oxidation of organic compounds by uranium to form alkanols then carboxylic acids and ketones. ii) Addition reactions leading to the formation of esters for *n*-alkanes reagents.

The low abundance of these ester molecules relative to the oxygenated molecules in GC-MS analyses results in a low yield of these addition reactions against oxidation-reduction reactions leading to the formation of alkanols, ketones and carboxylic acids (Table 2).

The duration of our experiments is too short to involve the role of radiolysis. Schlepp (2000) [44] attributed the changes in organic matter of Lodève deposit to the effect of radiolysis alone. In this study it was shown that the oxidation of the organic matter occurred in the short term (less than 2 months at 200°C and 500 bar). Faure (2003) showed the catalytic role of clays on the thermal degradation of hydrocarbons at low temperature.

Thus, the oxidative processes studied in this present work seem to have an important role in hydrocarbon degradation. However, this degradation does not seem to be the result of a

single process but of a combination of processes such as oxidative processes, radiolysis and catalytic phenomena.

When comparing this study carried out in the presence of an oxidizing medium with other works investigating the thermal cracking of alkanes [45], some similarities can be found: mechanisms involved are of free-radical type leading to products both smaller and larger than the starting material. But reactions are very different leading here to oxygenated compounds.

Weres (1988) have studied the hydrous pyrolysis of alkanes in presence of clay. They have reported that adding water shifted the process to a free radical mechanism and eliminated the catalytic effect of clay. Experiments carried out here with water and uranium do not exhibit the same inhibition effect of water probably because uranium and clay have a different reactivity.

6 CONCLUSIONS

This paper presents the first steps of the chemical behaviour of uranium in the ternary system Uranium - Organic Matter - D_2O under conditions close to the genesis of a uranium deposit. The study of organic compounds and their evolution revealed several phenomena: i) The following redox reaction (reduction of uranium and oxidation of organic matter) is the initiation mechanism of the reaction pathway and generates free radicals. ii) The oxidation of n-octane leads to the production of alcohol, ketones, aldehydes, carboxylic acids and esters molecules in different configurations and proportions. iii) The reactions with n-alkanes made it possible to show an increase in the phenomenon of gradual oxidation of the organic matter starting from the compound C6. The parameter of increase in the aliphatic chain is a

major factor of the increase in the oxidizing ability of the medium on the organic compound in balance with uranium trioxide.

The reaction model of n-octane passing through radical, oxidation and addition reactions could be extended to all compounds studied.

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