GENIORS

Research and Innovation Action (RIA)

This project has received funding from the European
Union's Horizon 2020 research and innovation programme
under grant agreement No 755171.

Start date : 2017-06-01 Duration : 48 Months
http://geniors.eu/

Destruction of organic

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GENIORS - Contract Number: 755171

Project officer: Roger Garbil

Document title	Destruction of organic
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Number of pages	11
Document type	Deliverable
Work Package	WP2
Document number	D2.3
Issued by	CEA
Date of completion	2020-05-15 13:13:50
Dissemination level	Public

Summary

The present deliverable collects the studies carried out by UNIPR and CEA concerning the thermal stability of the organic reagents used in the radioelements separating processes. The compounds studied are (i) stripping agents, their derivatives and their synthesis reagent with azide function (PTD, PTT (PyTriTetraol), PT EtHex, 2-ethyl-hexyl azide and 1-azido-4-iodo butane), and (ii) TODGA, pure or diluted in TPH, in contact with nitric acid. The stability of the compounds is studied by calorimetry methods (DSC and reaction calorimetry).

Approval

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CONTENT

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ABSTRACT

The present deliverable collects the studies carried out by UNIPR and CEA concerning the thermal stability of the organic reagents used in the radioelements separating processes. The compounds studied are (i) stripping agents, their derivatives and their synthesis reagent with azide function (PTD, PTT (PyTriTetraol), PT EtHex, 2-ethyl-hexyl azide and 1-azido-4-iodo butane), and (ii) TODGA, pure or diluted in TPH, in contact with nitric acid. The stability of the compounds is studied by calorimetry methods (DSC and reaction calorimetry).

INTRODUCTION

The stability of the organic reagents (stripping agent, extracting molecules and diluent) developed for the radioelements separating processes is an essential characteristic which can guide the choice of the molecules. While the degradation of compounds by hydrolysis and radiolysis under normal process operating conditions has already been the subject of numerous studies, other important aspects must also be considered in order to guarantee the safety of all the operations. In the context of these studies, it is a question of:

- The intrinsic reactivity of pure compounds, which can be crucial for example in the event of accumulation of the compounds in some parts of the process, or during their handling or their synthesis. The main compounds identified, are organic derivatives of azides, issuing from pyridine-2,6-bis (triazolyl propanol), the main hydrophilic stripping agent currently studied in GENIORS, as well as some analogous derivatives and reagents used for its synthesis.
- The reactivity of organic molecules under more severe conditions than those of the separating operations, in particular for the high acidities and/or high temperatures encountered during the treatment of liquid effluents. The scenario envisaged here, resulting from a degraded situation, is the presence of an organic phase (here *N*,*N*,*N*',*N*'-tetraoctyldiglycolamide (TODGA)) in an evaporator for the nitric acid concentration.

These two studies use calorimetry techniques, the DSC for the first, and the reaction calorimetry for the second.

THERMAL STABILITY OF PTD

(UNIPR: A. Casnati, M. C. Gullo, F. Sansone, L. Baldini)

A literature search for the implementation of a method to study the safety of PTD and of the chemicals for its production evidenced that it is well known that azide salts (e.g. AgN_3, $Pb(N_3)_2$) and even some azido derivatives of some organic compounds might show shock sensitive or explosion propagation behaviours. Many of the inorganic azides form ionic or partly ionic solids, so that an electron-transfer mechanism must operate during some stage of the decomposition to metal and nitrogen gas. In order to explain the difference in stability it is necessary to know the electronic levels in the solid concerned. On the other hand, the covalent azides such as hydrogen azide or hydrazoic acid, HN_3, decompose by a free-radical mechanism.

Organic azides are far less dangerous than inorganic ones, but care should be taken in their handling and preservation. Usually a practical so called “rule of six” might be use to qualitatively evaluate hazards: six carbons (or other atoms of about the same size) per energetic functional group (azide, diazo, nitro, etc.) should provide enough dilution to render the compound relatively safe to work with given appropriate controls and safety procedures. More in details, the “Carbon to Nitrogen Ratio” might be used. The total number of nitrogen atoms

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in the organic azide should not exceed that of carbon. The following ratio is used to help evaluate if an azide is stable enough to work with, with N equal to the number of atoms: $CO/N = (N_{Carbon} + N_{Oxygen}) / N_{Nitrogen}$

- When **CO/N > 3** the organic azide can be isolated and stored in its pure form (up to 20 grams).
- Azides with **1 > CO/N > 3** can be synthesized and isolated, but should be stored below room temperature at no more than 1 M concentration and at a maximum of 5 grams of material.
- Organic azides with **CO/N < 1** should never be isolated. It may be synthesized if the azide is a transient intermediate species AND the limiting reagent in the reaction mixture AND is limited to a maximum quantity of 1 gram.[1,2]

We have therefore identified Differential Scanning Calorimetry (DSC) and Accelerating Rate Calorimetry (ARC) as interesting and informative techniques to assess preliminary hazard level of organic azides and the ligand of interest (PTD).

Especially from DSC it is possible to assess the SS and EP parameters.[3] In fact, the test method evaluates the thermal behaviour of a material from the total measured energy (Q, $cal \cdot g^{-1}$) and onset temperature (T, °C) of exothermic decomposition.

$$SS = \log Q - 0.72 \cdot \log (T - 25) - 0.98$$

$$EP = \log Q - 0.38 \cdot \log (T - 25) - 1.67$$

According to these equations, if the value for Shock sensitivity (SS) or Explosion Propagation (EP) are ≥ 0.00, then the material is predicated to be shock sensitive or demonstrate explosive propagating properties, respectively.

The UNIPR partner, was in charge to synthesize (Figure 1) the pyridine-2,6-bis(triazolyl propanol) ligand, also named **PyTriDiol** or, shortly, **PTD**, used at POLIMI to carry out all the experimental activity reported in this first part. The synthesis starts with the commercially available 2,6-dibromopyridine **1** which was coupled under Sonogashira conditions with trimethylsilyl acetylene to afford compound **2**. The latter compound was deprotected to 2,6-diethynyl pyridine **3** which was clicked with 3-azido propanol **4** under Huisgen cycloaddition conditions and using a microwave oven. This synthesis is currently carried out on a 2-3 gram scale and work should be done in the future to scale-up the preparation and especially purification of the intermediates and final compound.

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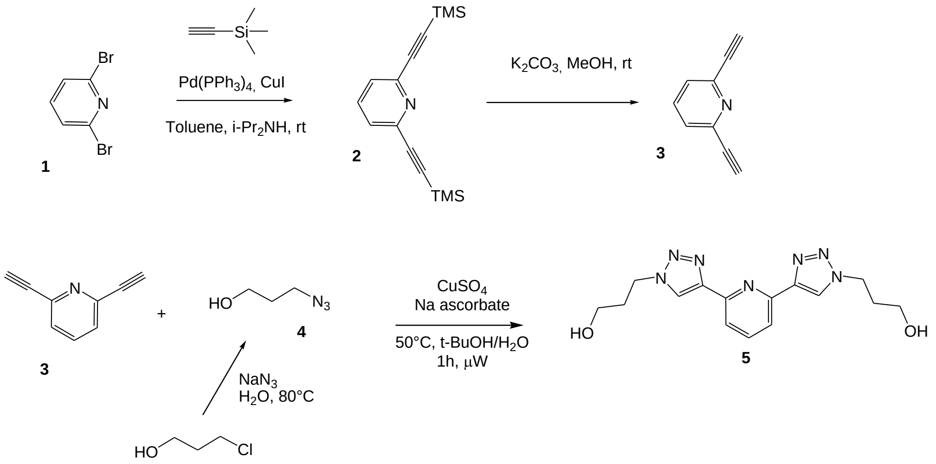
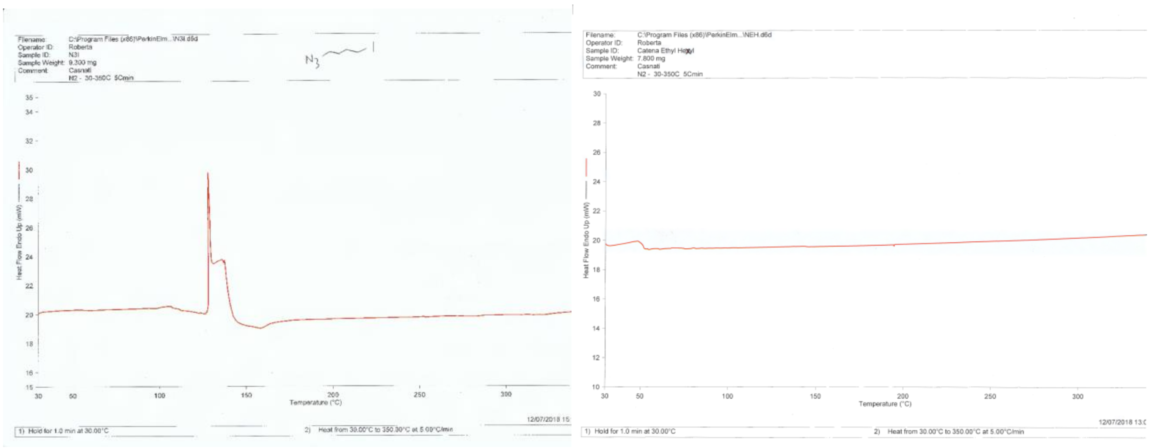


Figure 1: Synthesis of PTD ligand.

We have therefore carried out several DSC experiment, in particular using PTD (the most important hydrophilic stripping agent currently studied in GENIORS), PTT (PyTriTetraol), PT EtHex (a lipophilic version of PTD), 2-ethyl-hexyl azide and an azides, $ICH_2CH_2CH_2CH_2N_3$, with a structure similar to that used for the synthesis of PTD. We could not use directly the azide employed in the synthesis of PTD since the latter is rather volatile and suddenly evaporates from the sample escaping from the heating chamber.

A similar behavior was shown by 4-iodo-butane azide $ICH_2CH_2CH_2CH_2N_3$, which showed a slightly endothermic peak around 130 °C due to evaporation of the sample (Figure 2 left). The thermogram of 2-ethyl-hexyl azide was, on the other hand, completely flat (Figure 2 right) indicating the absence of decomposition even at >250°C.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Operator ID: Roberta
Sample ID: N3I
Sample Weight: 9.300 mg
Comment: Casnati
N2 - 30-350C 5Cmin

1) Hold for 1.0 min at 30.00°C
2) Heat from 30.00°C to 350.00°C at 5.00°C/min

Filename: C:\Program Files (x86)\PerkinElm...\NEH.d6d
Operator ID: Roberta
Sample ID: Catena Ethyl Hexyl
Sample Weight: 7.800 mg
Comment: Casnati
N2 - 30-350C 5Cmin

1) Hold for 1.0 min at 30.00°C
2) Heat from 30.00°C to 350.00°C at 5.00°C/min

Figure 2: Thermograms of 4-iodopropane azide (left) and of 2-ethyl-hexyl azide (right).

Quite interestingly, PTD and PTT (Figure 3 left and right, respectively) both show only endothermic peaks resulting from melting of the solids (correspondence with melting points in a capillary was verified). Melting of PTT at 150-160°C was accompanied by slight decomposition (doubling of peaks). No exothermic peaks, however, probes of highly energetic decompositions with release of heat, were observed suggesting that triazoles are rather stable to heating.

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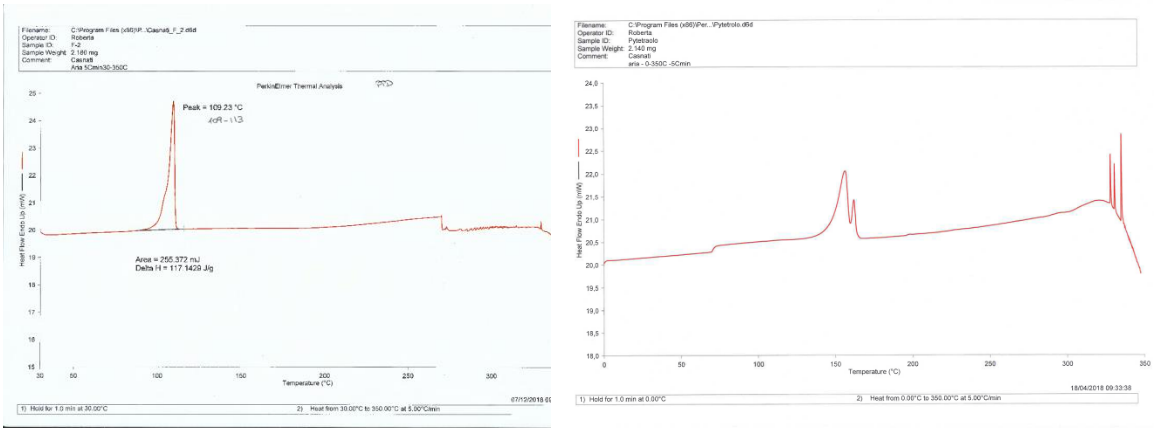

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Sample ID: F-2
Sample Weight: 2.180 mg
Comment: Casnati
Aria 5Cmin30-350C

Peak = 109.23 °C
108 - 113

Area = 255.372 mJ
Delta H = 117.1429 J/g

07/12/2018 09

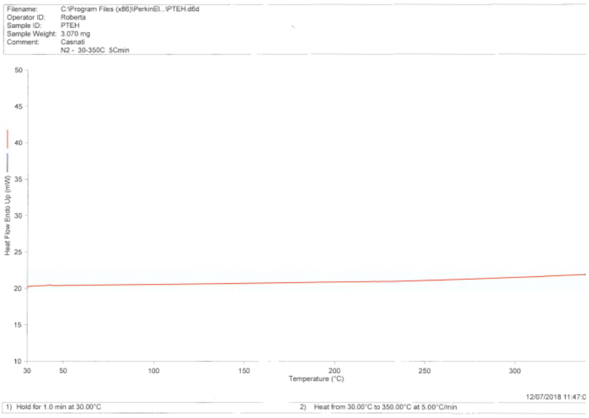
1) Hold for 1.0 min at 30.00°C
2) Heat from 30.00°C to 350.00°C at 5.00°C/min

Filename: C:\Program Files (x86)\Per...\Pytetrolo.d6d
Operator ID: Roberta
Sample ID: Pytetraolo
Sample Weight: 2.140 mg
Comment: Casnati
aria - 0-350C -5Cmin

18/04/2018 09:33:38

1) Hold for 1.0 min at 0.00°C
2) Heat from 0.00°C to 350.00°C at 5.00°C/min

Figure 3: Thermograms of PTD (left) and PTT (right) from room temperature to 250 °C.



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Sample ID: PTEH
Sample Weight: 3.070 mg
Comment: Casnati
N2 - 30-350C 5Cmin

12/07/2018 11:47:0

1) Hold for 1.0 min at 30.00°C
2) Heat from 30.00°C to 350.00°C at 5.00°C/min

Figure 4: Thermograms of PTEtHex from room temperature to 350 °C.

This was also confirmed with PTEtHex (Figure 4), the lipophilic form of PTD that shows a completely flat DSC profile. Being in fact a highly dense liquid at room temperature, even no endothermic peaks, signs of state transitions, are observed.

THERMAL STABILITY OF TODGA IN CONTACT WITH NITRIC ACID

(CEA: P. Pochon, M. C. Charbonnel)

The reactivity of TODGA was studied under conditions of high temperature and acidity, according to the hypothesis of an accidental introduction of organic phase in an evaporator during the concentration operations of the fission products (acidity of 2.5M) or recovery of nitric acid (acidity of 5 to 11M) in nuclear fuel reprocessing plants. Under these severe conditions, organic materials react with nitric acid by complex processes, often self-catalytic and generally very exothermic, with the participation of reactional intermediates such as alkyl nitrate. These reactions generate large quantities of non-condensable gases (nitrogen oxides and carbon oxides) and vapour due to temperature rise. Under certain conditions, in particular when the pressure can not be released quickly enough, the system evolves towards a violent reaction runaway. In the case of tributylphosphate (TBP), used as an extractant for the reprocessing of nuclear fuel in the uranium and plutonium extraction process (PUREX), these reactions are known as "Red-Oil" formation[4,5,6].

It is therefore important to study the reactivity of TODGA in conditions representative to evaporators (high temperature and high acidity). Two reaction calorimeters have been selected:

- The *Thermal Screening Unit* (TSU) from HEL[7], a non-adiabatic calorimeter for the comparison of chemical systems. Experimental conditions are the following ones: about 0.15 g of organic phase + 2 mL of nitric acid in an 8 cm^3 hastelloy cell,
- and the *Phi-Tec II* from HEL[8], a pseudo-adiabatic calorimeter for the acquisition of thermokinetics data usable by prediction models. Experimental conditions are: 0.5 to 1 mL of organic phase + 33 mL of nitric acid in a 100 cm^3 hastelloy cell.

A temperature ramp of 1°C/min was applied to the cell until the observation of a reaction characterized by a sudden increase in temperature and pressure during the measurement (Figure 5). From these evolutions, different thermokinetic quantities can be determined[9]: starting temperature of the reaction (T_{onset}), rates ($\Delta T/dt$ and $\Delta P/dt$), maximum values (ΔT_{max} and ΔP_{max}), enthalpy (ΔH) of the reaction (for pure compound) or total amount of energy released Q, activation energy E_a and pre-exponential factor A.

Because the reaction cells are closed, a reaction runaway takes place in all cases, unlike in the case of open reactors, which constitute temperate systems.

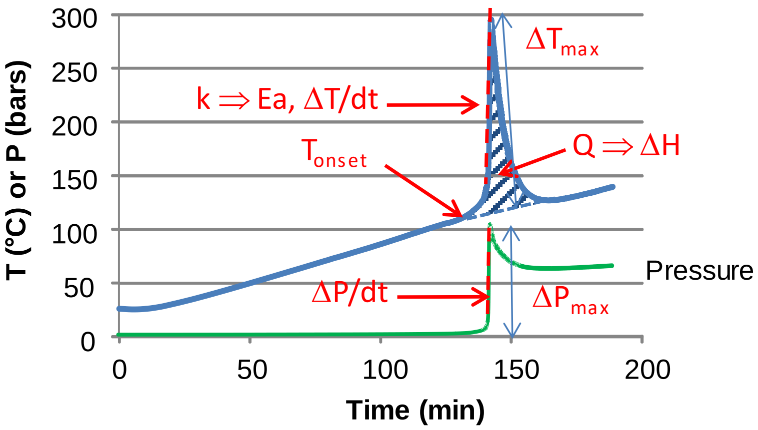

Figure 5: Typical changes in temperature and pressure obtained during organic phase decomposition tests in contact with nitric acid (example for the TSU calorimeter).

First experiments have been performed with the TSU calorimeter to compare the reactivity of TODGA, TEHDGA and TBP in the same conditions (0.16-0.17g of neat extractant in 2 mL HNO_3 11.4M). For a same mass of organic compound introduced, it seems that TODGA is more reactive than TEHDGA, and that the reactions for the DGA molecules accelerate faster and to higher values than TBP (Figure 6 left). For example, T_{onset} is about 10 °C lower, and the energy released per mole of organic compounds is nearly 5 times higher for TODGA than for TBP. The higher number of carbon in the TODGA molecule (36 compared to 12 for the TBP) may partly explain this difference. These compounds however exhibits both acceptable instability and reactivity.

The second series of experiments was devoted to the impact of the nitric acid concentration (2 mL of 2.5M, 5M, 7M, 5M, 9M and 11M nitric acid) on the reactivity of TODGA (0.18 g of neat compound) (Figure 6 right). Under these conditions, when the acidity of the aqueous phase increases, T_{onset} decreases from 120 °C to 108 °C. The apparent enthalpy of the reaction increases from 760 kJ/mol of TODGA to a threshold value around 5600 kJ/mol for 9M and 11M nitric acid (Figure 7 left). The energy of activation increases linearly while the speed of the reaction increases almost exponentially (Figure 7 right). The apparent stoichiometry of the reaction increases from 10 to 50 moles of HNO_3 consumed per mole of TODGA destroyed. The irregular evolution of the temperature and the pressure for the acidity at $[HNO_3] = 2.5M$ (slowest reaction) indicates that the decomposition of the TODGA is a very complex process.

In addition, the impact of the quantity or organic phase was studied. When the initial amount of TODGA increases, from 0.1 g to 0.3 g in 2 mL of 11M nitric acid, the starting temperature of the reaction (T_{onset}) decreases linearly, while the enthalpy, the activation energy and the rate of reaction increase also linearly (up to a threshold value of about 6000 kJ/mol for ΔH).

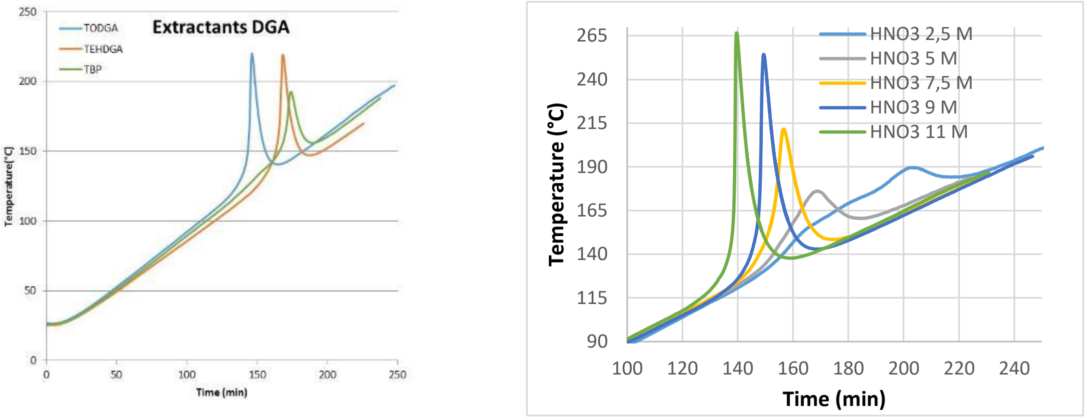

Figure 6 : Comparison of thermal reactivity of TODGA, TEHDGA and TBP in contact with 11.4M nitric acid (Experimental conditions: 2 mL HNO_3, 0.16-0.18 g of neat extractant, Ramp 1°C/min, cell 8 cm^3) (left) and thermal reactivity of TODGA in contact with 2.5M to 11M nitric acid (Experimental conditions: 2 mL HNO_3, 0.18 g TODGA, Ramp 1°C/min, cell 8 cm^3) (right). Only the evolutions of temperature are shown.

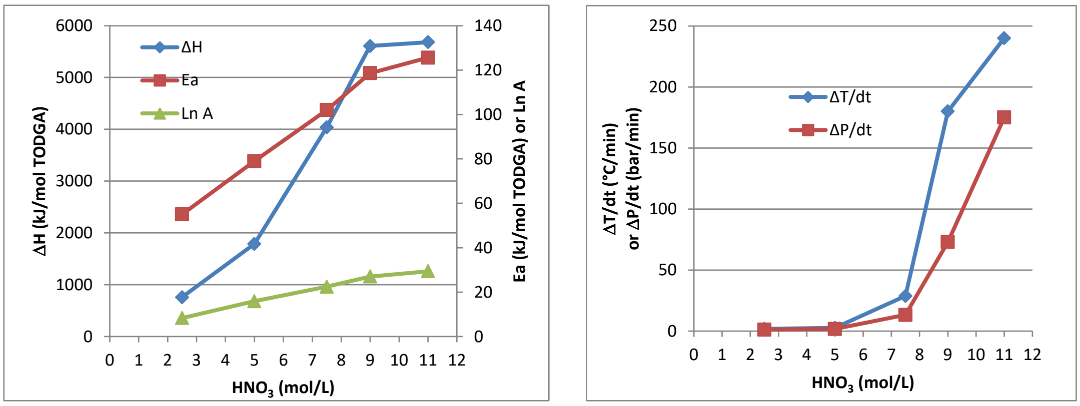

Figure 7 : Thermal reactivity of TODGA in contact with 2.5M to 11M nitric acid (Experimental conditions: 2 mL HNO_3, 0.18 g TODGA, Ramp 1°C/min, cell 8 cm^3). Enthalpy, energy of activation and pre-exponential factor (left), rate of temperature and pressure increase (right)

The last study carried out with the TSU calorimeter relates to the stability of TODGA solutions diluted in TPH, with equivalent concentrations to those involved in the separation processes:

- 0.1M TODGA in 5% octanol / 95% TPH equilibrated with 2.5M nitric acid,
- and 0.2M TODGA in 5% octanol / 95% TPH equilibrated with 2.5M nitric acid.

About 0.15 g of each organic solution in contact with 2 mL of 11M nitric acid were heated at 2°C/min. The temperature and pressure changes were compared with those obtained for neat TODGA.

The reactivity of TODGA solutions in TPH is higher than neat TODGA (Figure 8), a similar behavior to the one already observed with other extractants like TBP: the presence of TPH, and octanol, leads to lower reaction start-up temperatures around 105 °C instead of 120 °C measured with neat TODGA. However, the energy developed by the reaction is more important with neat TODGA, probably due to the greater proportion of carbon atoms in the organic solution. For example, in the selected conditions described, the energy of the reaction is 325 J/g with 0.2M TODGA in TPH, and 465 J/g with neat TODGA. The temperature and pressure rise rates are also higher with neat TODGA, respectively 1.1°C/s and 0.58 bar/s, against 0.31°C/s and 0.13 bar/s with 0.2M TODGA in TPH.

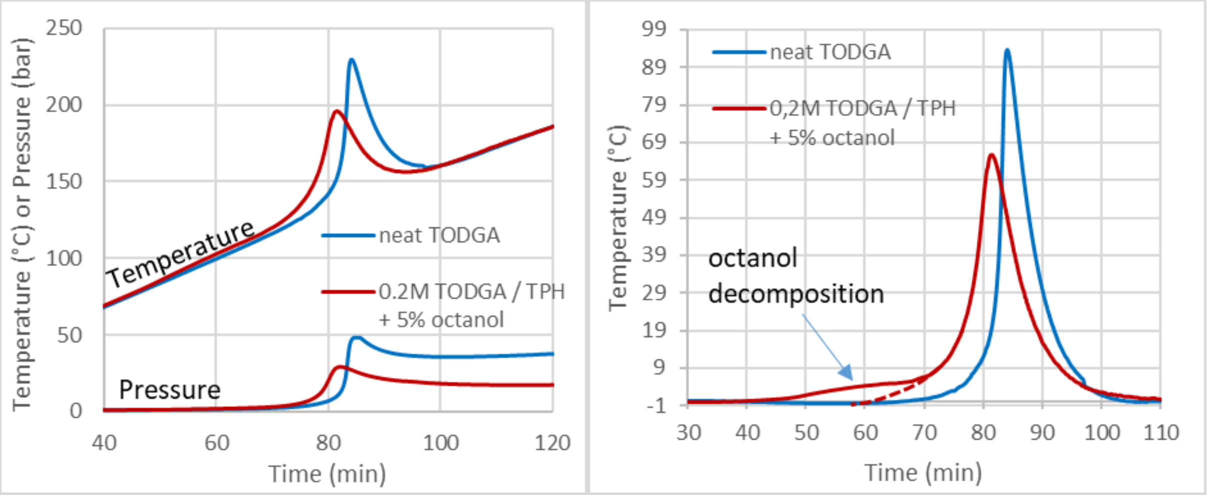

Figure 8. Thermal reactivity of neat TODGA and 0.2M TODGA in 95% TPH / 5% octanol in contact with 11M nitric acid: evolution of temperature and pressure (left) and evolution of temperature after subtraction of the baseline (right). (Experimental conditions: 2 mL HNO_3 11M, 0.15g TODGA solutions, Ramp 2°C/min, cell 8 cm^3)

After degradation of these organic solutions by γ radiolysis at 610 kGy, the behavior is similar to the non-irradiated solutions (Figure 9 left). Even for a solution of 0.2M TODGA in 5% octanol / 95% TPH equilibrated with 11M nitric acid, for which the higher acidity of the organic phase could lead to a greater formation of oxidizing species. Irradiation at around 600 kGy does not appreciably modify the stability of the chemical system. Therefore, whatever the initial acidity of the organic phase, an irradiation dose up to 600 kGy has no impact on the reactivity of the 0.1M or 0.2M TODGA solutions in TPH, in contact with 11M nitric acid at high temperature.

On the contrary, during an experiment carried out with neat TODGA equilibrated with 11 M nitric acid, a decrease in reactivity has been measured after irradiation at about 600 kGy (Figure 9 right). The enthalpy of the reaction measured by the TSU calorimeter are about 5000 kJ/mol of TODGA for the non-irradiated solution, and 3550 kJ/mol of TODGA for the irradiated solution. The reaction rate, characterized by the rate of rise in temperature and pressure, also decreases from 1.1°C/s and 0.6 bar/s to 0.45°C/s and 0.2 bar/s. This decrease in reactivity could be explained by the decrease of the concentration of the amide function in favor of less reactive functions with regard to nitric acid, and/or to a loss of potential energy of the chemical system due to the breaking of chemical bonds by radiolysis or hydrolysis. However, these hypotheses should be checked by more exhaustive studies.

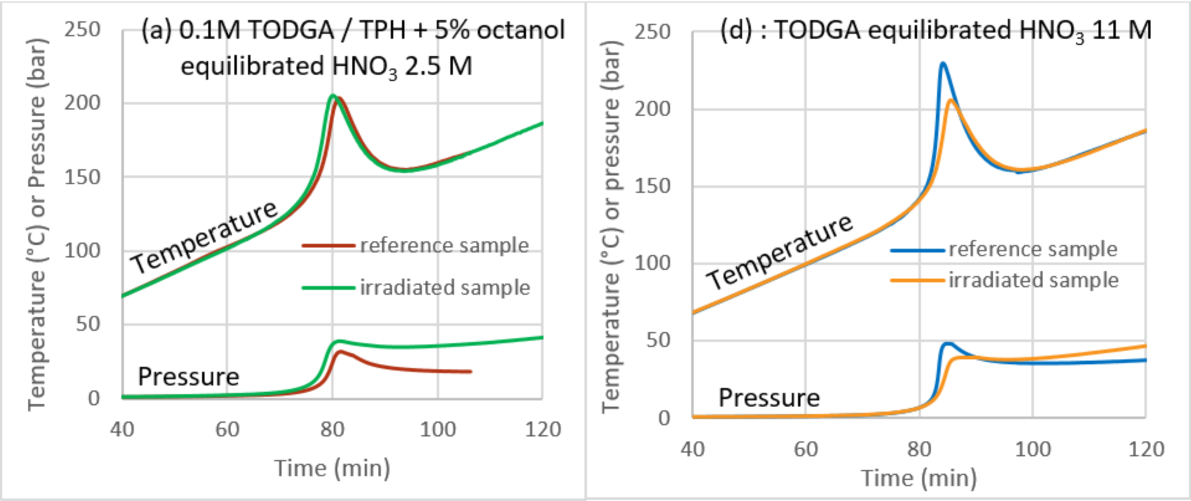

Figure 9. Thermal reactivity of irradiated or non-irradiated organic solutions in contact with 11M nitric acid: evolution of temperature and pressure for 0.1M TODGA in (95% TPH - 5% octanol) (left) or neat TODGA (right). Experimental conditions: 2 mL HNO_3 11M, 0.15g TODGA solutions, Ramp 2°C/min, cell 8 cm^3)

To obtain more reliable and accurate thermokinetics data of the reaction (T_{onset}, $\Delta T/dt$, $\Delta P/dt$, ΔH, Ea and pre-exponential factor A), experiments were performed in adiabatic conditions with the Phi-Tec II calorimeter. These quantitative data can be directly introduced in simulation models.

The experiments were carried out with neat TODGA in contact with nitric acid at different concentrations. The conditions tested were the following:

Organic phase	Aqueous phase	
Volume (mL)	Volume (mL)	C_{HNO3} (mol/L)
1	33	2.5 – 5 - 8.5 - 11
0.5 – 0.75 - 1	33	11

The values obtained are compared with those for neat TBP under the same experimental conditions.

With the same volume of organic phase, the enthalpy of the reaction increases from 5020 kJ/mol to about 6170 kJ/mol of TODGA when the acidity of the aqueous phase increases from 2.5M to 11M (Figure 10 left). In the same conditions, the enthalpy of the reaction for the TBP in contact with nitric acid increases from 1640 kJ/mol to 2130 kJ/mol. The factor 3 between TBP and TODGA could come from the fact that the TODGA molecule has 3 times more carbons than TBP, each carbon can produce energy by reacting with nitric acid to form CO_2. However further investigations on the final composition should be performed to better explain this behavior.

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The acidity has also an influence: an increase of the acidity raises the activation energy and the pre-exponential factor (Figure 10 left), and the reaction rate characterized by the rate of rise in temperature and pressure (Figure 10 right). On the contrary, the starting temperature of the reaction decreases from 138 °C to 120 °C when the acidity increases from 2.5M to 11M (Figure 10 right).

When the volume of organic phase increases from 0.5 mL to 1 mL (corresponding to a decrease of the volume ratio A/O from 66 to 33), the energies ΔH and E_a are similar (Figure 11 left), and the temperature T_{onset} stays constant around 120 °C. However, the total amount of energy of the reaction increases from 5.4 kJ to 9.3 kJ. The rates in temperature and pressure increase also quasi-linearly with the quantity of introduced TODGA (Figure 11 right).

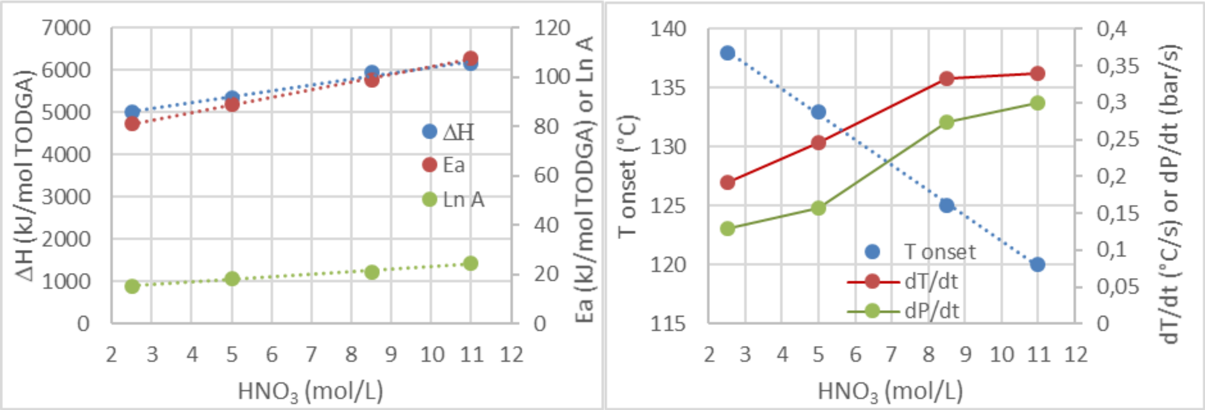

Figure 10. Thermal reactivity of TODGA in contact with 2.5M to 11M nitric acid in adiabatic conditions: enthalpy of the reaction, energy of activation and pre-exponential factor A (on the left), temperature of the reaction and rate of rise in temperature and pressure (on the right). Exp. conditions: VHNO$_3$ 2.5M to 11M 33 mL – V$_{TODGA}$ 1mL – Ramp 1°C/min – Volume of the cell 100 mL

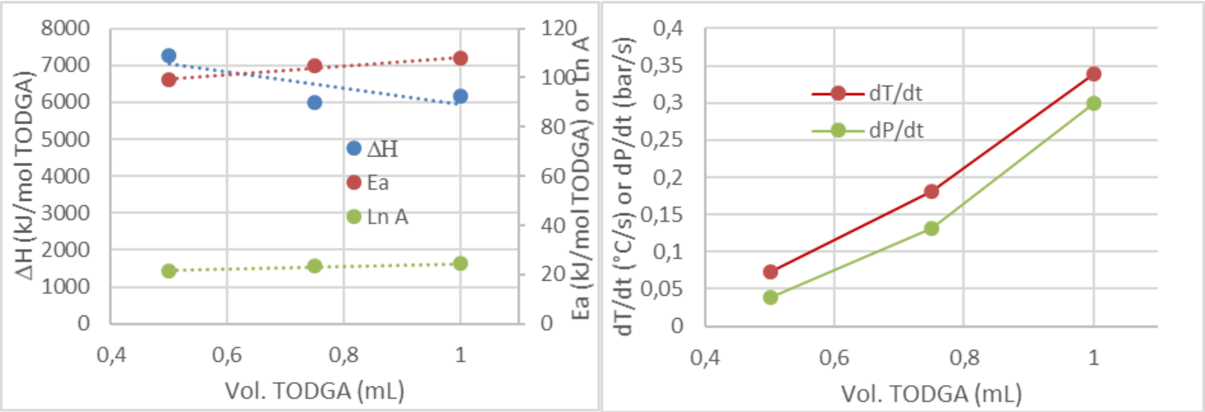

Figure 11. Thermal reactivity of TODGA in contact with 11M nitric acid in adiabatic conditions: enthalpy of the reaction, energy of activation and pre-exponential factor A (on the left), rise in temperature and pressure (on the right). Exp. conditions: V$_{HNO3\ 11M}$ 33 mL – V$_{TODGA}$ 0.5 mL to 1 mL – Ramp 1°C/min – Volume of the cell 100 mL

CONCLUSIONS

The stability of the organic reagents (stripping agent, extracting molecules and diluent) used in the radioelements separation processes is an important characteristic which must be verified in order to guarantee the safety of the operations.

Among the proposed compounds, attention was focused on those having azide functions because some are known to be very unstable. The thermal stabilities of pyridine-2,6-bis(triazolyl propanol) (PTD), PT EtHex, PyTriTetraol, 2-ethyl-hexyl azide and 1-azido-4-iodo butane (a reagent similar to that used in the synthesis of molecules), have been studied up to temperatures of 350 °C by DCS calorimetry. No significant decomposition was observed for any of these compounds, which demonstrates their good thermal stability, and suggests that the risk of spontaneous decomposition during their synthesis or manipulation is very low.

The second system studied was the TODGA extractant in contact with nitric acid at high temperature, representative of the severe conditions of the concentration operations applied in the effluents management processes. Even if the stability of the TODGA is a little lower, with energies and pressure released a little higher compared to TBP, the additional risk in the event of an organic phase entrainment in an evaporator of nitric acid (in closed reactor configuration) is not more problematic. In addition, when the TODGA is diluted in TPH, the diluent governs the stability of the organic phase, as for the TBP solutions. The degradation of extracting solutions (0.1M or 0.2M TODGA in TPH) by γ radiolysis up to 600 kGy does not modify the reactivity of the chemical system. The influence of the concentration of nitric acid (2.5M to 11M) and the amount of organic phase (ratio A/O from 66 to 33) was also considered. The thermokinetic quantities for the decomposition reaction of TODGA by nitric acid were measured under adiabatic conditions to obtain data usable in simulation codes.

REFERENCES

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[1] Bräse, S.; Gil, C.; Knepper, K.; Zimmermann, V. “Organic Azides: An Exploding Diversity of a Unique Class of Compounds,” Angew. Chem. Int. Ed., 2005, 44, 5188-5240

[2] Kolb, H.C.; Finn, M. G.; Sharpless, K.B. “Click Chemistry: Diverse Chemical Function from a Few Good Reactions,” Angew. Chem. Int. Ed., 2001, 40, 2004-2021.

[3] Richardson, M. B.; Brown, D. B.; Vasquez, C. A.; Ziller, J. W.; Johnston, K. M. and Weiss, G. A. “Synthesis and Explosion Hazards of 4-Azido-L-phenylalanine” *J. Org. Chem.* 2018, 83, 4525-4536.

[4] IRSN. “Risks of explosion associated with “red oils” in reprocessing plants,” Technical note, June 2008, www.irsn.fr/EN/publications/technical-publications/Documents/IRSN_Technical-Note_Red-Oils_062008.pdf

[5] DUKE COGEMA, STONE & WEBSTER. “Chemical consequences for potential chemical hazard events,” DCS01-RRJ-DS-CAL-H-35604-B.

[6] Usachev, V. N. and Markov, G. S. “Incidents caused by Red Oil phenomena at semi-scale and industrial radiochemical units,” *Radiochem*., 2003, 45, 1-8.

7 Singh, J. and Simms, C. “The Thermal Screening Unit. A tool for reactive chemical screening,” *Symposium Series*, 2001, 148, 67-79.

[8] Singh, J. “Reliable scale-up of thermal hazards data using the PHI-TEC II calorimeter,” *Thermochimica Acta*, 1993, 226, 211-220.

[9] McIntosh, R. D. and Waldram, S. P. “Obtaining more, and better, information from simple ramped temperature screening tests,” J. *Thermal Analysis and Calorimetry*, 2003, 73, 35-52.

This project has received funding from the EURATOM research and training programme 2014–2018 under grant agreement No 755171. The content of this deliverable reflects only the author’s view. The European Commission is not responsible for any use that may be made of the information it contains.