Speciation of palladium in nuclear fuel reprocessing operation

B. Simon, C. Bouyer, S. de Sio, A. Chagnes, L. Berthon

FROM RESEARCH TO INDUSTRY

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Speciation of palladium in nuclear fuel reprocessing operation

Kudowa Zdròj, August 26-30, 2018

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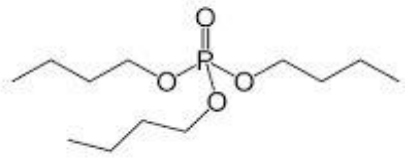
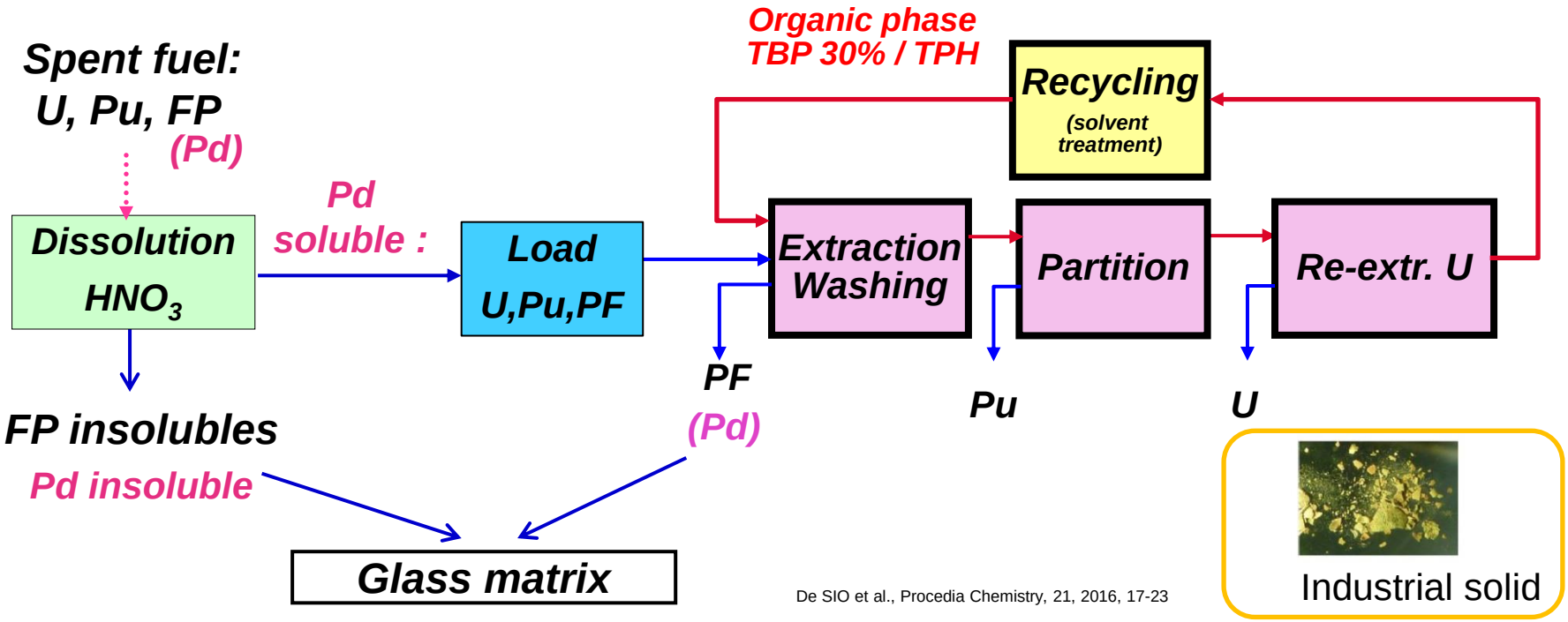
Unit of dissolution and separation processes

Context: PUREX process

- PUREX process = hydrometallurgical process
- Selective extraction of U and Pu present in the spent nuclear fuel by an organic phase TBP-TPH
- Palladium = fission product
- How to cope with aging equipment:
  → Presence of precipitate with palladium



TBP



De SIO et al., Procedia Chemistry, 21, 2016, 17-23

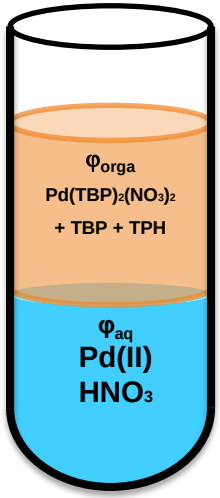
Industrial solid

Objective of the study

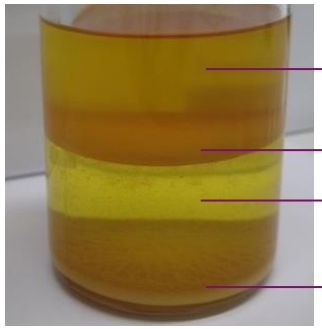
Understanding the formation of Pd precipitates in liquid-liquid extraction cycles

→ Identification of the compounds responsible for the precipitation of Pd

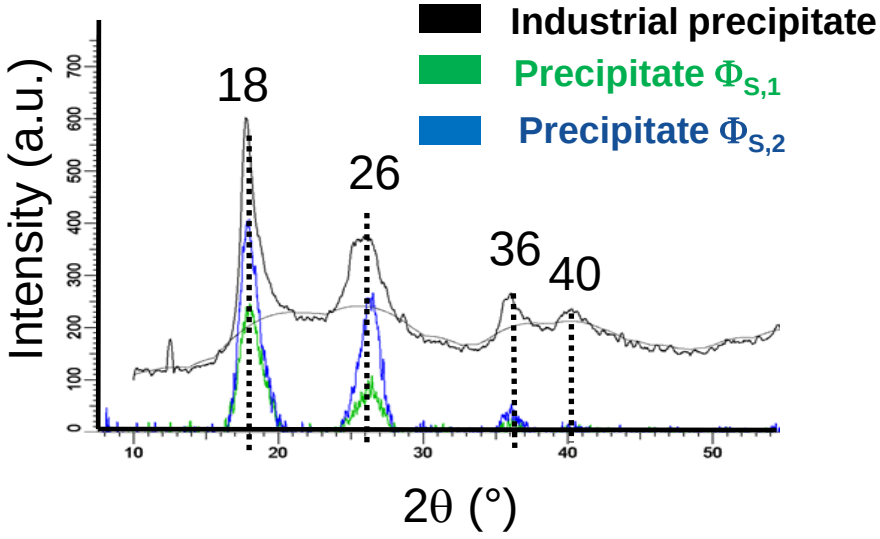
Role of the radiolysis



γ-irradiation
500 kGy



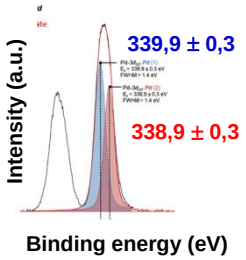
Characterization
by XRD powder diffraction



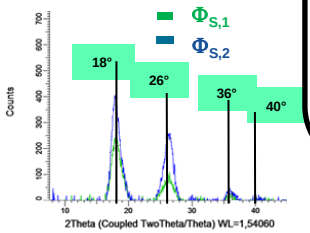
How to explain the presence of precipitate in liquide-liquid extraction cycles ?

➢ Speciation of precipitates formed by γ-irradiation

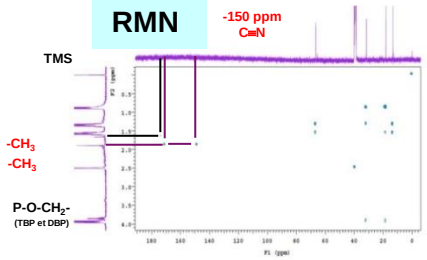
XPS



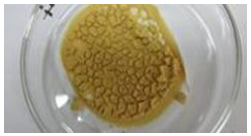
XRD



RMN

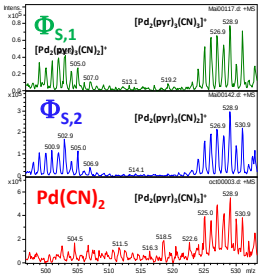


Precipitate $\Phi_{S,1}$

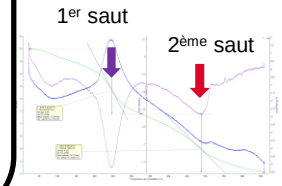


Precipitate $\Phi_{S,2}$

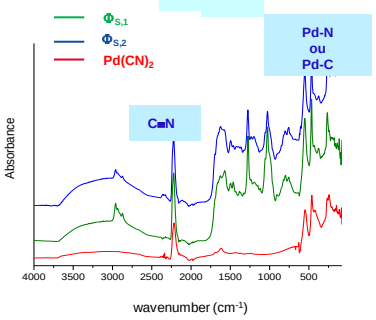
ESI-MS



ATG

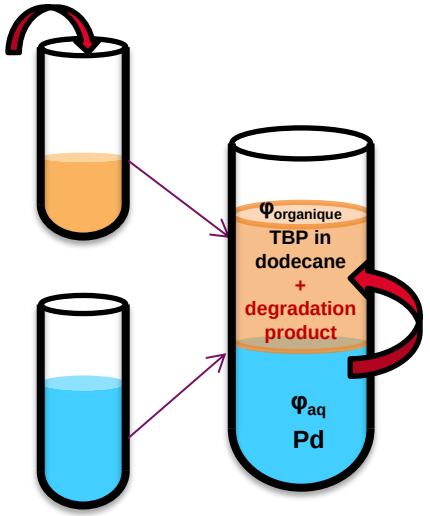


IRFT



➢ Extraction of Pd(II) in presence of degradation product (DP) of the solvent

degradation product



Identification of palladium species formed with degradation products (solid/complexe)

Characterization of precipitates formed by γ-irradiation

Precipitate

$\Phi_{S,1}$

Precipitate

$\Phi_{S,2}$

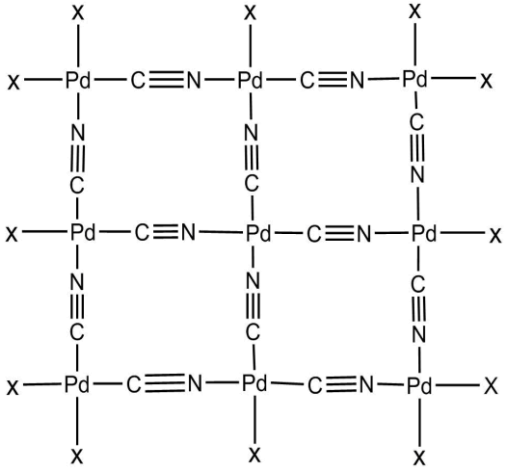
Functions present in the precipitates $\Phi_{S,1}$ et $\Phi_{S,2}$

XRD, XPS, ATG, ESI-MS

XPS, FTIR, NMR

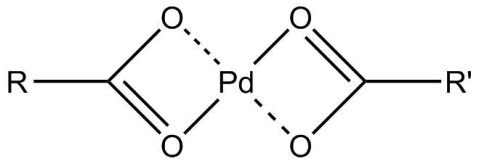
NMR, XPS, FTIR, ESI-MS

$Pd(CN)_2$

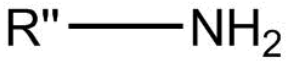


with X = H_2O, CN, others functions

Pd-carboxylate



Organic compounds



and Phosphorous compounds

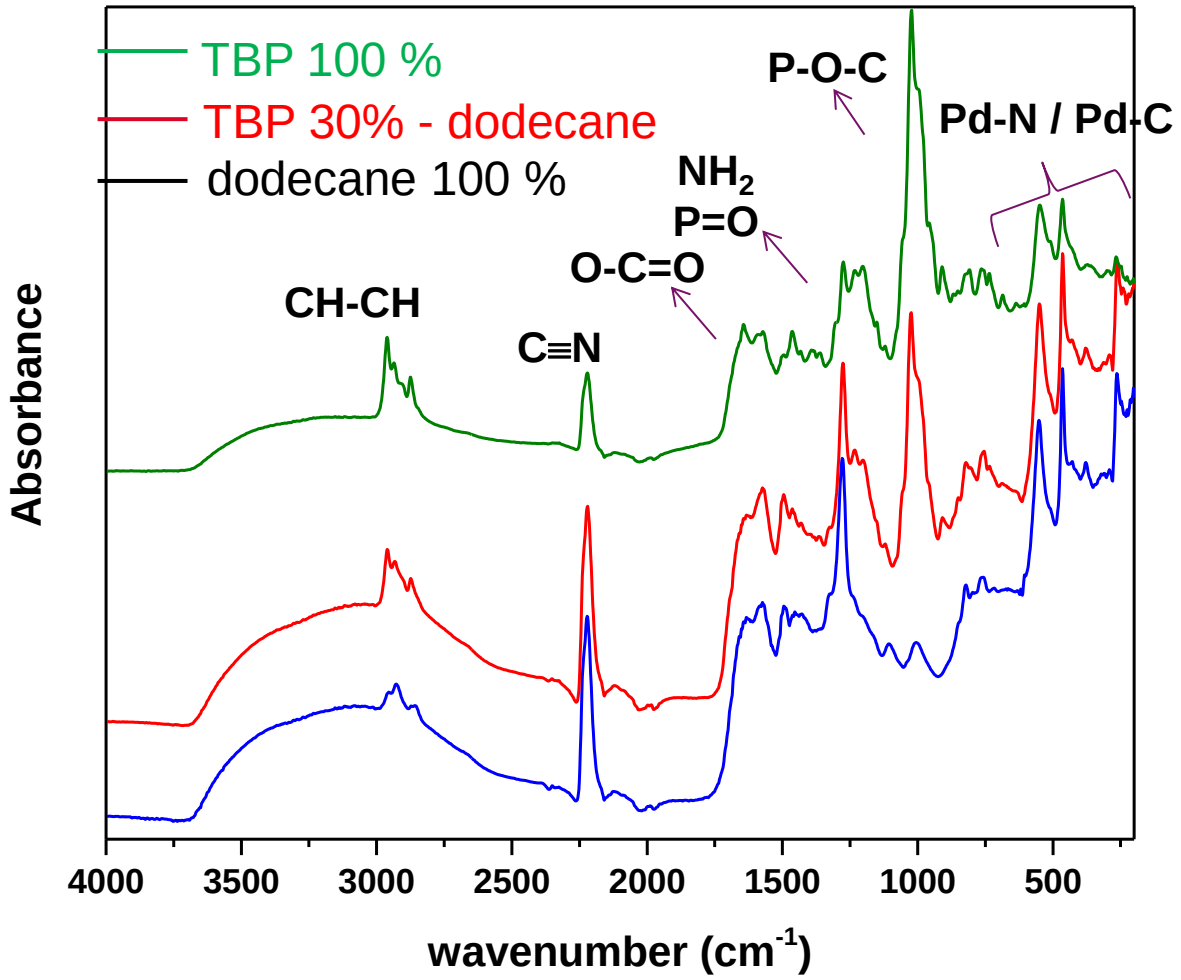
(TBP / HDBP)

Presence at least of 2 different compounds

S. J. Hibble, A. M. Chippindale, E. J. Bilbé, E. Marelli, P. J. F. Harris and A. C. Hannon, *Inorg. Chem.*, 2011, **50**, 104–113.

Published manuscript : "Characterization of palladium species after γ-irradiation of a TBP-alkane-$Pd(NO_3)_2$ system "
RSC Adv., 2018, 8, 21513-21527

Origin of degradation products leading to the formation of precipitates



Initial conditions:

φ_{aq}: $Pd(NO_3)_2$, HNO_3 3 mol.L^{-1}

φ_{orga}: variable composition

$\Phi_{S,2,TBP}$

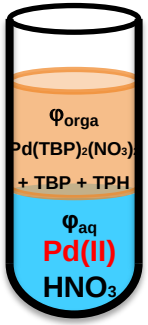
$\Phi_{S,2,TBP\text{-}dodecane}$

$\Phi_{S,2,dodecane}$

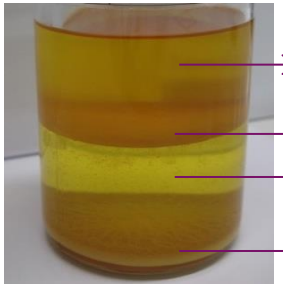
Degradation products from TBP or dodecane allowing the formation of precipitates

Distribution of degradation products leading to precipitation of palladium

Irradiation with Pd :



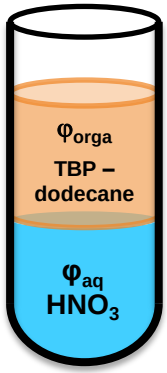
γ-irradiation
500 kGy



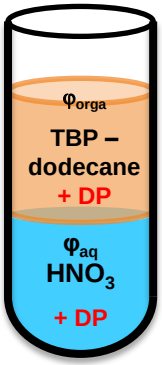
$\Phi_{S,2}$

Irradiation without Pd :

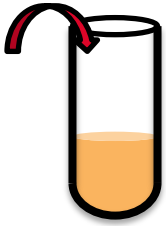
φ_{orga} irradiated



γ-irradiation
500 kGy



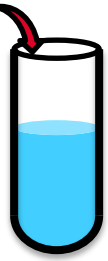
$Pd(NO_3)_2$



Stirring
Rest

$\Phi_{pp,\varphi orga}$

$Pd(NO_3)_2$



Stirring
Rest

$\Phi_{pp,\varphi aq}$

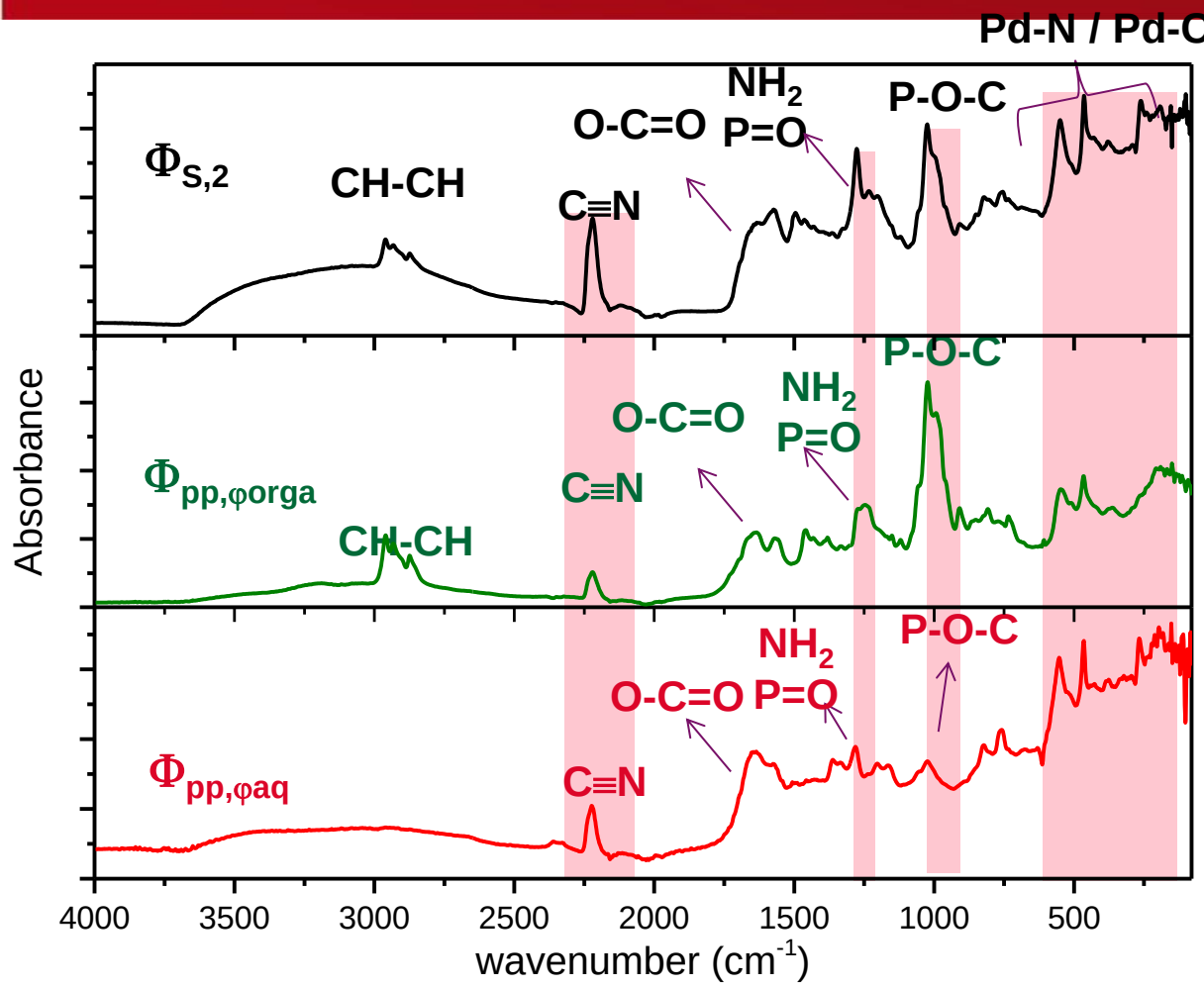
φ_{aq} irradiated

Initial conditions:

φ_{orga}: TBP 1 mol/L^{-1}- dodecane

φ_{aq}: HNO_3

Infra-red of $\Phi_{pp,\varphi orga}$ et $\Phi_{pp,\varphi aq}$ after the addition of $Pd(NO_3)_2$



- Precipitates $\Phi_{pp,\varphi orga}$ and $\Phi_{pp,\varphi aq}$ et $\Phi_{s,2}$ similar
  - CN, Pd-C/Pd-N → $Pd(CN)_2$
  - Functions O=C-O
  - NH_2, P=O et P-O-C
- For $\Phi_{pp,\varphi orga}$
  - $CH\text{-}CH_{alcane}$

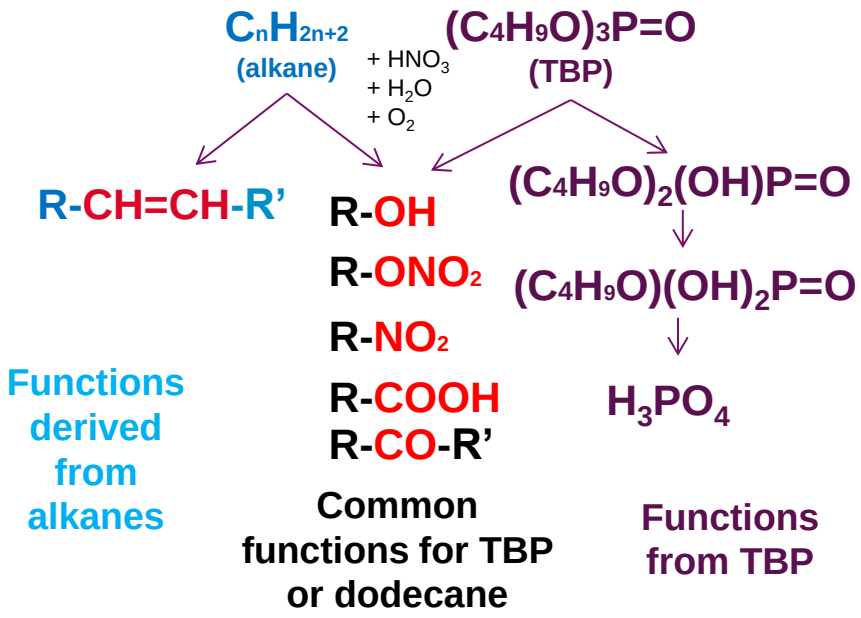
$\Phi_{pp,\varphi aq}$

$\Phi_{pp,\varphi orga}$

Degradation products responsible for the precipitation of Pd present in φ_{aq} et φ_{orga}

Extraction of Pd(II) in the presence of degradation products (DP)

Bibliographic review
on the degradation of TBP -TPH



D. Lesage, 1995
L. Berthon et M. C. Charbonnel, 2009
Tripathi et Sumathi, 1999

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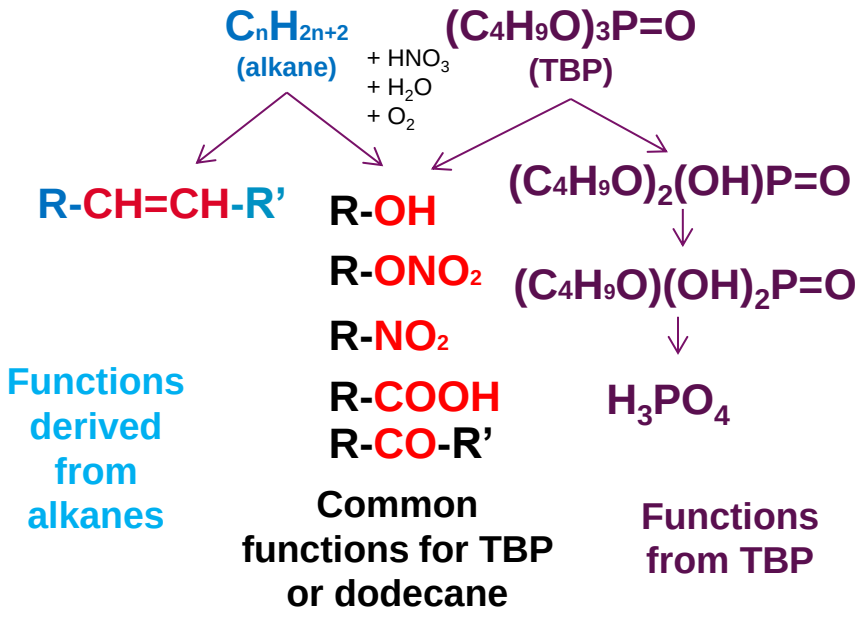
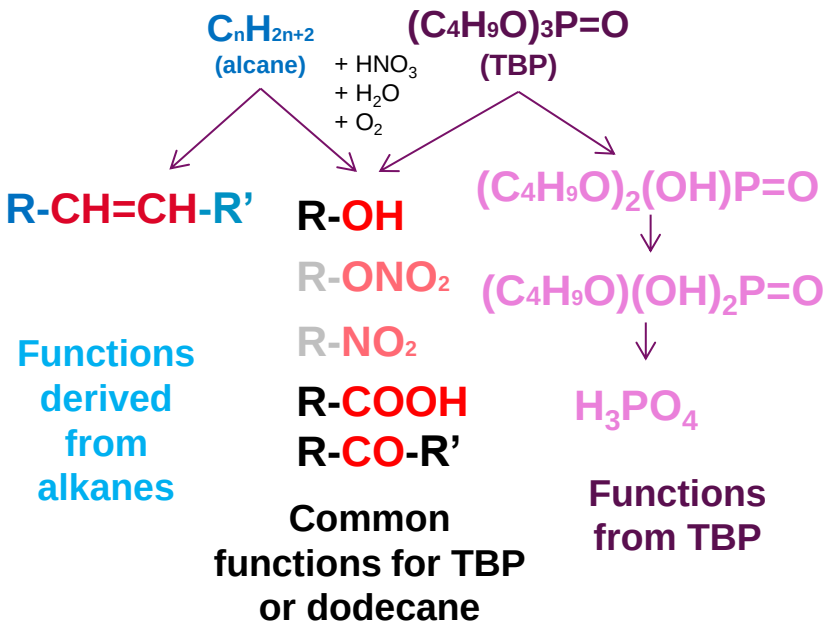


- DP tested:
  - 5-dodecene
  - dodecanoïc acid
  - 1-dodecanol
  - 5-dodecanone

D. Lesage, 1995
L. Berthon et M. C. Charbonnel, 2009
Tripathi et Sumathi, 1999

Extraction of Pd(II) in the presence of degradation products (DP)

Bibliographic review on the degradation of TBP -TPH



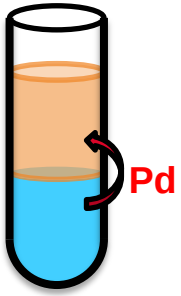
- DP tested:
  - 5-dodecene
  - dodecanoïc acid
  - 1-dodecanol
  - 5-dodecanone

D. Lesage, 1995
L. Berthon et M. C. Charbonnel, 2009
Tripathi et Sumathi, 1999

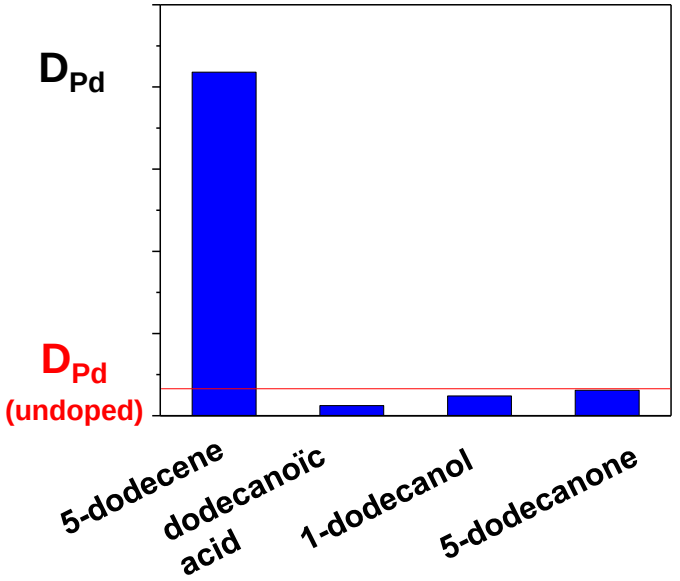
Identification of palladium species formed with these DPs (solids / complexes)

Organic phase:
TBP 1 mol.L^{-1} in dodecane
+ addition of DP

$$D_{Pd} = \frac{[Pd]_{orga}}{[Pd]_{aq}}$$



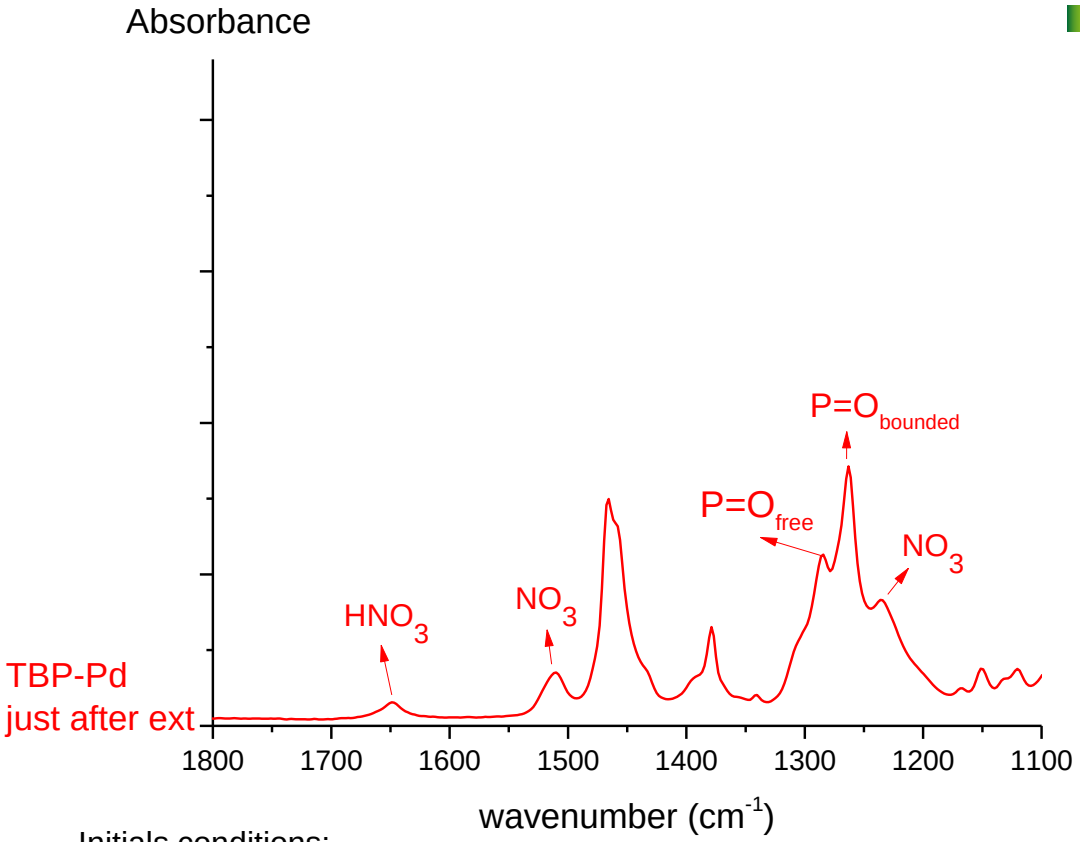
Aqueous phase:
HNO_3 + Pd(II)



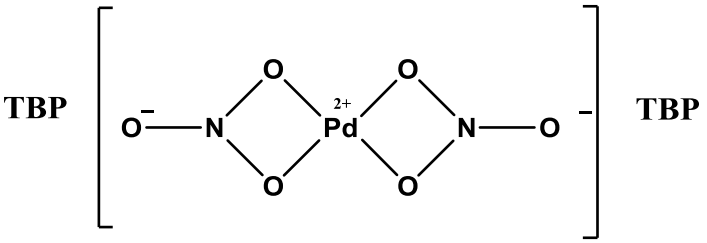
Only 5-dodecene:

1. D_{Pd}(TBP+alkene) >> D_{Pd}(undoped)
2. Presence black powder at the interphase Pd et PdO (XRD powder and XPS)

Infra-red of φ_{orga} after Pd(II) extraction in presence of absence of 5-dodecane



φ_{orga} of TBP-Pd :

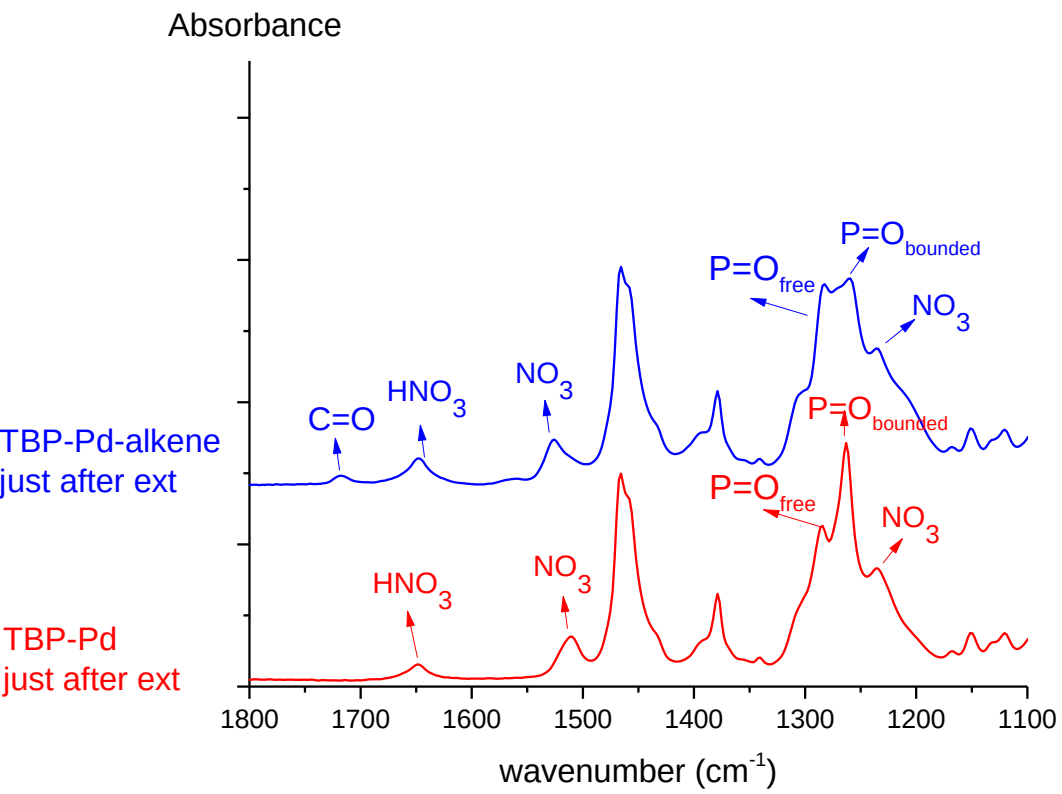


Initials conditions:

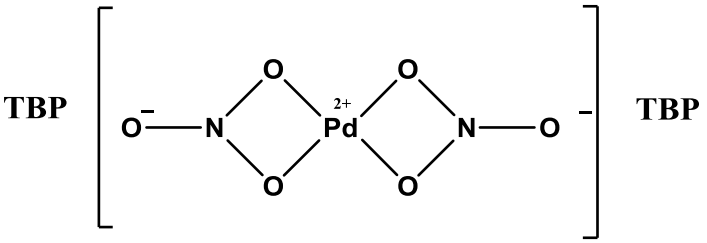
φ_{aq}: Pd(II), HNO_3

φ_{orga}: TBP 1 mol/L in dodecane with or without 5-dodecene

Infra-red of φ_{orga} after Pd(II) extraction in presence of absence of 5-dodecane



- φ_{orga} of TBP-Pd :

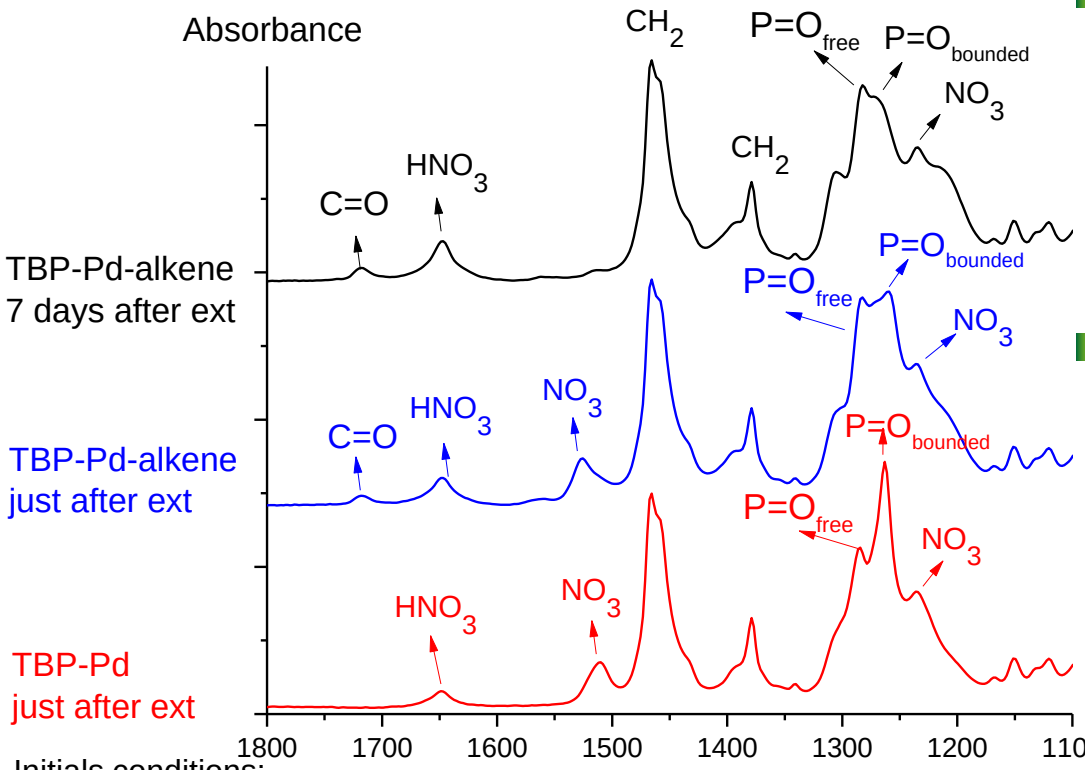


- φ_{orga} of TBP-Pd-5-dodecene :
  - Presence of C=O at 1718 cm^{-1}
    → function RCOH, R-CO-R' or R-COOH
  - NMN : presence of ketone
  - ESI-MS : complexes different from $Pd(TBP)_2(NO_3)_2$

→ Palladium complexes different with or without alkene

Initials conditions:
φ_{aq}: Pd(II), HNO_3
φ_{orga}: TBP 1 mol/L in dodecane with or without 5-dodecene

Infra-red of φ_{orga} after Pd(II) extraction in presence of absence of 5-dodecane

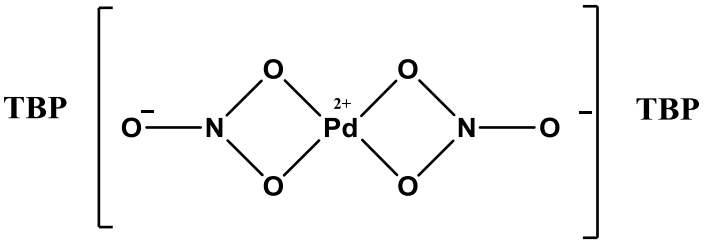


Initials conditions:

φ_{aq}: Pd(II), HNO_3

φ_{orga}: TBP 1 mol/L in dodecane with or without 5-dodecene

- φ_{orga} of TBP-Pd :



- φ_{orga} of TBP-Pd-5-dodecene :
  - Presence of C=O at 1718 cm^{-1}
    → function RCOH, R-CO-R' or R-COOH
  - NMN : presence of ketone
  - ESI-MS : complexes different from $Pd(TBP)_2(NO_3)_2$

→ Palladium complexes different with or without alkene

- Evolution φ_{orga} of TBP-Pd-alkene :

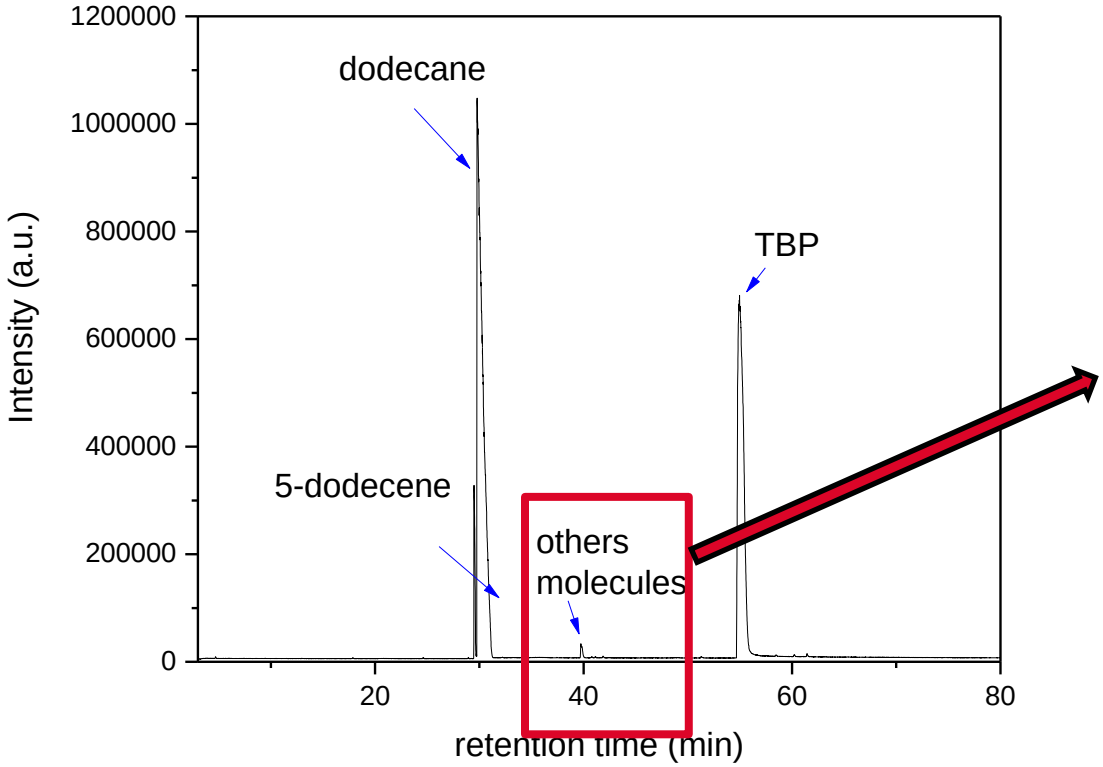
Functions C=O: C^{te} between t_0 et 7 days

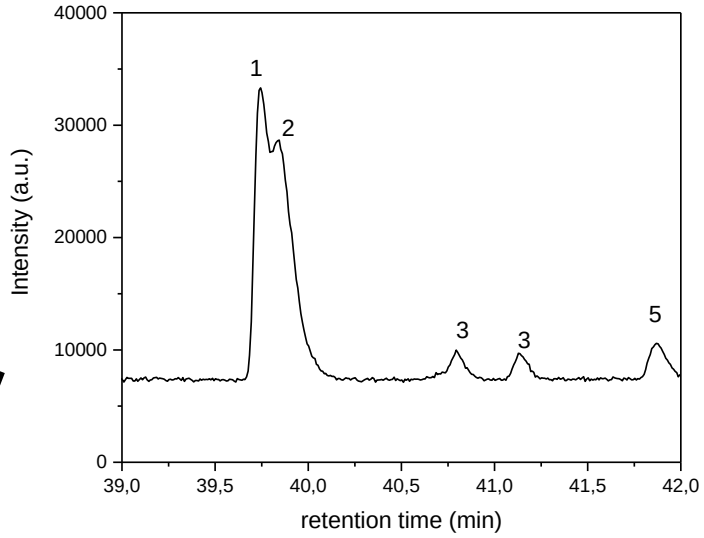
Disapperence of nitrate vibration bands (1527 cm^{-1})

  - ESI-MS : Presence of a mixed complexe of Pd-TBP-5-dodecene

Hyp : mixed complexes Pd-TBP-$C_{12}H_{24}$
Formation of C=O in presence of alkene

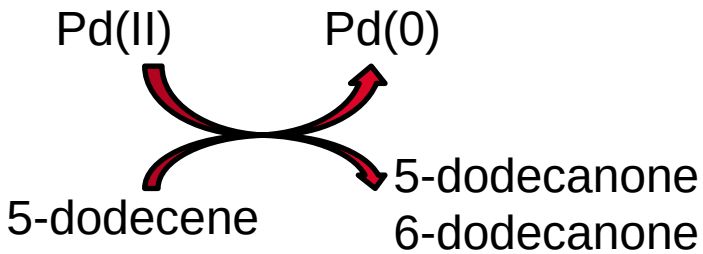
Characterization by GC-MS of an organic phase of TBP-dodecane-Pd-5-dodecene





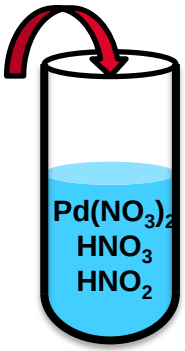
N°	Attribution
1	6-dodecanone
2	5-dodecanone
3	3-dodecanone
4	2-dodecanone
5	?

Oxydo-reduction reaction:



Behavior of ketone in presence of palladium

2-butanone
(DP from TBP)



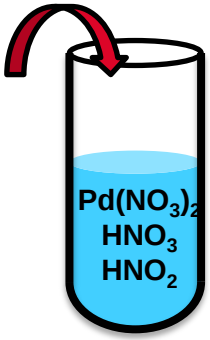
Mixture without stirring

$\Phi_{2\text{-butanone}}$

Initials conditions:
HNO_3, Pd(II), HNO_2, Ketone

M. Nonomura, *Toxicol. Environ. Chem.*, 1987, **17**, 47–57

2- dodecanone
or
5-dodecanone
(DP from dodecane)



Mixture stirred
T_{amb}

No precipitate

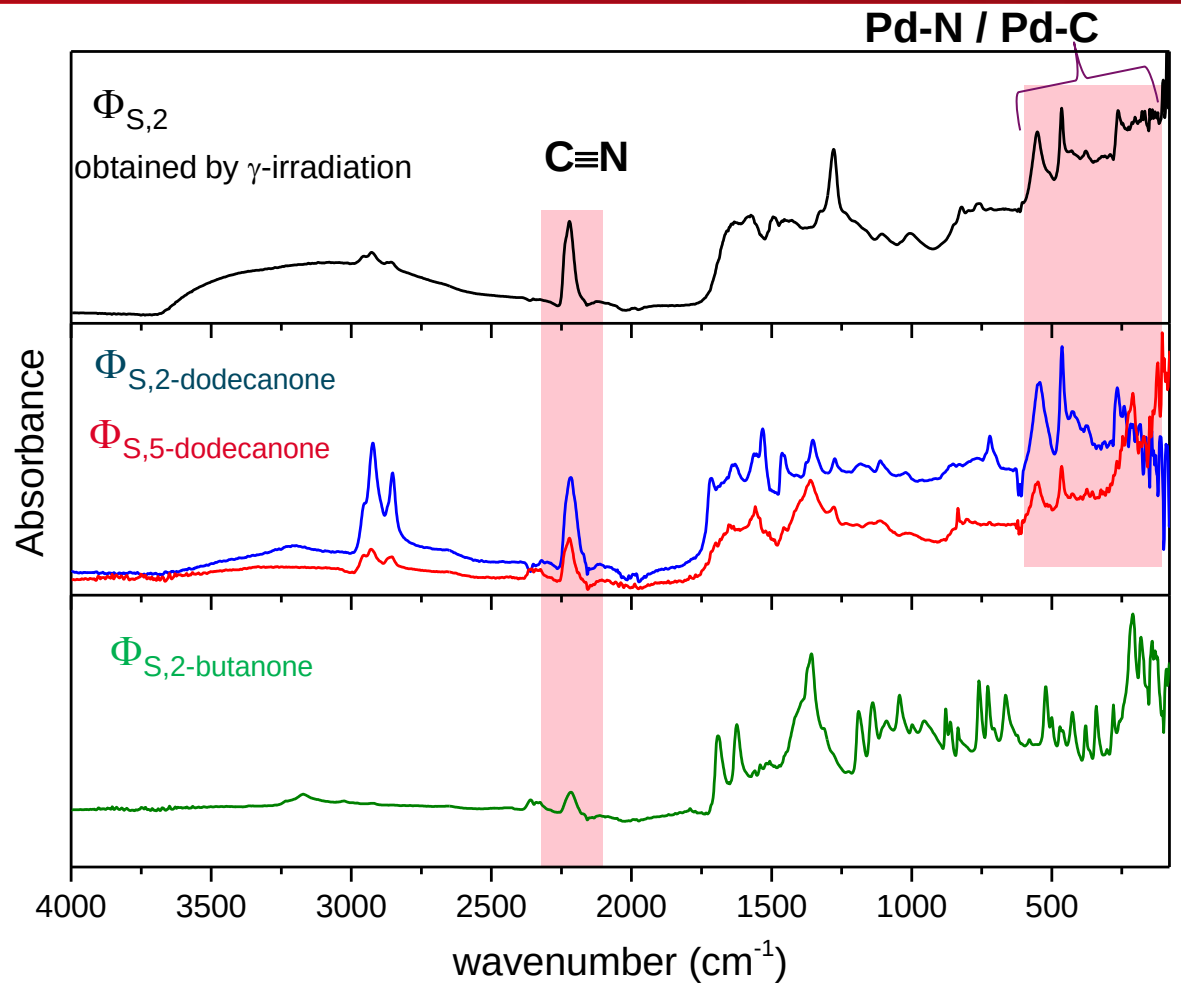
Stirred mixture
100°C

$\Phi_{S,5\text{-dodecanone}}$

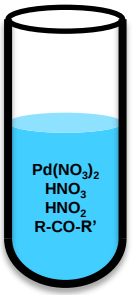
$\Phi_{S,2\text{-dodecanone}}$

- without ketone: no solid formation
- without HNO_2: no solid formation

Infra-red of $\Phi_{S,2\text{-dodecanone}}$, $\Phi_{S,5\text{-dodecanone}}$ et $\Phi_{S,2\text{-butanone}}$



Initials conditions:
HNO_3, Pd(II), HNO_2, Ketone



- Presence of C≡N in the 3 solids
  - whatever the length of the chain and the position of C=O, formation of $Pd(CN)_2$

Ketone and HNO_2: precursors in the $Pd(CN)_2$ formation

Conclusions and Prospects

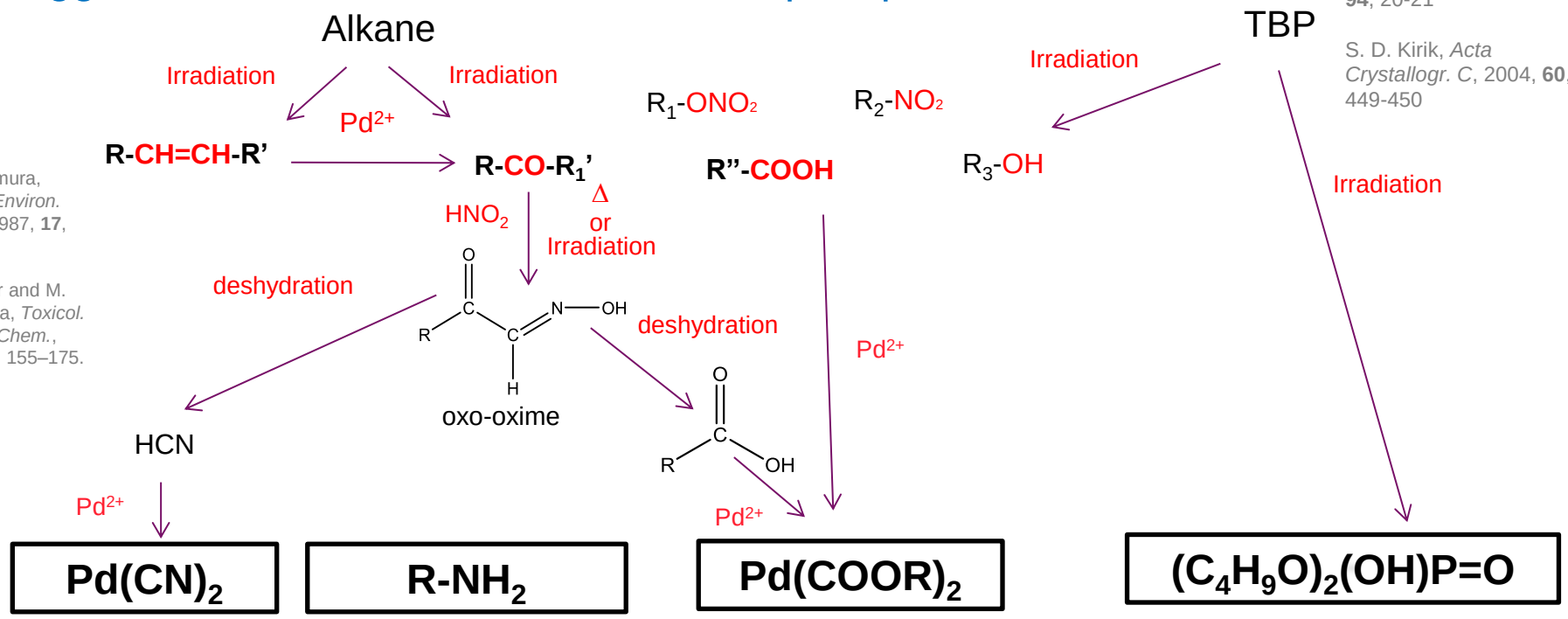
- Characterization of precipitates of palladium in {TBP-TPH-HNO_3} irradiated

  Several compounds : $Pd(CN)_2$, $Pd(COOR)_2$, TBP, HDBP, Amine

  DP come from TBP or dodecane

  DP leading to the precipitation of Pd present in φ_{aq} and φ_{orga}

- Suggestion of mechanisms formation of precipitates



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- Prospects: suggestion of NH_2 mechanism formation

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Thank you for your attention

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