Formation and Characterization of Gaseous Adducts of Carbon Dioxide to Magnesium, $(CO_2)MgX$ (X = OH, Cl, Br)

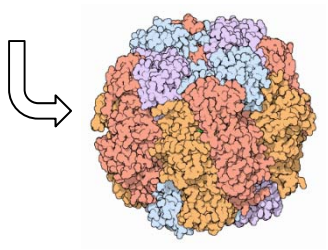
Héloïse Dossmann

18/09/2012

Introduction

- Photosynthesis: 2 steps
  - Photochemical step: storage of energy
  - Light-independent reactions:

    <u>fixation</u> then conversion of CO_2



Catalysed by the RuBisCO enzyme

Precise but not efficient!

- Fixation mechanism?
  - $RX + CO_2 + 2e^- \rightarrow RCO_2^- + X^-$ = formation of a C-C bond
  - RuBisCO: reaction takes place on the active Mg^{2+} site

→ $XMgCO_2^-$ complexes (X = OH, Br, Cl) : structure and reactivity in the gas phase?

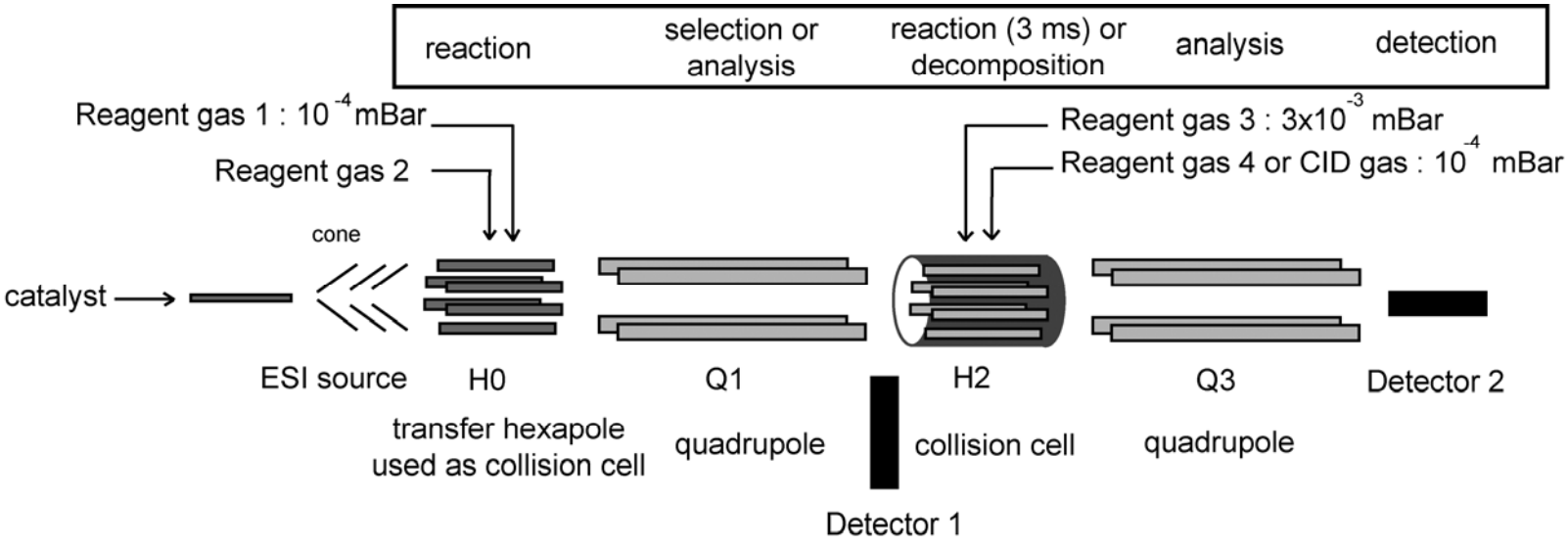
Methods

- Experimental method
  - Complexes formation: MgX_2 + $C_2H_2O_4$ in MeOH/H_2O (9/1)
  - Electrospray ionization in negative mode
  - Ion-molecule reaction (IMR)

- Electronic structure calculations (for X = OH)
  - GAUSSIAN, G4 compound method

Experimental method

- Homemade modified Quattro II mass spectrometer (Micromass, Manchester, U.K.)
  - Ion-molecule reactions (IMR) performed in the collision cell with gas or liquid reactants



Experimental method

- Hybrid quadrupole Fourier transform ion cyclotron resonance MS

  (hQh-FT/ICR; 7 T magnet)

  (Solarix, Bruker Daltonics, Bremen, Germany)

  - Sustained off-resonance irradiation collision-induced dissociations with Ar (SORI-CID)

Results

1- Formation of the complexes

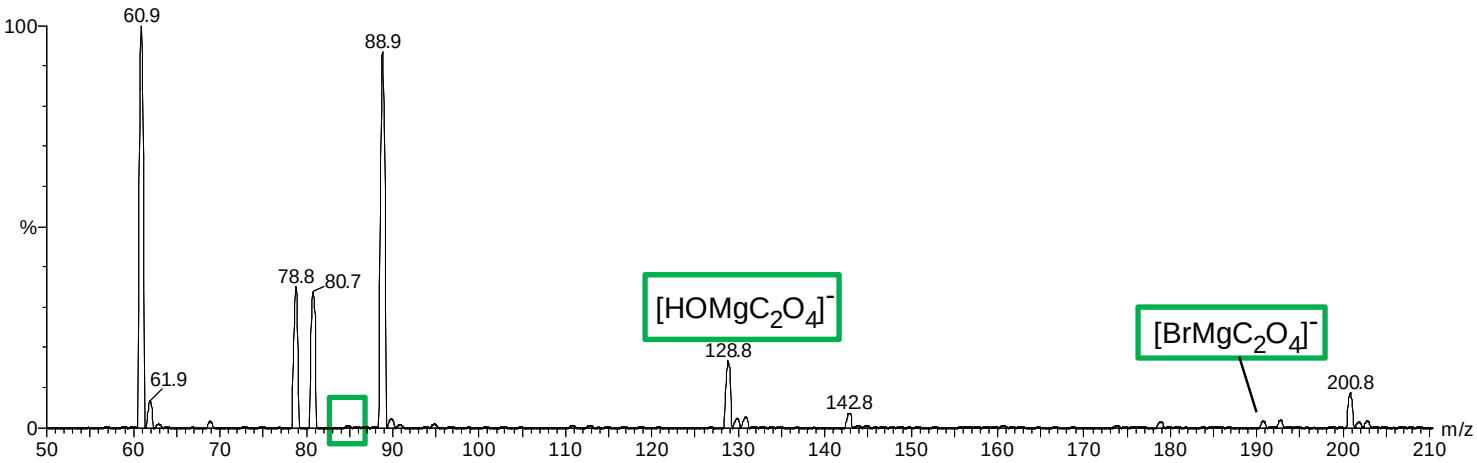
2- Reaction with H_2O

3- Reaction with CH_3Cl

1- Formation of the complexes

$$MgX_2 + \text{Oxalic acid} \xrightarrow[CH_3OH/H_2O]{\text{ESI-}} HOMgC_2O_4^-$$

X = Br or Cl

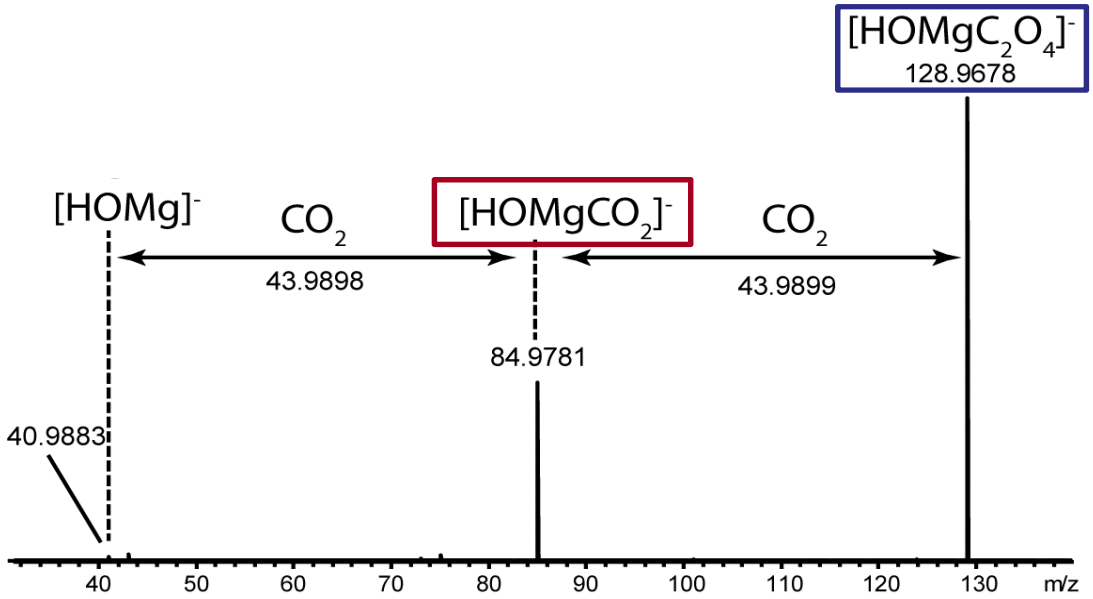


MS spectrum (TQ) of a mixture of MgX_2 and oxalic acid (1:10) in $MeOH/H_2O$ (9:1) ionized by ESI-

1- Formation of the complexes

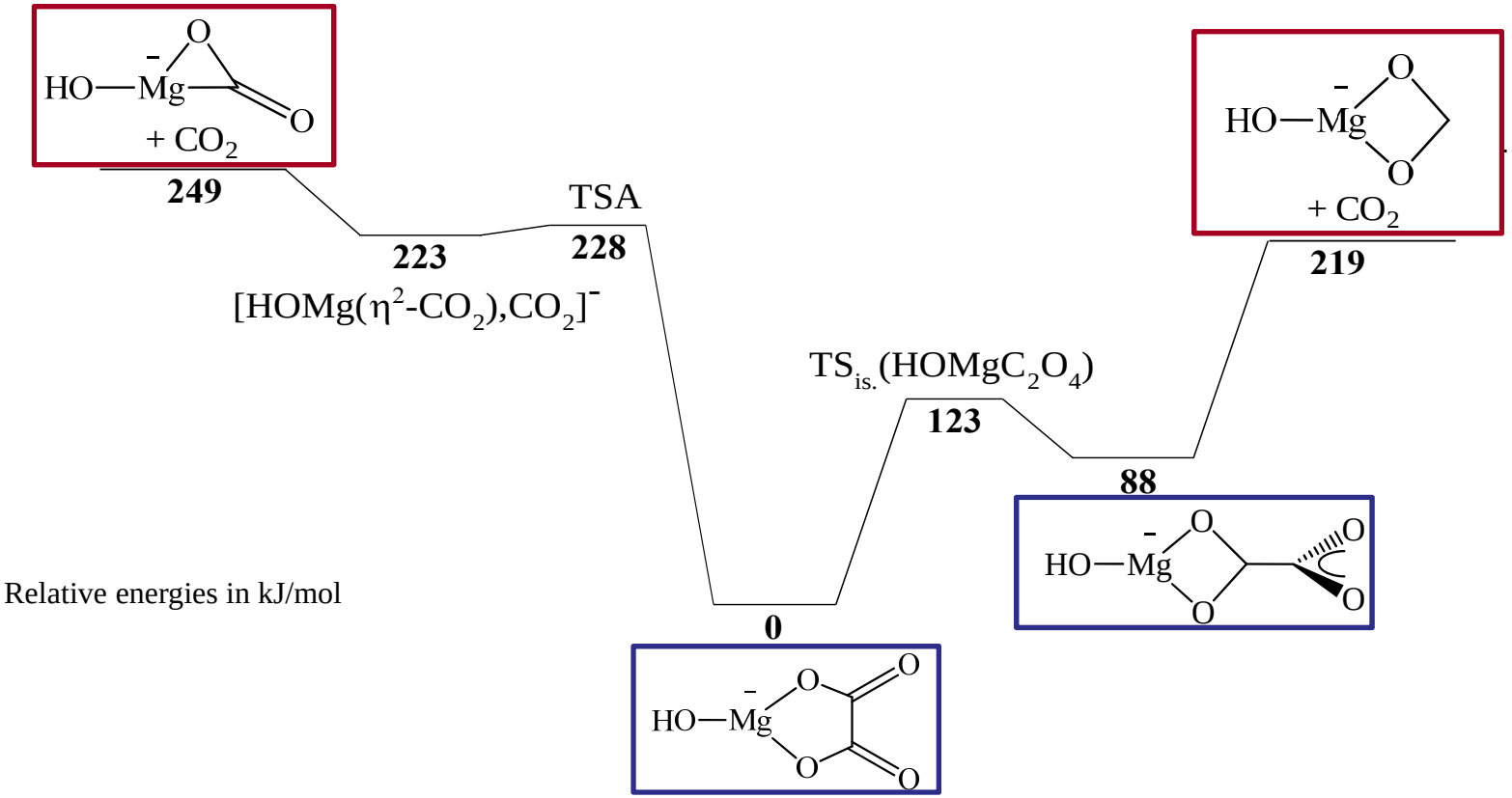
$$MgX_2 + \text{Oxalic acid} \xrightarrow[CH_3OH/H_2O]{\text{ESI-}} HOMgC_2O_4^-$$

X = Br or Cl

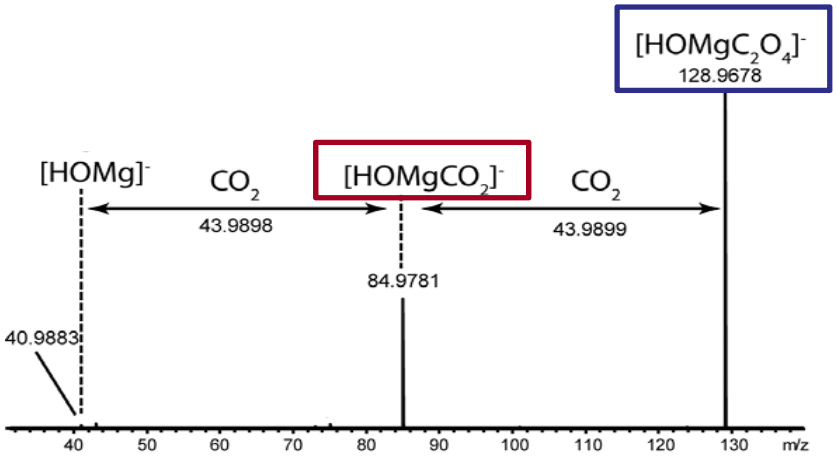


SORI-CID spectrum of the *m/z* 129 ion

1- Formation of the complexes



Relative energies in kJ/mol



SORI-CID spectrum of the *m/z* 129 ion

1- Formation of the complexes

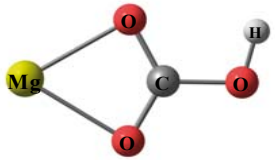
Relative energies in kJ/mol

$^{3}HOMg(\eta^{2}\text{-}O_{2}C)^{-}$

131

$^{3}HOMg(\eta\text{-}CO_{2})^{-}$

121

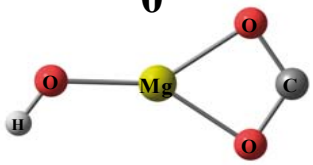


$^{3}Mg(\eta^{2}\text{-}OCO_{2}H)^{-}$

196

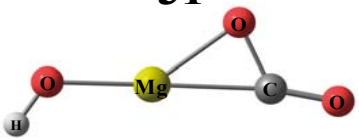
$^{1}HOMg(\eta^{2}\text{-}O_{2}C)^{-}$

0



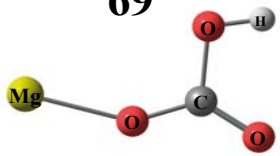
$^{1}HOMg(\eta^{2}\text{-}CO_{2})^{-}$

31

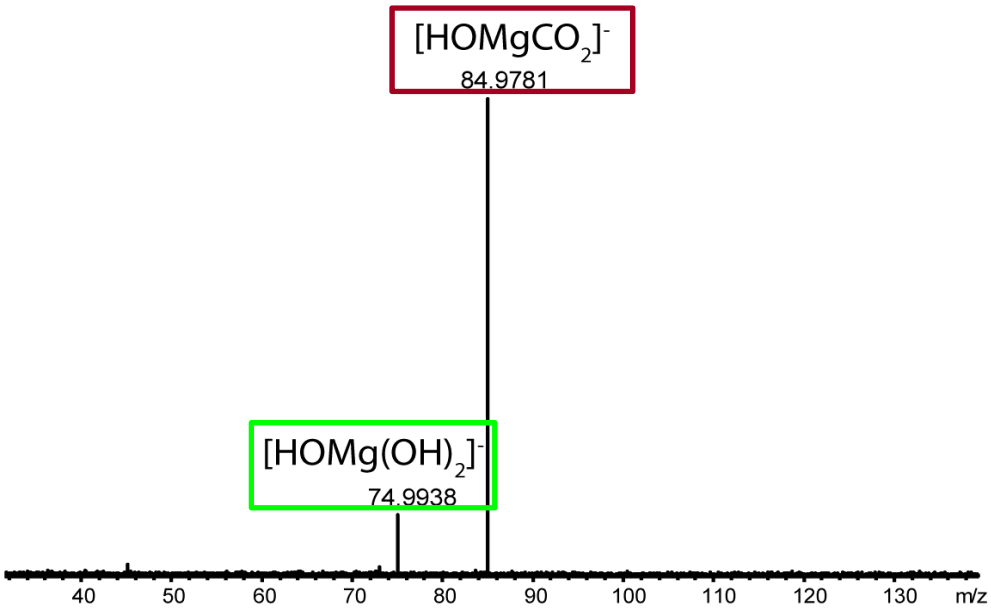


$^{1}Mg(\eta\text{-}OCO_{2}H)^{-}$

69



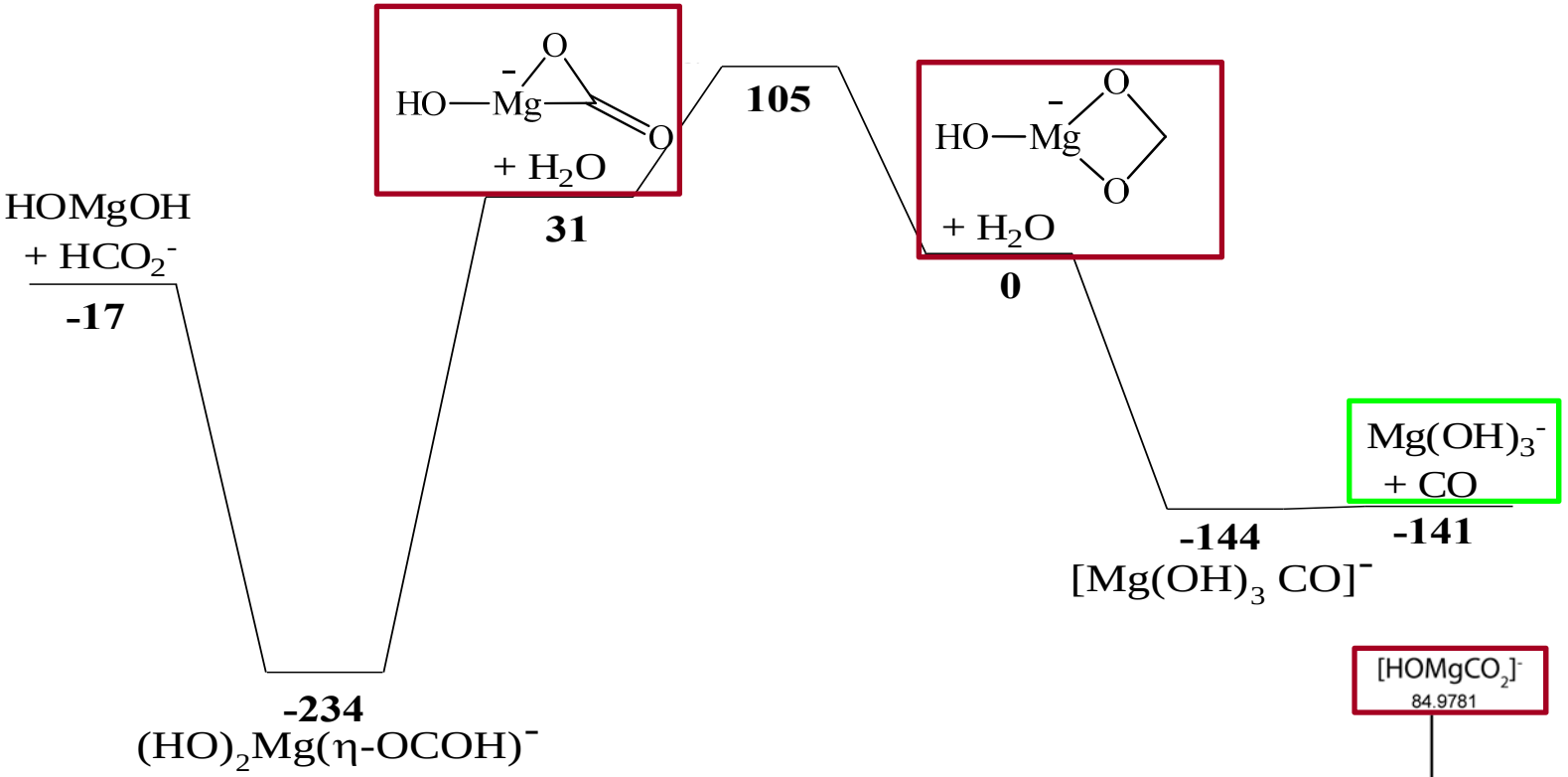
2- Reaction with H_2O



SORI-CID spectrum of the *m/z* 85 ion

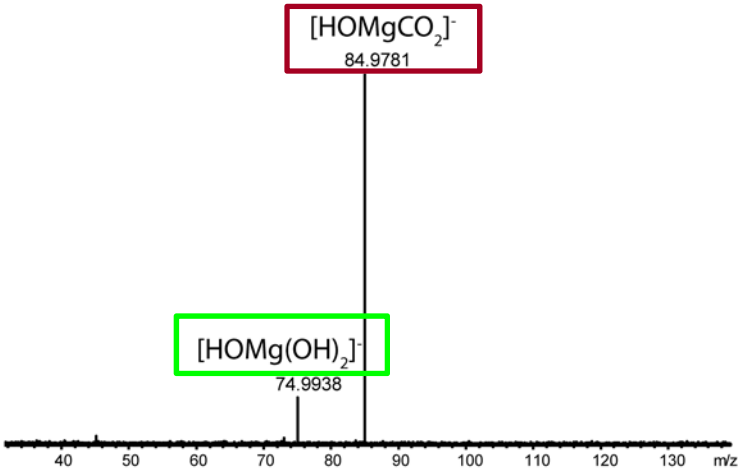
$$HOMgCO_2^- + H_2O \longrightarrow Mg(HO)_3^- + CO$$

2- Reaction with H_2O



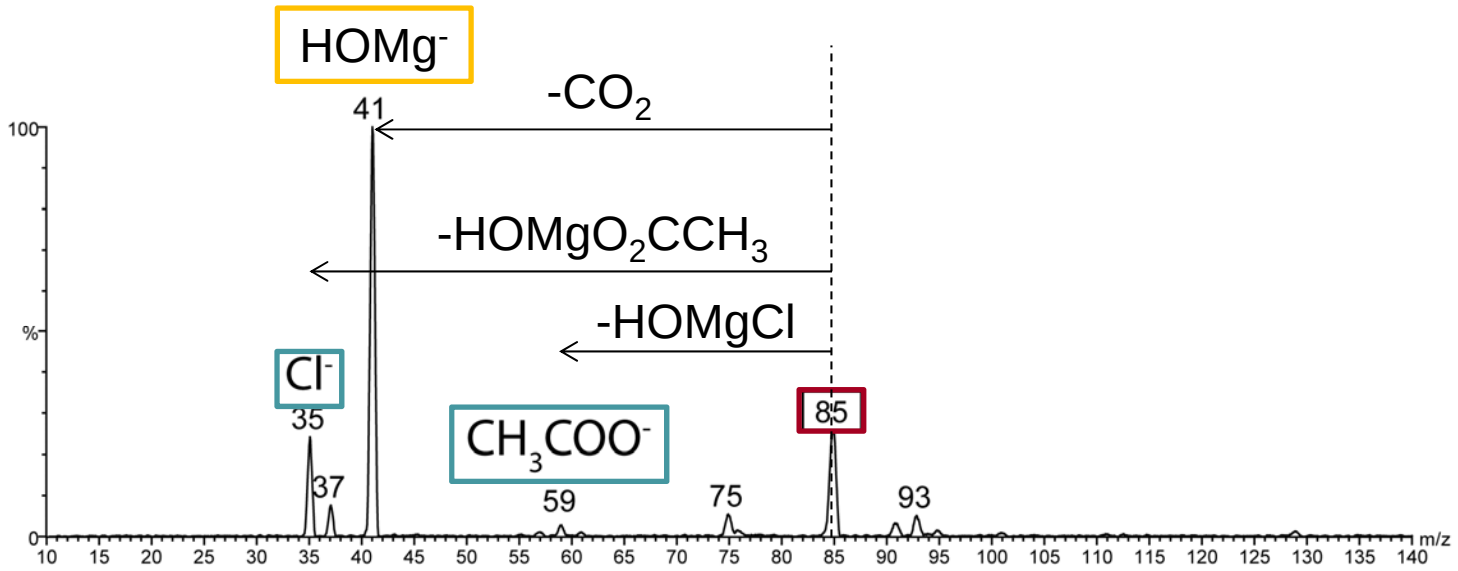
Relative energies in kJ/mol

$HOMgCO_2^- + H_2O \longrightarrow Mg(HO)_3^- + CO$



SORI-CID spectrum of the *m/z* 85 ion

3- Reaction with CH_3Cl



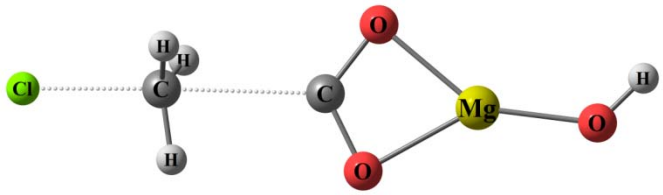
IMR spectrum (TQ) of the *m/z* 85 ion reacting with CH_3Cl

$$HOMgCO_2^- + CH_3Cl \longrightarrow HOMg^- + "CH_3ClCO_2"$$

$$\longrightarrow HOMgO_2C{-}CH_3 + Cl^-$$

$$\longrightarrow CH_3CO_2^- + HOMgCl$$

3- Reaction with CH_3Cl

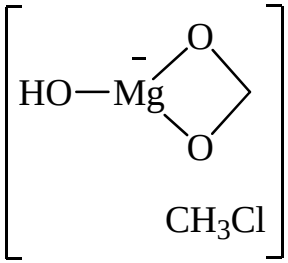


$HOMgCO_2^- + CH_3Cl$

0

-35

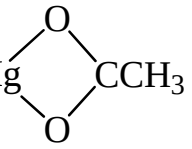
-10



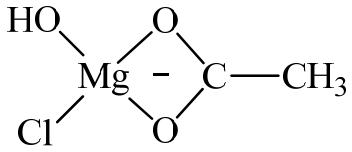
-135

$HOMgCl + CH_3CO_2^-$

-215

Cl^- + 

-434



Relative energies in kJ/mol

Conclusions

- Charge repartition analysis Mg(+ 1.5)
- Reaction with H_2O: structure of the complex is confirmed
- Reaction with CH_3Cl: exothermic C-C bond formation
- Next steps (in progress)
  - $XMgOH^- + CO_2$
  - $HOMg^-$ ➔ Mg(0)

Thank you for your attention !

This work was published under:
H. Dossmann (Soldi-Lose), C. Afonso, D. Lesage, J.-C. Tabet and E. Uggerud, *Angew. Chem. Int. Edition,* 51 **2012** 6938