Formation and Characterization of Gaseous Adducts of Carbon Dioxide to Magnesium, $(\text{CO}_2)\text{MgX}$ ($X = \text{OH, Cl, Br}$)

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Introduction

- Photosynthesis: 2 steps
  - Photochemical step: storage of energy
  - Light-independent reactions: fixation then conversion of CO₂

Catalysed by the RuBisCO enzyme
Precise but not efficient!

- Fixation mechanism?
  - RX + CO₂ + 2e⁻ → RCO₂⁻ + X⁻ = formation of a C-C bond
  - RuBisCO: reaction takes place on the active Mg²⁺ site

XMGCO₂⁻ complexes (X = OH, Br, Cl): structure and reactivity in the gas phase?
Methods

- **Experimental method**
  - Complexes formation: MgX₂ + C₂H₂O₄ in MeOH/H₂O (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)
1- Formation of the complexes
2- Reaction with H₂O
3- Reaction with CH₃Cl
1- Formation of the complexes

$$\text{MgX}_2 + \text{Oxalic acid} \xrightarrow{\text{ESI-}} \text{HOMgC}_2\text{O}_4^-$$

$$\text{CH}_3\text{OH}/\text{H}_2\text{O}$$

$$X = \text{Br or Cl}$$

MS spectrum (TQ) of a mixture of MgX₂ and oxalic acid (1:10) in MeOH/H₂O (9:1) ionized by ESI-

$[\text{HOMgC}_2\text{O}_4^-]$ $[\text{BrMgC}_2\text{O}_4^-]$
1- Formation of the complexes

\[ \text{MgX}_2 + \text{Oxalic acid} \xrightarrow{\text{ESI-CH}_3\text{OH/H}_2\text{O}} \text{HOMgC}_2\text{O}_4^- \]

\( X = \text{Br or Cl} \)

SORI-CID spectrum of the \( m/z \) 129 ion

[Schematic diagram showing the formation and dissociation of ions, with labeled masses and m/z values.]
1- Formation of the complexes

Relative energies in kJ/mol
1- Formation of the complexes

Relative energies in kJ/mol

\[
\begin{align*}
{^3}\text{HOMg}(\eta^2-\text{O}_2\text{C})^- & \quad 131 \\
{^3}\text{HOMg}(\eta-\text{CO}_2)^- & \quad 121 \\
{^1}\text{HOMg}(\eta^2-\text{O}_2\text{C})^- & \quad 0 \\
{^1}\text{HOMg}(\eta^2-\text{CO}_2)^- & \quad 31 \\
{^3}\text{Mg}(\eta^2-\text{OCO}_2\text{H})^- & \quad 196 \\
{^1}\text{Mg}(\eta-\text{OCO}_2\text{H})^- & \quad 69
\end{align*}
\]
2- Reaction with H$_2$O

\[ \text{HOMgCO}_2^- + \text{H}_2\text{O} \rightarrow \text{Mg(HO)}_3^- + \text{CO} \]
2- Reaction with H₂O

HOMgOH + HCO₂⁻ → (HO)₂Mg(η-OCOH)⁻

Relative energies in kJ/mol

HOMgCO₂⁻ + H₂O → Mg(HO)₃⁻ + CO
3- Reaction with $\text{CH}_3\text{Cl}$

HOMg$^-$ + CH$_3$Cl $\rightarrow$ HOMg$^-$ + "CH$_3$ClCO$_2$"

$\rightarrow$ HOMgo$_2$C$-$CH$_3$ + Cl$^-$

$\rightarrow$ CH$_3$CO$_2$$^-$ + HOMgCl
3- Reaction with CH₃Cl

HOMgCO₂⁻ + CH₃Cl

Relative energies in kJ/mol
Conclusions

- Charge repartition analysis Mg(+ 1.5)
- Reaction with H₂O: structure of the complex is confirmed
- Reaction with CH₃Cl: exothermic C-C bond formation

Next steps (in progress)

- XMgOH⁻ + CO₂
- HOMg⁻ \rightarrow Mg(0)

Thank you for your attention!