

# FORMATION, CHARACTERIZATION AND REACTIVITY OF GASEOUS ADDUCT OF CARBON DIOXIDE TO MAGNESIUM

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Activated forms of carbon dioxide are of great interest due to the relevance to photosynthetic CO<sub>2</sub> uptake and to sequestration of CO<sub>2</sub> from flue gases formed upon the burning of fossil fuels. One efficient fixation of carbon dioxide by covalent C-C bond formation is schematically described as  $RX + CO_2 + 2e^- \rightarrow RCO_2^- + X^-$ . In plant cells, electrons are provided from chlorophyll via NADPH<sub>2</sub> and formation of a bond between C-atoms of CO<sub>2</sub> and of another substrate occurs at the magnesium centered active site of the enzyme RuBisCO. In this context, we report here on the gas-phase characterization of a novel and fragile structural form of carbon dioxide bonded to magnesium, HOMgCO<sub>2</sub><sup>-</sup> showing interesting reactivity features.

Electrospray ionization was applied to mixtures of oxalic acid and magnesium salts MgCl<sub>2</sub> and MgBr<sub>2</sub> dissolved in CH<sub>3</sub>OH/H<sub>2</sub>O (v/v 90/10). From the recorded mass spectra, signal corresponding to the MgC<sub>2</sub>O<sub>5</sub>H<sup>-</sup> ion was observed. Upon collisional activation, this ion dissociates by losing CO<sub>2</sub>, 2CO<sub>2</sub> and MgC<sub>2</sub>O<sub>4</sub> leading to the formation respectively of HOMgCO<sub>2</sub><sup>-</sup>, HOMg<sup>-</sup> and HO<sup>-</sup>. Different structures are probed theoretically for the ion of interest, HOMgCO<sub>2</sub><sup>-</sup> as well as its mechanism of formation from the MgC<sub>2</sub>O<sub>5</sub>H<sup>-</sup> ion. Results show that two structures are conceivable for this ion, HOMg(η<sup>2</sup>-O<sub>2</sub>C)<sup>-</sup> and HOMg(η<sup>2</sup>-OCO)<sup>-</sup> whose energies are distinguished by a difference of by 31 kJ/mol, the other forms being higher by at least 69 kJ/mol. Furthermore, the complex shows a strong reactivity towards water which is present as a trace in the collision cell of the mass spectrometer. This reaction leads to the formation of a unique ion, Mg(OH)<sub>3</sub><sup>-</sup>. Theoretical study of the mechanism of formation of this ion reveals a very exothermic pathway specifically from the HOMg(η<sup>2</sup>-O<sub>2</sub>C)<sup>-</sup> form. As will be discussed, this supports the hypothesis of the presence of only one structure for HOMgCO<sub>2</sub><sup>-</sup>, *i.e.* HOMg(η<sup>2</sup>-O<sub>2</sub>C)<sup>-</sup>. Finally, the reaction of the complex with CH<sub>3</sub>Cl is investigated. Several product ions are observed, in particular Cl<sup>-</sup> and CH<sub>3</sub>CO<sub>2</sub><sup>-</sup> that are issued from a S<sub>N</sub>2-type reaction.