Reaction Intermediates

DOI: 10.1002/anie.201108477

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

*Héloïse Dossmann (Soldi-Lose), Carlos Afonso, Denis Lesage, Jean-Claude Tabet, and Einar Uggerud**

There is great current interest in the properties and reactivity of carbon dioxide and its activated forms owing to the relevance to photosynthetic CO_2 uptake[1] and to sequestration of CO_2 from flue gases formed upon the burning of fossil fuels;[2] the former process is essential to life on Earth, and the latter is important in sustaining it under balanced conditions.[3] Efficient fixation of carbon dioxide by covalent C–C bond formation requires two extra electrons [Equation (1)]:

$$RX + CO_2 + 2e^- \rightarrow RCO_2^- + X^- \qquad (1)$$

This general two-electron reduction is applicable to a range of different reactions. In plant cells, the formation of a bond between the carbon atom of CO_2 and one carbon atom of the other substrate, ribulose-1,5-bisphosphate (RuBP), occurs at the magnesium-centered active site of the enzyme RuBisCO,[4] the electrons being obtained from chlorophyll via $NADPH_2$. In electrochemical and photoelectrochemical CO_2 fixation, the electrons are supplied by coupling to an electrochemical process that is mediated by various metals.[5] Synthetic ways to fixate CO_2 are very often involving Grignard reaction.[6] This reaction proceeds with metals, traditionally magnesium, directly providing the electrons. In this context, we have undertaken the study of some elusive $[Mg + CO_2]$ complexes to characterize them and study their ability to form new C–C bonds. Mass spectrometry was an ideal tool as it makes possible to produce, isolate, and probe the structures and reactivities of elusive intermediates in the rarefied gaseous state; that is, in an chemical environment free from interference of neighboring molecules, including the effects of a solvent, which otherwise would make such intermediates too short-lived for observation.[7] In the following, we present the chemical characterization and reactivity of a novel and fragile structural form of carbon dioxide bonded to magnesium. The species in question are conveniently prepared by electrospray ionization of solutions containing magnesium(II) salts and oxalic acid. In parallel to the experiments, quantum-chemical calculations have been performed to gain more insights into the structures and mechanisms of the species under study.

Electrospray ionization (ESI) in the negative-ion mode was applied to mixtures of oxalic acid (Ox) and magnesium salts $MgCl_2$ and $MgBr_2$ dissolved in CH_3OH/H_2O (90:10 *v*/*v*) From the recorded mass spectra we observe signals that are due to $MgC_2O_5H^-$, $MgClC_2O_4^-$, and $MgBrC_2O_4^-$ ions. Upon collisional activation, these ions (see the Supporting Information) dissociate by loss of CO_2, $2\,CO_2$, and MgC_2O_4. The ions resulting from carbon dioxide loss, $MgCO_3H^-$, $MgClCO_2^-$, and $MgBrCO_2^-$, are presented herein. Accurate mass measurements and isotopic patterns confirm each of the molecular formulae. Three possible molecular structures for the $[MgCO_2X]^-$ ion have been considered: $XMg(\eta^2\text{-}O_2C)^-$, $XMg(\eta^2\text{-}CO_2)^-$, and $Mg(O_2CX)^-$ (X = OH, Cl, Br). Quantum-chemical calculations for X = OH show that of these isomeric forms, the former is lowest in potential energy (Figure 1) and that the electronic triplet is 131 kJ mol^{-1} higher in energy than the singlet. A potential energy diagram (Supporting Information) shows possible mechanisms of formation of these ions from the starting oxalic acid adduct. The application of decarboxylation as a method of forming

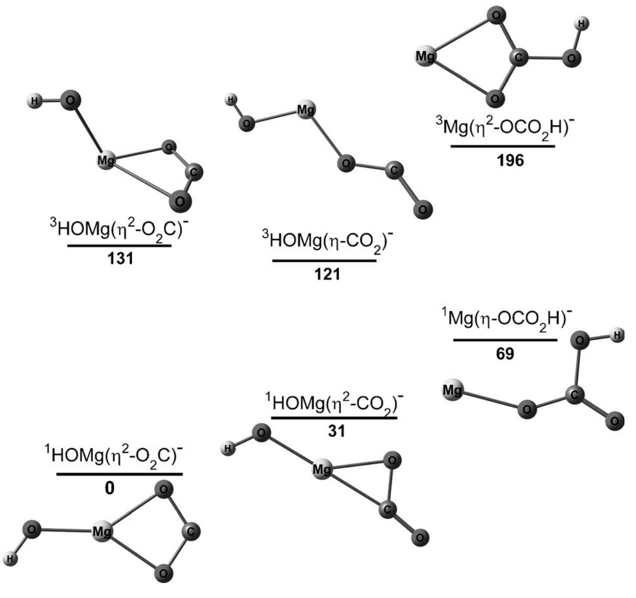

Figure 1. Relative energies [kJ mol^{-1}] for $HOMg(\eta^2\text{-}O_2C)^-$, $HOMg(\eta^2\text{-}CO_2)^-$, and $Mg(OCO_2H)^-$ in their electronic singlet (^1Mg) and triplet forms (^3Mg). Data obtained from G4-optimized structures.

---

[*] H. Dossmann (Soldi-Lose), C. Afonso, D. Lesage, J.-C. Tabet
Institut Parisien de Chimie Moléculaire
Université Pierre et Marie Curie-Paris 6, UMR 7201- FR2769
Place Jussieu, 75252 Paris Cedex 05 (France)
C. Afonso
Université de Rouen, UMR CNRS 6014 COBRA
1 rue Tesnière, 76130 Mont-Saint-Aignan (France)
E. Uggerud
Massespektrometrilaboratoriet og Senter for teoretisk og beregningsbasert kjemi (CTCC), Kjemisk institutt, Universitetet i Oslo
Postboks 1033 Blindern, 0315 Oslo (Norway)
E-mail: einar.uggerud@kjemi.uio.no

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201108477.

WILEY ONLINE LIBRARY

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

negatively charged metallic ions is known: Jacob et al.[8] used alkali and alkaline earth acetates to form organometallics, and Curtis et al.[9] and Attygalle et al.[10] have demonstrated that metal oxalate anions, for example $KC_2O_4^-$, dissociate upon collisional activation by successive losses of carbon dioxide, providing a useful method for making negatively charged atomic metal ions in the gas phase. The latter authors also suggested a bidendate structure for the MCO_2^- intermediate observed in their experiments and supported by quantum chemical calculations, in analogy with $XMg(\eta^2\text{-}O_2C)^-$ reported herein.

Isolation of $XMg(O_2C)^-$ inside the cell of an FT-ICR mass spectrometer leads to loss of the elements of carbon monoxide upon water addition [Figure 2; Equation (2)]:

$$XMg(O_2C)^- + H_2O \rightarrow XMg(OH)_2^- + CO \quad (X = OH, Cl, Br) \qquad (2)$$

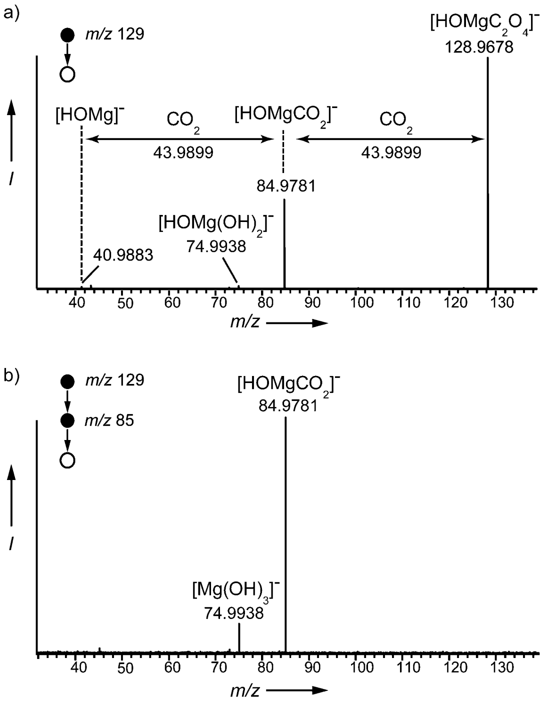

Figure 2. SORI-CID spectrum of a) $[HOMg(C_2O_4)]^-$ (*m/z* 129) and b) $[HOMg(CO_2)]^-$ (*m/z* 85) reacting with water. The $[HOMg(H_2O)]^-$ ion (*m/z* 75) is produced through loss of CO from $[HOMg(CO_2)]^-$ upon addition of H_2O.

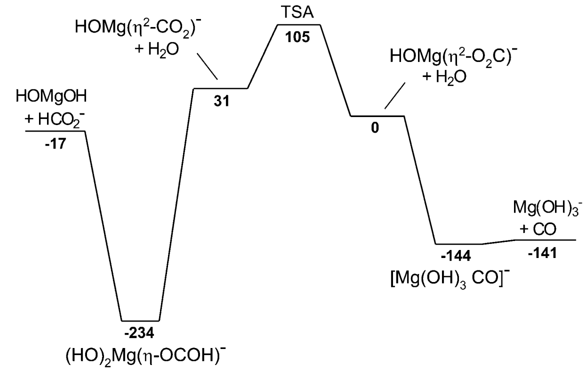

Figure 3. Potential energy diagram of $HOMg(CO_2)^-$ reacting with water. Relative energies are given in kJ mol^{-1}.

The same reaction is observed during tandem mass spectrometry collisional activation at extended times and slightly elevated background water pressures using either a triple-quadrupole mass spectrometer or a Paul ion trap. The reaction appears to be efficient, although the experimental setups provide no accurate estimates of the bimolecular rate coefficients. Figure 3 shows the computed potential energy diagram relevant to the case where X = OH. The right hand side of the diagram, which is most relevant to the experimental observation, shows that water addition essentially occurs in one step, however in a concerted but clearly nonsynchronous sequence of bond formation and dissociation that is best explained as a dissociative hydration reaction. In the first stage, the incoming water forms an O–Mg bond to the central magnesium atom, whereupon one of the water hydrogen atoms gradually transfers to one of the basic oxygen atoms of the CO_2 moiety. At the G4 level of theory, this hydrogen transfer proceeds without barrier, which explains why no $[HOMgCO_2{\cdot}H_2O]^-$ intermediate complex is displayed on the potential energy diagram in Figure 3. A weakly bonded $[Mg(OH)_3^-{\cdot}CO]$ complex is thus formed, which finally dissociates. The driving forces of the reaction are formation of a strongly bonded magnesium oxide form and the concurrent hydration. The former is similar to the well-known highly exothermic reaction between magnesium metal and CO_2.[11] As a consequence, the $Mg(OH)_3^-$ product is extremely stable. A related mechanism was found in reactions between $[CH_3MgL_2]^-$ and water.[12] The left-hand side of Figure 3 shows an alternative route, namely the possible reaction between the isomeric $HOMg(\eta^2\text{-}CO_2)^-$ and water, which indicates that the expected reaction ionic product would be formate anion rather than the observed $Mg(OH)_3^-$, substantiating our structural and mechanistic assignment. Figure 3 also shows that the two isomers are separated by a considerable energy barrier of 105 kJ mol^{-1}.

Evidence for carbon–carbon bond formation is found in reactions between $XMg(CO_2)^-$ and alkyl halides, which is supported by quantum-chemical model calculations. Figure 4 shows that the product ion in this reaction is Cl^-. In the case of the reaction with CH_3I, the ionic product is I^-. Furthermore, depending on the ion translational energy and observation time window (which are different in the triple quadrupole, the FT-ICR, and the Paul trap), variable amounts of XMg^- owing to collision-induced CO_2 loss are observed. Only small amounts of acetate ion are observed (see below). The computed energy diagram of Figure 5 reveals the interesting details. The calculations substantiate the idea that the reaction is due to an C–C bond-forming S_N2 reaction, via the transition structure TSB (see Figure 6) at −10 kJ mol^{-1} relative to the separated reactants, demonstrating the increased nucleophilic character of the carbon atom of $HOMg(\eta^2O_2C)^-$ compared to CO_2. The ion displaces the

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

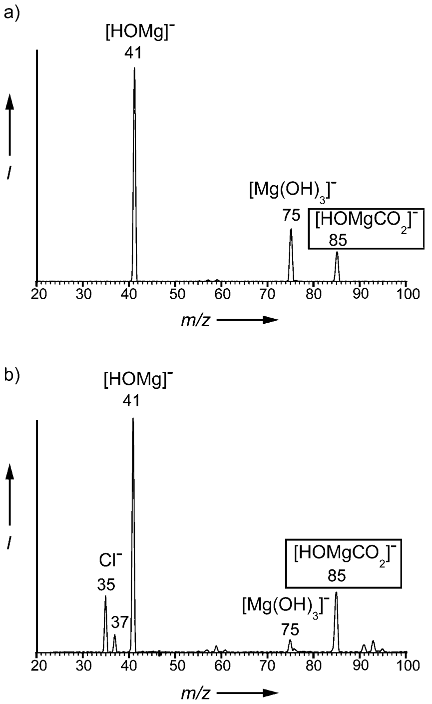

Figure 4. a) CID of $[HOMgCO_2]^-$ (m/z 85) and b) CAR of $[HOMg(CO_2)]^-$ (m/z 85) with CH_3Cl introduced into the collision cell using a triple-quadrupole mass spectrometer.

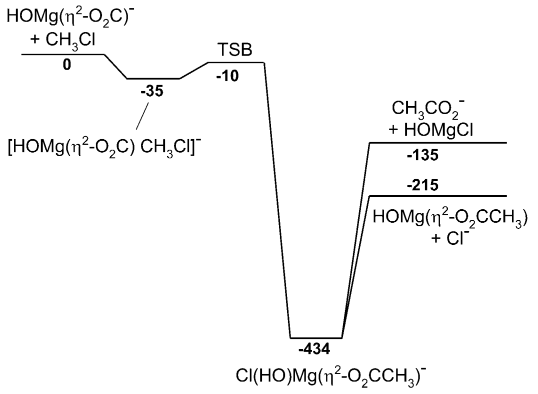

Figure 5. Potential energy diagram of $HOMg(CO_2)^-$ reacting with CH_3Cl. Relative energies are given in $kJ\,mol^{-1}$.

chloride upon which the complex of magnesium acetate hydroxide and Cl^- is formed, whereupon Cl^- separates:

$$HOMg(\eta^2\text{-}O_2C)^- + CH_3Cl \rightarrow HOMg(O_2CCH_3) + Cl^- \quad (3)$$

The alternative loss of acetate from the product complex is energetically less favorable and entropically more demanding, which is evident from the insignificant peaks at m/z 59 in the product mass spectra, as reported above.

The experimental evidence presented herein together with the insights of the quantum chemical calculations indicate unique electronic properties of the $HOMg(\eta^2\text{-}O_2C)^-$ structure. Formally it is a complex of one OH^-, one CO_2^{2-}, and one Mg^{2+} ion. In practice, the electronic situation is of course more complex, but straightforward enough to describe. According to the NBO population analysis, the CO_2 moiety carries almost two negative charges (−1.7), implying that magnesium is in a semi-reduced Mg^I state (+1.5). Interestingly, a negatively charged CO_2 molecule is a requirement for electrochemical conversion of CO_2 into CO, in accordance with the reaction with water reported above.[13] Upon collisionally induced dissociation, we observe that $XMg(\eta^2\text{-}O_2C)^-$ loses CO_2 in all cases. We have not been able to establish the experimental conditions required to study the reverse association reactions $XMg^- + CO_2$ because of the very low XMg^- signal, although in the case of X = OH, our quantum-chemical calculations clearly shows that formation of $HOMg(\eta^2\text{-}O_2C)^-$ is the more energetically favored product. The addition starts with the formation of a bond between magnesium and one of the oxygen atoms of the CO_2, whereupon the linear O=C=O starts to bend, eventually leading to a second Mg–O contact and formation of a four membered ring. There are no local minima or transition structures along this path.

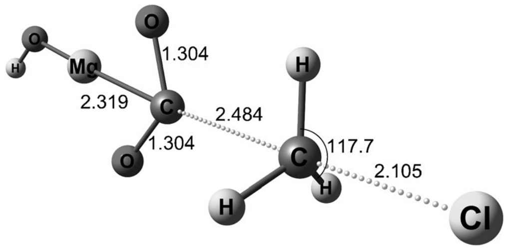

Figure 6. G4-optimized structure of TSB with bond lengths [Å] and angles [°] indicated.

The nucleophilic character of $XMg(\eta^2\text{-}O_2C)^-$ demonstrated in the reactions with alkyl halides reported above is also evident from an MO analysis. The highest occupied orbital (HOMO) clearly has a carbon lone-pair character (Supporting Information). Although the prototypical carbene, singlet CH_2, is less stable than its triplet form in the isolated gas phase, it is known to be persistent even when interacting with hydrogen-bond donors in various complexes.[14] Moreover, upon substitution by electron-donating substituents and protective groups, singlet carbenes are stable and isolable.[15] For example, spectroscopic evidence has been presented for gas-phase dihydroxymethylene, HOCOH,[16] which contains the same central structural element. We will emphasize that the compound at hand is a carbene (having one lone pair at carbon), rather than a carbon having two lone pairs,[17] as a second frontier MO having carbon lone pair character is not found.

We speculate that the findings presented herein have some relevance to the mechanism of the dark reaction of photosynthesis. In the carbon–carbon bond-formation step of this reaction, CO_2 is incorporated into a carbohydrate catalyzed by the magnesium-centered enzyme RuBisCo. A key issue of this reaction is the difficulty by which CO_2 is able to adapt a structure close to that of a carboxylate group at the transition state.[4] We propose that electron transfer (from $NADPH_2$) to the magnesium atom prior to or during this

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

event will allow this to happen by the quasi-magnesium(I) intermediate that we have described herein.

Received: December 1, 2011
Revised: May 7, 2012
Published online: June 6, 2012

Keywords: carbon dioxide fixation · computational chemistry · gas-phase reactions · nucleophilic substitution · photosynthesis

---

[1] D. O. Hall, K. K. Rao, *Photosynthesis*, *6th ed.*, Cambridge University Press, Cambridge, **1999**.
[2] M. Halmann, *Chemical Fixation of* CO_2, CRC, Boca Raton, **1993**.
[3] D. B. Dell'Amico, F. Calderazzo, L. Labella, F. Marchetti, G. Pampaloni, *Chem. Rev.* **2003**, *103*, 3857 – 3898.
[4] G. G. B. Tcherkez, G. D. Farquhar, T. J. Andrews, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 7246 – 7251.
[5] a) S. Derien, E. Dunach, J. Perichon, *J. Am. Chem. Soc.* **1991**, *113*, 8447 – 8454; b) Y. Tang, L. N. Zakharov, A. L. Rheingold, R. A. Kemp, *Organometallics* **2004**, *23*, 4788 – 4791; c) M. Tokuda, *J. Nat. Gas Chem.* **2006**, *15*, 275 – 281; d) D. A. Dickie, E. N. Coker, R. A. Kemp, *Inorg. Chem.* **2011**, *50*, 11288 – 11290; e) C. M. Mömming, E. Otten, G. Kehr, R. Fröhlich, S. Grimme, D. W. Stephan, G. Erker, *Angew. Chem.* **2009**, *121*, 6770 – 6773; *Angew. Chem. Int. Ed.* **2009**, *48*, 6643 – 6646.
[6] V. Grignard, *Ann. Chim. Phys., Ser. 7*, **1901**, *24*, 433.
[7] H. Schwarz, *Angew. Chem.* **2011**, *123*, 10276 – 10297; *Angew. Chem. Int. Ed.* **2011**, *50*, 10096 – 10115.
[8] A. P. Jacob, P. F. James, R. A. J. O'Hair, *Int. J. Mass Spectrom.* **2006**, *255 – 256*, 45 – 52.
[9] S. Curtis, J. Renaud, J. Holmes, P. Mayer, *J. Am. Soc. Mass Spectrom.* **2010**, *21*, 1944 – 1946.
[10] A. B. Attygalle, F. U. Axe, C. S. Weisbecker, *Rapid Commun. Mass Spectrom.* **2011**, *25*, 681 – 688.
[11] U. Gol'dshleger, E. Shafirovich, *Combust. Explos. Shock Waves* **1999**, *35*, 637 – 644.
[12] R. A. J. O'Hair, A. K. Vrkic, P. F. James, *J. Am. Chem. Soc.* **2004**, *126*, 12173 – 12183.
[13] B. A. Rosen, A. Salehi-Khojin, M. R. Thorson, W. Zhu, D. T. Whipple, P. J. A. Kenis, R. I. Masel, *Science* **2011**, *334*, 643 – 644.
[14] E. Uggerud, *J. Am. Chem. Soc.* **1994**, *116*, 6873 – 6879.
[15] a) H. W. Wanzlick, *Angew. Chem.* **1962**, *74*, 129 – 134; *Angew. Chem. Int. Ed. Engl.* **1962**, *1*, 75 – 80; b) A. Igau, H. Grutzmacher, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.* **1988**, *110*, 6463 – 6466; c) A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361 – 363.
[16] P. R. Schreiner, H. P. Reisenauer, *Angew. Chem.* **2008**, *120*, 7179 – 7182; *Angew. Chem. Int. Ed.* **2008**, *47*, 7071 – 7074.
[17] R. Tonner, G. Frenking, *Chem. Eur. J.* **2008**, *14*, 3260 – 3272.

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim