

LIGAND AND METAL EFFECTS IN THE GAS PHASE REACTIONS OF ALKALINE EARTH ORGANOEMETALLATES

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Organometallic "ate" species are formed in the gas phase via decarboxylation of the corresponding metal acetates (eq. 1) [1]. These organometallics undergo reactions consistent with their known condensed phase reactivity. For example, the organomagnesium species act as bases (eq. 2 where M = Mg and L = Cl or CH₃CO₂; X = OH) [1a]. Here we use a combination of multistage mass spectrometry experiments and DFT calculations to examine the effects of both the ligand as well as the metal on reactivity.

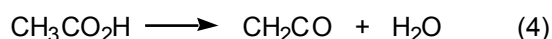
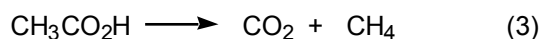


Electrospray ionization (ESI) of simple metal acetates [Metal(CH₃CO₂)_n] yields [Metal(CH₃CO₂)_{n+1}]⁻ ions. Using multi-stage mass spectrometry experiments in a modified ion trap (LCQ), these anions can be subjected to CID and the resultant organometallic anions can be mass selected and subject to additional stages of CID or ion-molecule reactions with neutral reagents such as methanol and carbonyl compounds. Rate measurements can be made to compare reactivity trends [2].

Ligand Effects: The reactivity of the organomagnesium species towards water and other acids (eq. 2 where M = Mg and L = Cl or CH₃CO₂) is attenuated for the acetate ligand. This is consistent with DFT calculations, which suggest an increase in coordination number caused by the bidentate binding of the acetate ligand.

Metal Effects: The organocalcium species react substantially faster with water and other acids than their organomagnesium counterparts, consistent with their enhanced reactivity in the condensed phase.

Catalysis: [CH₃ML₂]⁻ ions reacted with CH₃CO₂H to complete a catalytic cycle for the decarboxylation of acetic acid (eq. 3). In contrast, the [(HO)₂Ca(CH₃CO₂)]⁻ ion catalyses the dehydration of the acetic acid (eq. 4), highlighting the importance of ligand effects.



References:

- (1a) O'Hair, R. A. J.; Vrkic, A. K.; James, P. F., *J. Am. Chem. Soc.*, **2004**, *126*, 12173; (1b) James, P. F.; O'Hair, R. A. J., *Org. Lett.*, **2004**, *6*, 2761.
(2) Waters, T.; O'Hair, R. A. J.; Wedd, A. G. *J. Am. Chem. Soc.*, **2003**, *125*, 3384.