

# Gas Phase Synthesis of Neutral Rare Earth Metal Alkoxides as « High Tech » Materials

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Need of **new synthetic routes** of **neutral rare earth alkoxides**



Reaction of monovalent ion **M<sup>+</sup>** with potential alkoxy or aryloxy group suppliers

## INTRODUCTION

Today rare earths are involved in a variety of "**high tech**" materials [1] : electro-optical ceramics, superconductors, optical materials, sensors, catalysts or catalyst promoters



The formulations of rare earth-based materials are various **but** oxide-based materials represent the most developed class today

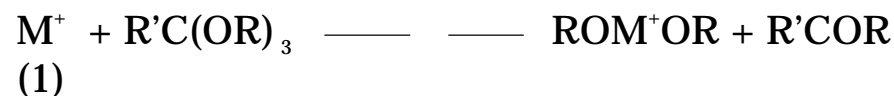


Metal alkoxides and aryloxides are the best class of **precursors** for these oxide-based materials



## Reactions observed in the cell of a FT-ICR Mass Spectrometer

M = Sc<sup>+</sup> [2-3], Y<sup>+</sup> [3], Lu<sup>+</sup> [3]



(if stable)

*R = CH<sub>3</sub> - R' = H, CH<sub>3</sub>, Ph (orthoesters) - R' = OCH<sub>3</sub> (carbonate)*

In this work, we show preliminary results on the gas phase reactions

between the neutral compound **methyl orthoformate** [ $\text{HC}(\text{OCH}_3)_3$ ] and the lanthanide metal ions  $\text{Ln}^+$  ( $\text{Ln} = \text{La}$  to  $\text{Lu}$ , except  $\text{Pm}$ ).

## EXPERIMENTAL SECTION

All experiments in Sacavém were conducted in a Finnigan FT/MS 2001-DT **FT-ICR** mass spectrometer, equipped with a 3 T superconducting magnet and interfaced with a Spectra-Physics Quanta-Ray GCR-11 Nd:YAG laser operated at the fundamental wavelength (1064 nm). The rare earth cations were produced by direct **laser desorption/ionisation** (LDI) of

Tb	30		10	15		45			<b>0.70</b>
Dy					50	50			<b>0.62</b>
Ho					35	65			<b>0.59</b>
Er			10		40	50			<b>0.65</b>
Tm				10	50	40			<b>0.50</b>
Yb				35			15	50	<b>0.53</b>
Lu	15	25		20	25	15			<b>0.77</b>

commercially obtained pure metal pieces. The detailed experimental procedures concerning neutral pressure measurements, thermalization of reactant ions and rate constant determinations, have been described previously [4].

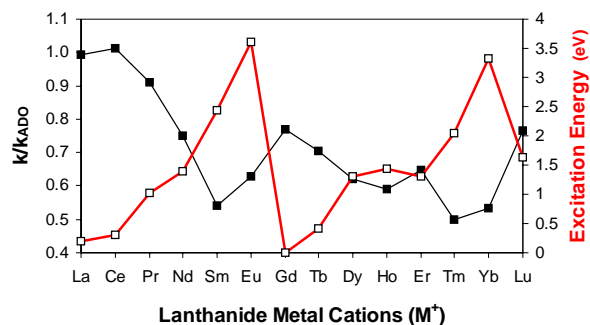
## RESULTS and DISCUSSIONS

**Primary product distributions (%) obtained in the reaction of  $\text{Ln}^+$  metal ions and  $\text{HC}(\text{OCH}_3)_3$**

$\text{M}^+$	Primary product distributions (%)								$k/k_{\text{ABo}}$
	$\text{MO}^+$	$\text{MOH}^+$	$\text{MOCH}_2^+$	$\text{MOCH}_3^+$	$\text{HMOCH}_3^+$	$\text{M}(\text{OCH}_3)_2^+$	$\text{M}(\text{C}_2\text{H}_7\text{O}_2)^+$	$\text{M}(\text{C}_4\text{H}_9\text{O}_3)^+$	
La	25	10	5	10		50			<b>0.99</b>
Ce	35	5	15	20		25			<b>1.01</b>
Pr	25		20	20		35			<b>0.91</b>
Nd	10		10	20		60			<b>0.75</b>
Sm				75		25			<b>0.54</b>
Eu				80				20	<b>0.63</b>
Gd	10		25	25		40			<b>0.77</b>

The primary product distributions (%) obtained in the reaction of  $\text{Ln}^+$  metal ions and  $\text{HC}(\text{OCH}_3)_3$  show the existence of important **differences** in the relative **reactivity** of these metal cations, like we have observed previously with other oxygenated organic molecules [5].

For example, the primary  $\text{MO}^+$  ion is not formed for all  $\text{Ln}^+$  cations. The formation of  $\text{MO}^+$  probably requires an initial **insertion** of the **metal** ion in the **C-O bond** of the **neutral**. The ability of the lanthanide metal cations to follow such a bond insertion mechanism depends on the excitation energies ground state  $\rightarrow d^1s^1$  state (see Figure 1), and it appears that the  $\text{MO}^+$  ion is only **formed** for those  $\text{Ln}^+$  ions with **lower excitation energies**.



**Figure 1 :** Efficiencies  $k/k_{ADO}$  of the reactions of lanthanide cations  $M^+$  with  $HC(OCH_3)_3$  (filled squares - left axis) and excitation energies ground state  $\rightarrow d^1s^1$  state of the metal cations (open squares - right axis; values from [2]).  $k_{ADO}$  was calculated according to [6] using estimated values for the dipole moment [7] and for the polarizability [8] of  $HC(OCH_3)_3$

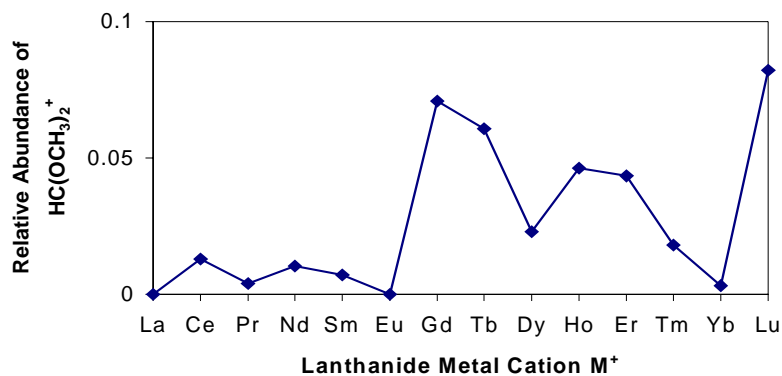
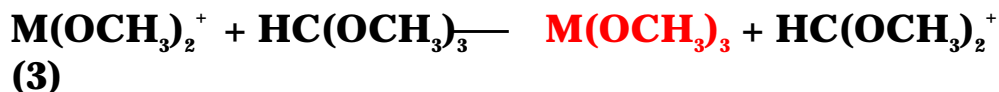
The reaction efficiencies  $k/k_{ADO}$  determined for the lanthanide ions also seem to **correlate** with the

**excitation energies**, as we can see in Figure 1 which shows **inversely parallel** trends for the two quantities.

## Formation of $M(OCH_3)_3$

The formation of the dimethoxy metal ion  $M(OCH_3)_2^+$ , both as a primary product and in subsequent reactions, is observed for all lanthanide ions except  $Eu^+$  and  $Yb^+$ , which are the ones that have more stable **2+** formal **oxidation states**.

The principal subsequent reaction of  $M(OCH_3)_2^+$  with  $HC(OCH_3)_3$  is the presumed formation of the neutral metal trismethoxide :



**Figure 2 :** Relative abundance of  $HC(OCH_3)_2^+$  calculated from the overall reactions  $M^+ + HC(OCH_3)_3$  for the same reaction time and pressure, as a function of the lanthanide metal cation

Figure 2 shows the relation between the formation of neutral  $M(OCH_3)_3$ , as measured by the relative abundance of  $HC(OCH_3)_2^+$ , and the nature of metal ion. It appears that this process is favored for the second part of the lanthanides series.

The observation of reaction (3) implies that the **ionisation energy** of neutral  $M(OCH_3)_3$  is larger than that of  $HC(OCH_3)_2$ . If we admit that  $IE[M(OCH_3)_3]$  follows the same trend as  $IE(M)$  along the lanthanide series, we can see from Figure 3 that it is the second part of the series that shows higher values. This is in agreement with the observations presented in Figure 2.

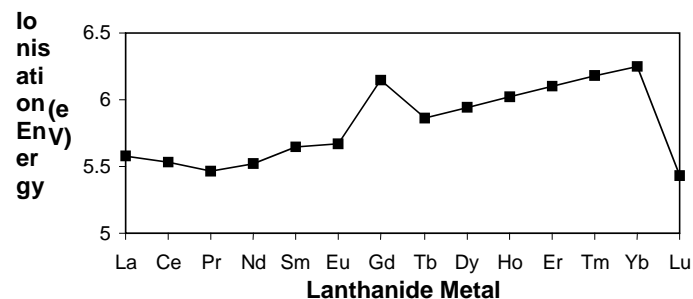


Figure 3 : Ionisation energies for the different lanthanide metals [9]

**Two main questions remain :**  
**How to prove unambiguously the formation of  $M(OR)_3$ ?**  
**How to prepare the  $M(OR)_3$  compounds in macroscopic quantities by this route ?**

## CONCLUSIONS

In this work, we have shown that the **gas phase reactions** of  $Ln^+$  with  $HC(OCH_3)_3$  lead to the **dialkoxy metal ions** which subsequently react with methyl orthoformate to form the  **$HC(CH_3)_2^+$**  ion, and presumably  $Ln(OCH_3)_3$ .

The reactions of monovalent rare earth ions  **$M^+$**  with potential alkoxy or aryloxy group suppliers, such as **esters** or **carbonates**, appear to be a possible route for the gas phase synthesis of neutral rare earth metal alkoxides.

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