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

N. MARCHANDÉ#, S. BRETON#,
M. DECOUZON#, S. GERIBALDI#,
J. MARÇALO*, J. M. CARRETAS*,
A. PIRES DE MATOS*

G.R.E.C.F.O.-Chimie Physique Organique
Université de Nice-Sophia Antipolis

* Instituto Tecnológico e Nuclear
Departamento de Química

Rare Earth Metals "High Tech" Materials

sensors / superconductors / optical materials / catalyst promoters

Metal Alkoxides

Best Class of Precursors Oxide-Based Materials

New Synthetic Routes of neutral rare earth alkoxides

$$M^+ + RC(OR')_3$$

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

M = Sc^+, Y^+, Lu^+ (*)

$$M^+ + R'C(OR)_3 \longrightarrow ROM^+OR + R'COR \quad (1)$$

$$ROM^+OR + R'C(OR)_3 \longrightarrow (RO)_3M + R'C(OR)_2^+$$

(if stable) ***(2)***

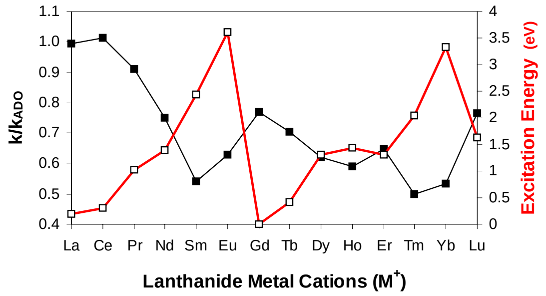
R = CH_3 *R' = H, CH_3, Ph (orthoesters)*
R' = OCH_3 (carbonate)

(*) : Experiences in Université de Nice-Sophia Antipolis

Ln^+ (Ln = La to Lu, except Pm) + $HC(OCH_3)_3$

	Primary product distributions (%)								
M^+	MO^+	MOH^+	$MOCH_2^+$	$MOCH_3^+$	$HMOCH_3^+$	$M(OCH_3)_2^+$	$M(C_2H_7O_2)^+$	$M(C_4H_9O_3)^+$	k/k_{ADO}
La	25	10	5	10		50			0.99
Ce	35	5	15	20		25			1.01
Pr	25		20	20		35			0.91
Nd	10		10	20		60			0.75
Sm				75		25			0.54
Eu				80				20	0.63
Gd	10		25	25		40			0.77
Tb	30		10	15		45			0.70
Dy					50	50			0.62
Ho					35	65			0.59
Er			10		40	50			0.65
Tm				10	50	40			0.50
Yb				35			15	50	0.53
Lu	15	25		20	25	15			0.77

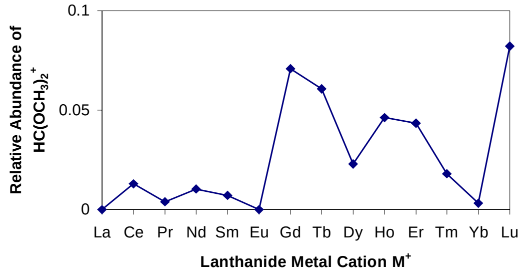
Efficiencies k/k_{ADO} of the reactions of lanthanide cations M^+ with $HC(OCH_3)_3$ (filled squares - left axis) and excitation energies ground state → d^1s^1 state of the metal cations (open squares - right axis)



Formation of $M(OCH_3)_3$

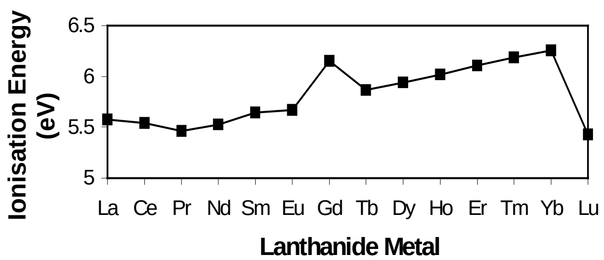
$M(OCH_3)_2^+ + HC(OCH_3)_3$ —— $M(OCH_3)_3 + HC(OCH_3)_2^+$ ***(3)***

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



IE ($M(OCH_3)_3$ > IE ($HC(OCH_3)_2$)

Ionisation energies for the different lanthanide metals



CONCLUSIONS

$Ln^+ + HC(OCH_3)_3$ → ⟶ $HC(OCH_3)_2^+$ + **$Ln(OCH_3)_3$**

M^+ + esters or carbonates ⟶ stable ion + $Ln(OCH_3)_3$

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 ?**

Acknowledgment :
This work was supported by a Portuguese-French Scientific Cooperation Programme, administered by ICCTI/Portugal and the French Embassy in Portugal.

Joaquim MARÇALO
(Instituto Tecnológico e Nuclear (P))

Serge GERIBALDI
(Université de Nice – Sophia Antipolis (F))