Can the cell of a FT-ICR spectrometer be used as a gas phase micro-reactor for synthesis of rare earth alkoxides ?

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Today lanthanides are involved in a variety of "high tech" materials[1] : electrooptical ceramics, high tech superconductors, optical materials, sensors, catalysts or catalyst promoteurs.

The formulations of lanthanide-based materials are various but oxide-based materials represent the most-developped class today

Metal alkoxides and aryloxydes is the best class of precursors for these oxide-based materials

Need of new synthetic routes of lanthanide alkoxides and aryloxides

1 : (a) Hubert-Pfalzgraf, L. G. *New J. Chem*. **1987**, *11*, 6623. (b) Yamane, H.; Mabumoto, H.; Hirai, T. *Appl., Phys. Lett*. **1988**, *53*, 1548. (c) Carretas, J. M.; Pires de Matos, A. *Materials Chem. Phys*. **1992**, *31*, 123.(d) Hubert-Pfalzgraf, L. G. *New J. Chem*. **1995**, *19*, 727.

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

1) Ln^+ + alcohol $\longrightarrow$ various $\longrightarrow$ $ROLn^+OR$
or ether primary compounds

2) $ROLn^+OR$ + X-OR $\longrightarrow$ $(RO)_3Ln^+$ + X^+
(if X^+ stable)

Nature of X-OR compounds :

- tBu-OR (R = CH_3※, C_2H_5※)
- R'_2-CH-$(OR)_2$ (R' = CH_3; R = CH_3)
- R'-CH-$(OR)_3$ R'= H※, CH_3
  R = CH_3※, C_2H_5※, C_3H_7※

※ : compounds already do (cf. results)

a) Formation of $M(OR)_3$ from alkyl ethers

The formation of dialkoxy metal ion are observed for the three metal ions in subsequent reactions :

$$M^+ + (CH_3)_3COR \longrightarrow \longrightarrow M(OR)_2^+ + \text{neutral}$$

(M = Sc, Y, Lu ; R = Me, Et)

The subsequent reaction of $M(OR)_2^+$ with ethers is :

$$M(OR)_2^+ + (CH_3)_3COR \longrightarrow M(OR)_3 + (CH_3)_3C^+$$
$$\longrightarrow \text{other compounds}$$

When M = Y and R = Me **:**
the formation of $(CH_3)_3C^+$ ion is not observed

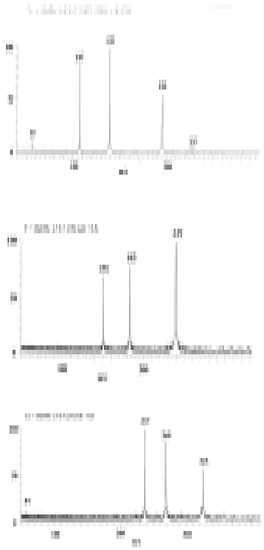
When M = Y and R = Et **:**
the formation of $(CH_3)_3C^+$ ion is infinitesimal (< 5%)

This reaction does not form only the $(CH_3)_3C^+$ ion with the three metal and the two alkyl groups.

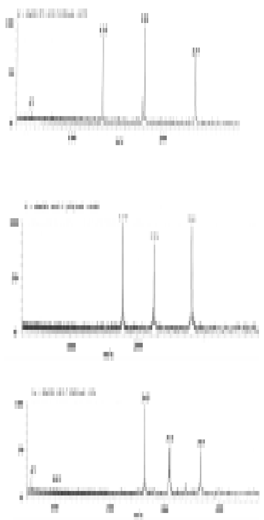
> **To date, the formation of the metal trialkoxides is demonstrated indirectly by the formation of $(CH_3)_3C^+$ ions from the reaction of $M(OR)_2^+$ and tertiobutyl alkyl ethers.**

a) $M^+(OR)_2$ (M=Sc, Y, Lu) with tertiobutyl alkyl ethers tBuOR (R= CH_3, C_2H_5)

$M^+(O\,CH_3)_2$ + tBuO CH_3



$M^+(O\,C_2H_5)_2$ + tBuO C_2H_5



CONCLUSION

The gas phase reactions of M^+ with alkyl orthoformates lead to the dialkoxy-metal ions which subsquently react with the orthoformates to form the $HM(OR)_2^+$ ions.

The gas phase reactions of M^+ with tertiobutyl alkyl ethers lead to the dialkoxy - metal ions which subsquently react with the ethers to form the $C(CH_3)_3^+$ ions.

Is the reaction between M^+ and alkoxy organic compounds, such as orthoformates or ethers or others, a possible route for gas phase synthesis of rare earth metal alkoxides ?

Now the question is :

How to prove unambiguously the formation of $M(OR)_3$ in the FT-ICR cell ?