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# Gas-phase reactions of lanthanide cations with alcohols

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All readers know the excellent contribution of Alan Marshall to the mass spectrometry community all over the world. We would like to recall his first visit to our Institute where, with his impressive hat, as an "American in Sacavém" (not in Paris), he stimulated the FTICR music in Portugal. It has occurred almost fifteen years ago that we sent him the first spectra of uranium ions obtained in Sacavém. We (A.P.M. and J.M.) visited him in Columbus and Tallahassee, and forgetting about the work, we remember well the friendly atmosphere and excellent food at his home. Thanks Alan for all these years. We enjoyed and still enjoy the FTICR work.

## Abstract

The gas-phase reactions of the lanthanide series cations $Ln^+$ (Ln = La–Lu, except Pm) with methanol, ethanol, and 2-propanol were studied by Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS). The majority of the lanthanide cations react exothermically with the alcohols, with formation of $LnO^+$ and $LnOH^+$ ions as main primary products. These ions participate in subsequent reactions with the alcohols that lead to $Ln(OR)_x(HOR)_y{}^+$ species, where $x = 1$–$2$ and $y = 0$–$3$. The study of the reaction sequences and of the corresponding kinetics showed the existence of important differences in the relative reactivity of the lanthanide series cations, in agreement with the known data on the reactivity of these metal cations with other organic molecules. The results obtained also evidenced the similarities between the reactivity of the lanthanide series cations and of group 3 metal cations.

*Keywords:* Lanthanide ions; Alcohols; Gas phase; FTICR-MS

## 1. Introduction

The chemistry of lanthanide alkoxides has received considerable attention in recent years, particularly due to the use of these compounds in the synthesis of new materials [1–7]. One of the main synthetic methods used, metal organic chemical vapor deposition (MOCVD), involves gas-phase procedures and efforts continue to be made to prepare lanthanide alkoxides that meet the requirements of the method, especially in terms of volatility. One of the features of lanthanide alkoxides (as well as of early transition metals) is that only for bulky or functionalised alcohols can discrete monomeric compounds be prepared. For small aliphatic alcohols the formation of oligomeric compounds is typical, sometimes with the presence of oxo or hydroxo ligands, which does not depend on the method used for the synthesis of the compound [2–5,7]. In our group, efforts have been made in the preparation of lanthanide alkoxides and aryloxides using different synthetic methods [8–12].

Gas-phase studies of the reactions of metal ions with organic molecules can sometimes provide hints on the mechanisms operative in condensed phases [13–16]. In joint work with Géribaldi and co-workers, we have recently reported on the gas-phase reactivity of lanthanide and group 3 metal cations with phenol [17], and on the reactivity of $Y^+$ and $Ln^+$ (Ln = La–Lu, except Pm) cations with trimethylorthoformate, and of $Y^+$ and $Lu^+$ ions with triethyl and tripropyl orthoformates [18]. The latter study had the purpose of probing the possible formation of neutral rare earth (lanthanide and group 3) trisalkoxides, following preliminary studies with $Sc^+$ cations by Géribaldi et al. [19].

In the present work, we describe gas-phase reactions of the lanthanide series cations $Ln^+$ (Ln = La–Lu, except Pm) with methanol, ethanol, and 2-propanol, studied by means of Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) [20–22], expanding previous work by Géribaldi and co-workers with related group 3 metal cations $Sc^+$, $Y^+$, and $Lu^+$ [23,24]. The studies involving methanol

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may have an additional relevance if they are to be compared with an interesting recent study of the reactivity of lanthanide cations with methanol clusters [25]. Moreover, these studies with alcohols also complement recent comprehensive studies of the gas-phase reactivity of lanthanide cations with hydrocarbons and other organic molecules [26–36]. Among the studies that have been revealing several interesting aspects of lanthanide chemistry, a mention is made to the first systematic study including all the lanthanide series cations that was done in a joint work of our group with Marshall and co-workers [29]. The work reported below has been briefly described in a recent review of our gas-phase studies with lanthanide cations [37].

## 2. Experimental

The experiments were carried out using a Finnigan FT/MS 2001-DT FTICR 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 metallic ions were produced by laser ionization of commercially obtained pure metal pieces. The reagent alcohols were dried by standard methods [38] prior to use and were introduced in the spectrometer through Andonian Cryogenics or Granville–Phillips leak valves. All experiments were carried out on the “source” side of the dual ion trap of the instrument. Reaction sequences were identified by means of double-resonance and MS/MS techniques. Isolation of the desired ions was achieved with the SWIFT technique [39]. The reactant ions were thermalized by collisions with argon, typically with 1 s collisional cooling periods after the introduction of the gas into the vacuum chamber of the instrument through General Valve Series 9 pulsed solenoid valves to pressures of ca. $10^{-5}$ Torr. The reproducibility of the reaction kinetics as well as the linearity of the semilog plots of the normalized reactant ion intensities versus time were used as indications of the thermalization of reactant ions. In the case where there was more than one product ion, absence of changes in the product distributions for different collisional cooling periods or collision gas pressures were also considered as indicative of the thermalization effectiveness. Neutral pressures were measured by a Bayard–Alpert type ionization gauge and were in the range of $3 \times 10^{-8}$ to $3 \times 10^{-7}$ Torr. Pressure calibration was made using the reactions $CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$ [40] and $CH_3COCH_3^+ + CH_3COCH_3 \rightarrow$ products [41] and included corrections for the ionization efficiencies of the alcohols [42], based on experimental molecular polarizabilities [43]. Rate constants were determined from the pseudo-first order decay of the reactant ion relative intensity as a function of time at constant reagent pressure. These constants are reported as reaction efficiencies, that is, as fractions of the average dipole orientation theory (ADO) collisional rates [44], calculated using tabulated dipole moments and molecular polarizabilities for the alcohols [43]. Uncertainties in the pressure calibration procedure may lead to errors in the absolute rate constants that we estimate to be ±50%, but the relative magnitudes of the reaction efficiencies should have errors lower than 20%.

## 3. Results and discussion

### 3.1. Primary reactions of lanthanide cations with methanol, ethanol and 2-propanol

In Tables 1–3 we summarize the primary product distributions, the rate constants ($k$) and the efficiencies ($k/k_{ADO}$) of the reactions of the lanthanide series ions $Ln^+$ ($Ln = La–Lu$, except Pm) with methanol (Table 1), ethanol (Table 2) and 2-propanol (Table 3). For some of the cations of the second half of the lanthanide series the primary reactions with

Table 1
Primary product distributions (%), rate constants ($k$) and efficiencies ($k/k_{ADO}$) of the reactions of lanthanide metal cations with methanol

| $Ln^+$ | Product ion | | | | $k$ ($\times 10^9$) ($cm^3$/molecule·s) | $k/k_{ADO}$ |
|---|---|---|---|---|---|---|
| | $LnO^+$ | $LnOH^+$ | $LnOCH_2^+$ | $LnOCH_3^+$ | | |
| $La^+$ | 20 | 20 | 30 | 30 | 0.62 | 0.34 |
| $Ce^+$ | 15 | 15 | 45 | 25 | 0.62 | 0.34 |
| $Pr^+$ | 20 | 20 | 25 | 35 | 0.27 | 0.15 |
| $Nd^+$ | 15 | 35 | 10 | 40 | 0.163 | 0.09 |
| $Sm^+$ | 25 | 75 | – | – | 0.02 | 0.01 |
| $Eu^+$ | – | 100 | – | – | 0.002 | 0.001 |
| $Gd^+$ | 15 | 20 | 65 | – | 0.61 | 0.34 |
| $Tb^+$ | 20 | 10 | 70 | – | 0.49 | 0.27 |
| $Dy^+$ | (70) | – | – | (30) | 0.004 | 0.002 |
| $Ho^+$ | (40) | – | (60) | – | 0.009 | 0.005 |
| $Er^+$ | (20) | – | (80) | – | 0.09 | 0.05 |
| $Tm^+$ | – | – | – | – | 0.0016 | <0.001 |
| $Yb^+$ | – | – | – | – | 0.0005 | <0.001 |
| $Lu^+$ | 10 | 70 | – | 20 | 0.46 | 0.26 |

The numbers in brackets are estimated values.

Table 2
Primary product distributions (%), rate constants ($k$) and efficiencies ($k/k_{ADO}$) of the reactions of lanthanide metal cations with ethanol

| $Ln^+$ | Product ion | | | | | | $k$ ($\times 10^9$) (cm$^3$/molecule·s) | $k/k_{ADO}$ |
|---|---|---|---|---|---|---|---|---|
| | $LnO^+$ | $LnOH^+$ | $LnOH_2{}^+$ | $LnOCH_2{}^+$ | $LnOCH_3{}^+$ | $LnOC_2H_5{}^+$ | | |
| $La^+$ | 60 | 20 | – | – | – | 20 | 0.69 | 0.41 |
| $Ce^+$ | 70 | 15 | – | – | – | 15 | 0.69 | 0.41 |
| $Pr^+$ | 45 | 30 | – | – | – | 25 | 0.47 | 0.28 |
| $Nd^+$ | 30 | 40 | – | – | – | 30 | 0.30 | 0.18 |
| $Sm^+$ | 10 | 90 | – | – | – | – | 0.10 | 0.06 |
| $Eu^+$ | – | 100 | – | – | – | – | 0.099 | 0.06 |
| $Gd^+$ | 65 | 25 | – | – | 10 | – | 0.64 | 0.39 |
| $Tb^+$ | 65 | 15 | – | – | 20 | – | 0.61 | 0.37 |
| $Dy^+$ | (70) | (10) | – | – | – | (20) | 0.2 | 0.1 |
| $Ho^+$ | (70) | (15) | – | (15) | – | – | 0.07 | 0.4 |
| $Er^+$ | (75) | (10) | – | (15) | – | – | 0.20 | 0.12 |
| $Tm^+$ | – | – | – | – | – | – | 0.002 | <0.001 |
| $Yb^+$ | – | – | – | – | – | – | 0.0003 | <0.001 |
| $Lu^+$ | 5 | 25 | 50 | – | 10 | 10 | 0.60 | 0.37 |

The numbers in brackets are estimated values.

methanol and ethanol were rather inefficient and slower than subsequent reactions; therefore, we were unable to determine with confidence the corresponding product distributions (the numbers in brackets in Tables 1 and 2 indicate tentative determinations for $Dy^+$, $Ho^+$ and $Er^+$). $Tm^+$ and $Yb^+$ were unreactive with the three alcohols.

The majority of the lanthanide cations reacted exothermically with the alcohols, with formation of $LnO^+$ (Eq. (1)) and $LnOH^+$ (Eq. (2)) ions as main primary products. The ionic species $LnOH_2{}^+$ (Eq. (3)), $LnOCH_2{}^+$ (Eq. (4)) and $LnOR^+$ ($R = CH_3$, $C_2H_5$ and $C_3H_7$) (Eqs. (5) and (6)) have also been obtained in some cases.

$$Ln^+ + ROH \rightarrow [LnO]^+ + RH \quad (R = CH_3, C_2H_5, C_3H_7) \tag{1}$$

$$Ln^+ + ROH \rightarrow [LnOH]^+ + R^\bullet \quad (R = CH_3, C_2H_5, C_3H_7) \tag{2}$$

$$Ln^+ + ROH \rightarrow [LnOH]^+ + R\text{–}H \quad (R = C_2H_5, C_3H_7) \tag{3}$$

$$Ln^+ + ROH \rightarrow [LnOCH_2]^+ + H_2 \quad (R = CH_3), \quad CH_4 \quad (R = C_2H_5) \tag{4}$$

$$Ln^+ + ROH \rightarrow [LnOCH_3]^+ + CH_3{}^\bullet \quad (R = C_2H_5) \tag{5}$$

$$Ln^+ + ROH \rightarrow [LnOR]^+ + H^\bullet \quad (R = CH_3, C_2H_5, C_3H_7) \tag{6}$$

Comparing these results with the ones obtained by Géribaldi and co-workers [23,24] on the reactivity of $Sc^+$, $Y^+$, and $Lu^+$ with aliphatic alcohols, it can be said that there is a general accordance between the two studies, in terms of primary products formed. The principal differences in the previous studies [23,24] are the absence of

Table 3
Primary product distributions (%), rate constants ($k$) and efficiencies ($k/k_{ADO}$) of the reactions of lanthanide metal cations with 2-propanol

| $Ln^+$ | Product ion | | | | $k$ ($\times 10^9$) (cm$^3$/molecule·s) | $k/k_{ADO}$ |
|---|---|---|---|---|---|---|
| | $LnO^+$ | $LnOH^+$ | $LnOH_2{}^+$ | $LnOC_3H_7{}^+$ | | |
| $La^+$ | 50 | 45 | – | 5 | 0.88 | 0.57 |
| $Ce^+$ | 55 | 40 | – | 5 | 0.89 | 0.58 |
| $Pr^+$ | 50 | 50 | – | – | 0.63 | 0.41 |
| $Nd^+$ | 40 | 60 | – | – | 0.52 | 0.34 |
| $Sm^+$ | – | 100 | – | – | 0.25 | 0.16 |
| $Eu^+$ | – | 100 | – | – | 0.06 | 0.4 |
| $Gd^+$ | 60 | 35 | 5 | – | 0.81 | 0.53 |
| $Tb^+$ | 70 | 20 | 10 | – | 0.63 | 0.42 |
| $Dy^+$ | 85 | 10 | 5 | – | 0.06 | 0.4 |
| $Ho^+$ | 95 | – | 5 | – | 0.18 | 0.12 |
| $Er^+$ | 95 | – | 5 | – | 0.36 | 0.24 |
| $Tm^+$ | – | – | – | – | 0.013 | <0.001 |
| $Yb^+$ | – | – | – | – | 0.0003 | <0.001 |
| $Lu^+$ | 5 | 45 | 50 | – | 0.58 | 0.39 |

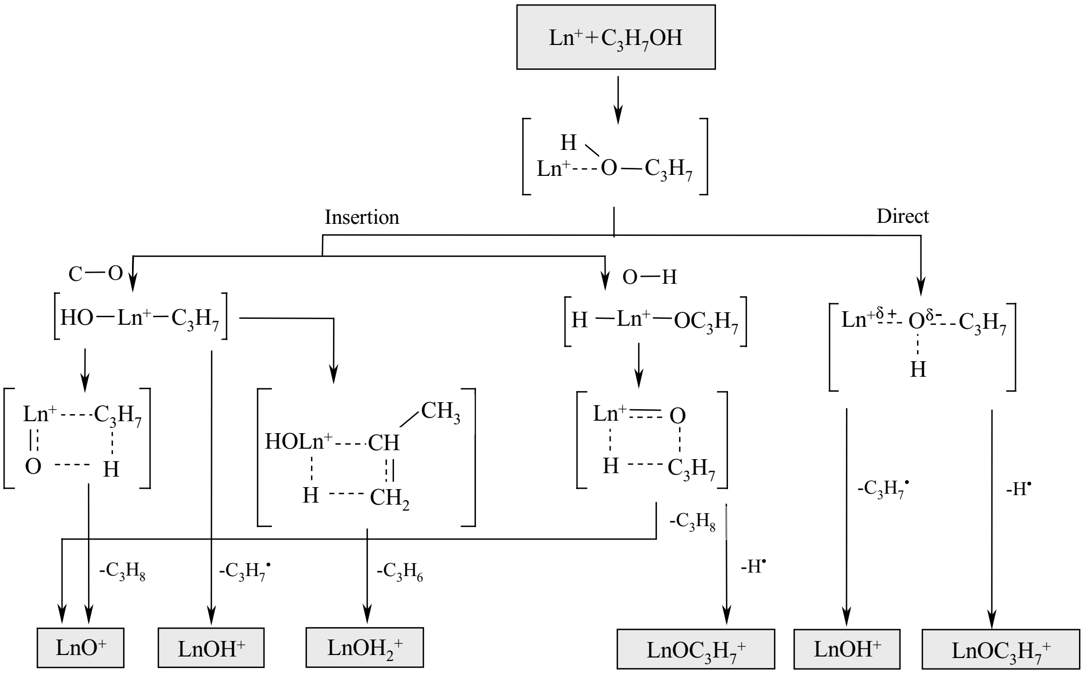
$LuO^+$ and the formation of the minor products $MH_2{}^+$ in the case of $Y^+$ with $CH_3OH$ and $C_2H_5OH$, and $MOC_3H_4{}^+$ in the reactions of $M^+$ (M = Sc, Y, Lu) with 2-propanol. The other gas-phase reactivity study of $Ln^+$ cations with methanol [25] did not focus on the reactions of metal ions with single molecular substrates, but within a cluster environment. Despite the fact that the experimental conditions are completely different from ours, we can emphasize the formation of the dehydrogenation products $LnOCH_2{}^+$ and $LnOCH_3{}^+$ with the most reactive ions $La^+$, $Ce^+$, $Pr^+$, $Nd^+$, $Gd^+$, $Tb^+$, $Ho^+$, $Er^+$ and $Lu^+$, besides the normal association products $Ln(CH_3OH)^+$. For $Lu^+$ other products such as $LuOH^+$ are also produced. The formation of $LnO^+$ was also observed but the authors attributed the presence of these oxide species to the quick oxidation of the lanthanide metal, and therefore they did not consider them as alcohol reaction products. On the other hand, the relatively unreactive $Sm^+$, $Eu^+$, $Dy^+$, $Tm^+$ and $Yb^+$ ions could not initiate dehydrogenation of methanol molecules and only association products $Ln(CH_3OH)^+$ were formed.

Table 4
Excitation energies (eV) ground state → $4f^{n-1}6s^15d^1$ state of the lanthanide cations $Ln^+$, second ionization energies (eV) of the lanthanide metals Ln, and lanthanide metal cation–oxygen bond dissociation enthalpies $D(Ln^+–O)$ (kJ/mol)

| $Ln^+$ | Excitation energy (eV)[a] | Second ionization energy (eV)[b] | $D(Ln^+–O)$ (kJ/mol)[c] |
|---|---|---|---|
| $La^+$ | 0.19 | 11.060 | 866 ± 14 |
| $Ce^+$ | 0.3 | 10.85 | 867 ± 16 |
| $Pr^+$ | 1.02 | 10.55 | 801 ± 20 |
| $Nd^+$ | 1.4 | 10.73 | 756 ± 16 |
| $Sm^+$ | 2.43 | 11.07 | 582 ± 16 |
| $Eu^+$ | 3.6 | 11.241 | 389 ± 18 |
| $Gd^+$ | 0 | 12.09 | 754 ± 17 |
| $Tb^+$ | 0.42 | 11.52 | 733 ± 16 |
| $Dy^+$ | 1.31 | 11.67 | 600 ± 43 |
| $Ho^+$ | 1.44 | 11.80 | 597 ± 27 |
| $Er^+$ | 1.31 | 11.93 | 589 ± 23 |
| $Tm^+$ | 2.05 | 12.05 | 535 ± 22 |
| $Yb^+$ | 3.32 | 12.176 | 389 ± 13 |
| $Lu^+$ | 1.63 | 13.9 | 560 ± 20 |

[a] Values from [47].
[b] Values from [43].
[c] Values from [48].

In our study different types of mechanisms could be simultaneously operative in the formation of the various primary products summarized in Tables 1–3. In Scheme 1 we show a representation of the proposed mechanisms in the case of 2-propanol. Previous gas-phase reactivity studies [17,18,23,24,26–35,37,45] of lanthanide metal cations with different organic molecules have shown that the ability of the lanthanide series ions to activate single bonds in different organic molecules correlates with the magnitude of the excitation energies from the ground state electron configurations, generally $4f^n6s^1$, to configurations with two unpaired non f electrons, particularly $4f^{n-1}6s^15d^1$ [46,47] (although $4f^{n-1}5d^2$ can also be considered), that are a necessary condition if a bond insertion mechanism is considered. These excitation energies from the ground state configurations to the $4f^{n-1}6s^15d^1$ configurations of the lanthanide ions are listed in Table 4. In the case of the alcohols, the oxophilicity of the metal ions was invoked as the major factor controlling the overall reactivity [23,24], although recent work done in our group involving phenols [17] indicates that besides the excitation energy, the second ionization energy of the metal could



Scheme 1.

also be important in explaining the formation of several ionic species, namely by a direct mechanism, in agreement with lanthanide reactivity studies with fluorinated hydrocarbons [32,34,45]. The values of the second ionization energy for the lanthanide metals are also listed in Table 4.

Formation of $LnO^+$ (Eq. (1)) can be explained as in previous studies [23,24] by a mechanism that started with a C–O or O–H insertion, followed by four-center electrocyclic elimination of RH. The fact that the O–H bonds are stronger than the C–O bonds (in methanol $D(CH_3O–H) = 435.1 \pm 2.9$ kJ/mol and $D(CH_3–OH) = 386.4 \pm 1.6$ kJ/mol, in ethanol $D(C_2H_5O–H) = 436 \pm 4$ kJ/mol and $D(C_2H_5–OH) = 392 \pm 4$ kJ/mol and in 2-propanol $D(C_3H_7O–H) = 438 \pm 4$ kJ/mol and $D(C_3H_7–OH) = 404.8 \pm 2.8$ kJ/mol) [48] could indicate that C–O insertion is the favored step. The formation of $LnO^+$ metal oxide was observed for all lanthanide cations, except $Eu^+$, $Tm^+$ and $Yb^+$. The very high excitation energy of these ions could be responsible for the non occurrence of a bond insertion mechanism, and consequently the absence of the referred ions. Moreover, admitting that only exothermic reactions could be observed, we may find the reason for the absence of $EuO^+$ and $YbO^+$ by comparing the values presented in Table 4 for $D(Eu^+–O)$ ($389 \pm 18$ kJ/mol) and $D(Yb^+–O)$ ($389 \pm 13$ kJ/mol) with the thermodynamic thresholds for the observation of reaction (1) in the case of the three alcohols [48]: $CH_3OH$, $D(Ln^+–O) = 376.3 \pm 0.5$ kJ/mol; $C_2H_5OH$, $D(Ln^+–O) = 400.0 \pm 0.3$ kJ/mol; and $C_3H_7OH$, $D(Ln^+–O) = 417.2 \pm 0.5$ kJ/mol. These thermodynamic thresholds indicate that the tendency for the formation of $LnO^+$ decreases in the series methanol > ethanol > 2-propanol. With 2-propanol the formation of $LnOH^+$ is favored compared with the formation of $LnO^+$: $CH_3OH$ [$D(Ln^+–OH) = 386.4 \pm 1.6$ kJ/mol]; $C_2H_5OH$ [$D(Ln^+–OH) = 392 \pm 4$ kJ/mol]; $C_3H_7OH$ [$D(Ln^+–OH) = 404.8 \pm 2.8$ kJ/mol] [48]. The absence of $SmO^+$ with 2-propanol and the lower abundance of $SmO^+$ in the case of ethanol as compared with the case of methanol may be related to these thermodynamic trends. The non observation of the ionic product $LuO^+$ reported by Géribaldi and co-workers [23,24] was not confirmed in our experiments, and the formation of the $LuO^+$ oxide ion was observed, possibly due to differences in the thermalization process.

Formation of $LnOH^+$ (Eq. (2)) can be explained as before [23,24] by a direct mechanism, with the coordination of the metal ion to the electronegative oxygen atom, followed by electron density transfer from the metal cation to the hydroxo group, facilitating the homolytic cleavage of the R–OH bond. The formation of $LnOH^+$ could also result from a C–O insertion followed by elimination of a radical $R^\bullet$. The high values for the excitation energy and also for the second ionization energy could be responsible for the absence of $TmOH^+$ and $YbOH^+$. However, this argument is no longer valid for the formation of $LuOH^+$ and for the different behavior of the ions $Dy^+$, $Ho^+$ and $Er^+$ toward the three alcohols. Metals that have high stability in the formal oxidation state 2+ formed exclusively (Eu) or predominantly (Sm) the hydroxide ion $LnOH^+$. For these metals $LnOR^+$ ($R = CH_3, C_2H_5, C_3H_7$) ions were not observed as primary products. It appears that the formation of $LnOH^+$ is favored in comparison with the formation of $LnOR^+$, and this may be related to the fact that the O–H bonds are stronger than the C–O bonds in the three alcohols.

Formation of $LnOH_2^+$ (Eq. (3)) is possible by an insertion of the metal ion in the C–O bond of the alcohol, followed by four-center electrocyclic elimination of alkene [24]. The occurrence of $LnOH_2^+$ was only observed with alcohols containing one hydrogen atom bonded to a β-carbon, excluding for this reason the formation of $LnOH_2^+$ in the case of methanol. Labeling experiments with deuterated alcohols confirmed the presence of a hydride hydroxide species [$H–Lu^+–OH$] [24]. Formation of $LnOCH_2^+$ seems to be related with alcohols containing two hydrogen atoms bonded to one α-carbon, excluding the possibility of obtaining that primary product with 2-propanol. The formation of $LnOCH_2^+$ (Eq. (4)) can be explained [23,24] by a mechanism involving metal cation insertion into the O–H bond of the alcohol, followed by a β-hydrogen atom transfer and elimination of $H_2$ for methanol, or β-methyl group transfer and elimination of $CH_4$ for ethanol. The observation of the presumed lanthanide formaldehyde complex requires $D(Ln^+–OCH_2) = 92.9 \pm 0.7$ kJ/mol [48]. The formation of $LnOCH_3^+$ (Eq. (5)) in the case of ethanol could start by an O–H insertion, followed by a β-methyl group transfer. The ion-dipole complex $[(CH_3)(H)Ln^+ \cdots OCH_2]$ could coexist in equilibrium with $[H_3C–Ln^+–OCH_3]$, and the latter losing a methyl group could originate the mono-methoxide ion [24]. Formation of $LnOR^+$ (Eq. (6)) could be explained [23,24] by a direct mechanism with hydrogen elimination, or by an O–H insertion followed by elimination of the same specie.

The reaction efficiencies $k/k_{ADO}$ determined for the different lanthanides ions toward each studied alcohol are listed in Tables 1–3, and seem to correlate with the excitation energies presented in Table 4: lanthanide cations with the highest values for the excitation energy are the less reactive. However, some discrepancies to this general correlation were also detected, namely the higher reactivity of $Sm^+$ and $Eu^+$ in comparison with $Tm^+$ and $Yb^+$, which, as pointed out before, may be associated with the lower values of second IE for Sm and Eu. An anomalous behavior was also observed for $Lu^+$, which has an excitation energy similar to $Dy^+$, $Ho^+$ and $Er^+$, and a rather high IE. In Fig. 1 we compare plots of the reaction efficiencies $k/k_{ADO}$ toward the three alcohols as a function of the metal ion. For all the reactive lanthanide cations, an increase in the reaction efficiencies $k/k_{ADO}$ is observed from methanol to ethanol and 2-propanol. In view of the results of the present work it appears that several features of the alcohols, namely dipole moment [43] and polarizability [43], are enough to justify the observed differences. For these examples an increase in the size of the alcohol and consequently an increase in the polarizability

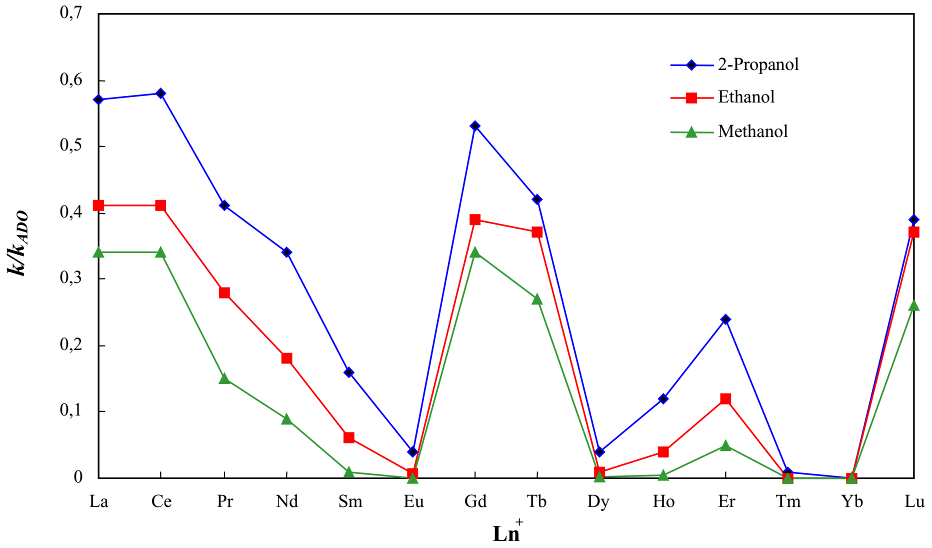


Fig. 1. Efficiencies $k/k_{ADO}$ of the reactions of lanthanide metal cations $Ln^+$ with methanol, ethanol, and 2-propanol.

are sufficient to place the ion-neutral collision complexes in deeper potential energy wells, making the ion-neutral bonding more strong and providing more energy for chemical activation.

### 3.2. *Reactions of primary and subsequent product ions with methanol, ethanol and 2-propanol*

The primary products formed in the reactions of lanthanide cations with the alcohols react further with the substrates by different pathways, and so do the subsequent products. In the case of methanol and ethanol the reactions of $Ln^+$ cations were only studied with the aim of observing the general tendencies of reaction, while in the case of 2-propanol all the gas-phase reactions were studied step by step and therefore the reactions sequences were fully identified. Having in mind the known similarities in the behavior of the ions ($La^+ \approx Ce^+$; $Pr^+ \approx Nd^+$; $Tb^+ \approx Gd^+$; $Ho^+ \approx Dy^+$, $Er^+$) identified in previous work [17,18,29,30,37] and also observed in the overall reactions, the formation of secondary and subsequent products and the corresponding reaction efficiencies $k/k_{ADO}$ with 2-propanol were determined in the specific cases of $La^+$, $Pr^+$, $Sm^+$, $Eu^+$, $Tb^+$ and $Ho^+$. The reactivity of $Lu^+$ ions with 2-propanol has been previously studied in detail by Géribaldi and co-workers [24,49]. In the case of methanol and ethanol we try to describe the reaction sequences considering the work of the same author [23,24,49] with the group 3 metal cations, and also our systematic study involving lanthanide ions and 2-propanol.

### 3.3. *Reactions with 2-propanol*

#### 3.3.1. *Reactions of LnO+*

Three primary reactions of the $LnO^+$ ions with 2-propanol were observed (Eqs. (7)–(9)):

$$LnO^+ + C_3H_7OH \rightarrow [LnOHCH_3]^+ + CH_3CHO \quad (Ln = Gd, Tb, Ho, Er) \tag{7}$$

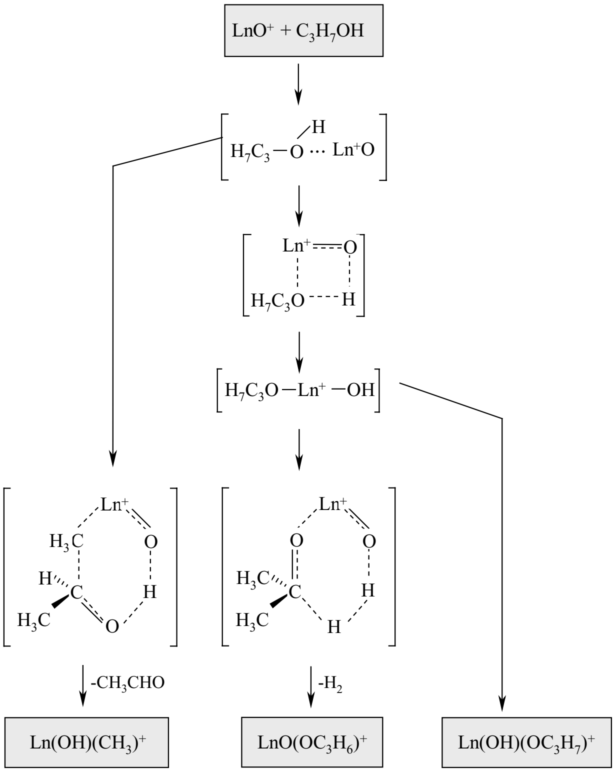
$$LnO^+ + C_3H_7OH \rightarrow [LnOOC_3H_6]^+ + H_2 \quad (Ln = La\text{–}Nd, Gd\text{–}Er) \tag{8}$$

$$LnO^+ + C_3H_7OH \rightarrow [LnOHOC_3H_7]^+ \quad (Ln = La\text{–}Nd, Dy) \tag{9}$$

For the ions studied in detail, the relative contributions of each reaction in those cases where more than one pathway was observed were: $LaO(OC_3H_6)^+$ (85%) and $La(OH)(OC_3H_7)^+$ (15%), $PrO(OC_3H_6)^+$ (85%) and $Pr(OH)(OC_3H_7)^+$ (15%), $Tb(OH)(CH_3)^+$ (45%) and $TbO(OC_3H_6)^+$ (55%).

In Scheme 2 we present possible mechanisms for the formation of the three product ions. Formation of $Ln(OH)(CH_3)^+$ could be explained by the addition of 2-propanol in the double bond of the oxide ion, followed by six-center electrocyclic elimination of acetaldehyde. The formation of $LnO(OC_3H_6)^+$ and $Ln(OH)(OC_3H_7)^+$ was possible by four-centered type transition state. The intermediate species could give the ionic product $LnO(OC_3H_6)^+$ by six-center electrocyclic elimination of dihydrogen, or it could be stabilized in the form $Ln(OH)(OC_3H_7)^+$. In the case of Lu it was reported the formation of $Ln(OH)(CH_3)^+$ and $LnO(OC_3H_6)^+$ [49].

The reaction efficiencies $k/k_{ADO}$ for the metal oxide ions $LnO^+$ in the case of La, Pr, Tb and Ho were, respectively, 0.30, 0.41, 0.47 and 0.45. While for La and Pr there was a decrease in reactivity as compared to the metal ion, for Tb the oxide and the metal ions showed similar reactivities, and for Ho the oxide ion was significantly more reactive than the metal ion (see Table 3). These results appear to be related with the strength of the $Ln^+$–O bonds for the different



Scheme 2.

metals (Table 4), in accordance with previous studies of the reactivity of $LnO^+$ ions with phenol [17] and other organic molecules [30,33]. Schröder and Schwarz, in their review of the gas-phase reactivity of transition metal oxide ions [50], remarked that ionic oxides with the highest values for the bond dissociation enthalpies $D(M^+–O)$ were more stable, and consequently revealed lower reactivities in comparison with the metallic ions $M^+$.

### 3.3.2. *Reactions of $LnOH^+$*

Three primary reactions of the $LnOH^+$ ions with 2-propanol were observed (Eqs. (10)–(12)):

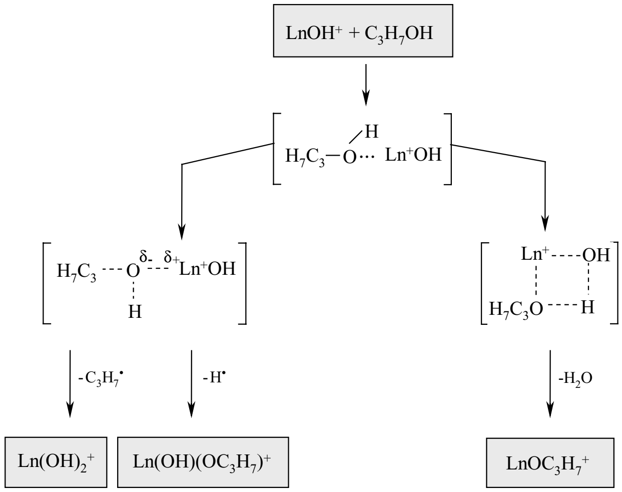
$$LnOH^+ + C_3H_7OH \rightarrow [LnOHOH]^+ + C_3H_7^\bullet \quad (Ln = La, Ce, Gd, Tb) \qquad (10)$$

$$LnOH^+ + C_3H_7OH \rightarrow [LnOC_3H_7]^+ + H_2O \quad (Ln = Pr–Dy) \qquad (11)$$

$$LnOH^+ + C_3H_7OH \rightarrow [LnOHOC_3H_7]^+ + H^\bullet \quad (Ln = La, Ce) \qquad (12)$$

The relative contributions of each reaction in the cases of La and Tb were: $La(OH)_2^+$ (60%) and $La(OH)(OC_3H_7)^+$ (40%), $Tb(OH)_2^+$ (75%) and $TbOC_3H_7^+$ (25%).

In Scheme 3 we present possible mechanisms for the formation of these ionic products. Formation of $Ln(OH)_2^+$ and $Ln(OH)(OC_3H_7)^+$ could be explained by a direct mechanism with eliminations of one isopropyl radical and one hydrogen, respectively. The formation of $LnOC_3H_7^+$ was possible by four-center electrocyclic elimination of one water molecule. The origin of $Lu(OH)_2^+$ was attributed to $LuOH^+$ [49]. The reaction efficiencies $k/k_{ADO}$ calculated for the $LnOH^+$ ions [Ln = La (0.53), Pr (0.50), Sm (0.39), Eu (0.47), Tb (0.45)] were close to the reaction efficiencies for $Ln^+$ cations, except for $SmOH^+$ and $EuOH^+$, that were exclusively formed in the primary reactions and revealed an increased reactivity in comparison with $Sm^+$ and $Eu^+$.



Scheme 3.

### 3.3.3. *Reactions of $LnOH_2^+$*

Three primary reactions of $LnOH_2^+$ ions with 2-propanol were observed (Eqs. (13)–(15)):

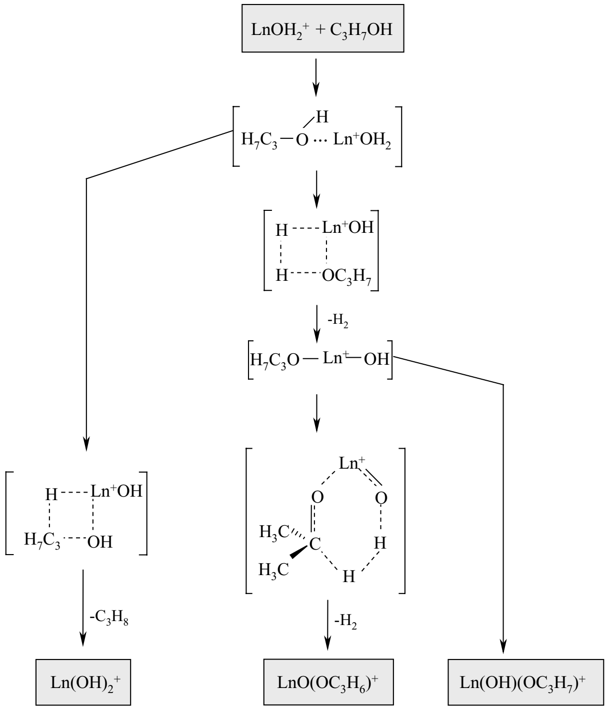
$$LnOH_2^+ + C_3H_7OH \rightarrow [LnOHOH]^+ + C_3H_8 \quad (Ln = Gd, Tb, Ho, Er) \qquad (13)$$

$$LnOH_2^+ + C_3H_7OH \rightarrow [LnOOC_3H_6]^+ + 2H_2 \quad (Ln = Gd–Er) \qquad (14)$$

$$LnOH_2^+ + C_3H_7OH \rightarrow [LnOHOC_3H_7]^+ + H_2 \quad (Ln = Gd–Er) \qquad (15)$$

The relative contributions of each reaction in the case of Tb were: $Tb(OH)_2^+$ (30%), $TbO(OC_3H_6)^+$ (45%) and $Tb(OH)(OC_3H_7)^+$ (25%).

In Scheme 4 we present possible mechanisms for the formation of the three product ions. Formation of $Ln(OH)_2^+$ could be explained by four-center electrocyclic elimination of propane. The formation of $LnO(OC_3H_6)^+$ and $Ln(OH)(OC_3H_7)^+$ was possible by four-center type transition state with elimination of dihydrogen. The intermediate specie could give the ionic product $LnO(OC_3H_6)^+$ after six-center electrocyclic elimination of dihydrogen, or it could be stabilized in the form $Ln(OH)(OC_3H_7)^+$. In the case of Lu the $LnOH_2^+$ ion yielded $Ln(OH)_2^+$, $LnO(OC_3H_6)^+$ and $Ln(OH)(OC_3H_7)^+$ ions [49]. The reaction efficiency calculated for the $TbOH_2^+$ ion was 0.50.



Scheme 4.

### 3.3.4. Reactions of $LnOC_3H_7^+$

The observed reactions of $LnOC_3H_7^+$ with 2-propanol are presented in Eqs. (16)–(18).

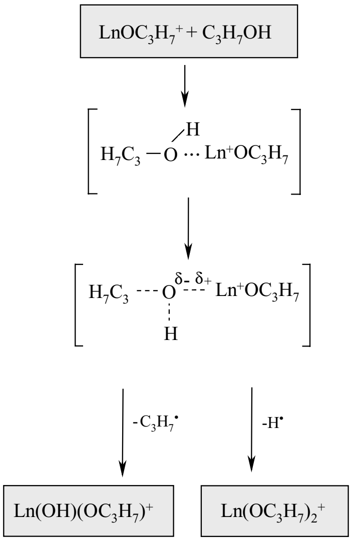
$$LnOC_3H_7^+ + C_3H_7OH \rightarrow [LnOHOC_3H_7]^+ + C_3H_7^\bullet \quad (Ln = La–Nd, Gd–Dy) \qquad (16)$$

$$LnOC_3H_7^+ + C_3H_7OH \rightarrow [LnOC_3H_7OC_3H_7]^+ + H^\bullet \quad (Ln = La–Nd) \qquad (17)$$

$$LnOC_3H_7^+ + C_3H_7OH \rightarrow [LnOC_3H_7C_3H_7OH]^+ \quad (Ln = Sm, Eu) \qquad (18)$$

The relative contributions of each reaction in the case of La and Pr were: $La(OH)(OC_3H_7)^+$ (40%) and $La(OC_3H_7)_2^+$ (60%), $Pr(OH)(OC_3H_7)^+$ (35%) and $Pr(OC_3H_7)_2^+$ (65%).

In Scheme 5 we present possible mechanisms for the formation of the ionic products $Ln(OH)(OC_3H_7)^+$ and $Ln(OC_3H_7)_2^+$, that could be explained by a direct mechanism with elimination of one isopropyl radical and one hydrogen, respectively. In the case of Sm and Eu, the $LnOC_3H_7^+$ species yielded the adducts $Ln(OC_3H_7)(C_3H_7OH)_n^+$ ($n$ = 1–3), due to the large tendency of these metals to maintain the formal oxidation 2+. The reaction efficiencies $k/k_{ADO}$ calculated for the $LnOC_3H_7^+$ ions were 0.45 (La), 0.27 (Pr), 0.04 (Sm), 0.04 (Eu) and 0.49 (Tb). The rather low reaction efficiencies revealed by the Sm and Eu mono-alkoxide ions are in agreement with the fact that they react only by adduct formation.



Scheme 5.

The Sm and Eu mono-alkoxides ions were inert in comparison with the mono-hydroxides ions, although in both types of species the metals are in the formal oxidation 2+. In the case of the $LnOH^+$ ions, the formation of $LnOC_3H_7^+$ with elimination of $H_2O$ is exothermic by ~60 kJ/mol [48], if we consider that $D(Ln^+–OH) \approx D(Ln^+–OC_3H_7^+)$, and therefore, an increased reaction efficiency for the Sm and Eu mono-hydroxide ions could be expected.

### 3.4. Reactions of $Ln(OH)_2^+$, $Ln(OH)(CH_3)^+$, $Ln(OH)(OC_3H_7)^+$ and $Ln(OH)(OC_3H_7)(OC_3H_6)^+$

The product ions that presumably contained the hydroxo ligand reacted with 2-propanol probably by four- or six-centered electrocyclic mechanisms. Previous work [49] involving Lu cations and 2-propanol is also included in the following summary of observed reactions: $Ln(OH)_2^+$ (Ln = La, Ce, Gd, Tb, Ho, Er, Lu) yielded $Ln(OH)(OC_3H_7)^+$ and $Ln(OH)_2(H_2O)^+$ (Ln = Lu); $Ln(OH)(CH_3)^+$ gave $Ln(OH)_2^+$ (Ln = Gd, Tb, Ho, Er, Lu), $Ln(OH)(OC_3H_7)^+$ (Ln = Gd, Tb, Lu) and $LnO(OC_3H_6)^+$ (Ln = Gd, Tb, Ho, Er, Lu); $Ln(OH)(OC_3H_7)^+$ originated $Ln(OC_3H_7)_2^+$ (Ln = La–Nd, Gd–Dy) and $Ln(OH)(OC_3H_7)(OC_3H_6)^+$ (Ln = Gd–Er, Lu); $Ln(OH)(OC_3H_7)(OC_3H_6)^+$ yielded $Ln(OC_3H_7)_2(OC_3H_6)^+$ (Ln = Gd–Er, Lu). Most of these ionic species reacted by substitution of the hydroxo ligand by an alkoxo, with elimination of water, a pathway also observed for the mono-hydroxide ions $LnOH^+$. The reaction efficiencies of the ions studied in detail (Ln = La, Pr, Tb, Ho) containing the hydroxo ligand were in the range (0.35–0.57), revealing values that were close to the values for $Ln^+$, except the ions of Ho which were more reactive than $Ho^+$.

### 3.4.1. Reactions of $LnO(OC_3H_6)^+$ and $LnO(OC_3H_6)_2^+$

The ionic product $LnO(OC_3H_6)^+$, that presumably contained the ketone function (but could also be formulated as a hydroxide propenoxide, $Ln(OH)(OC_3H_5)^+$), yielded the $Ln(OH)(OC_3H_7)^+$ (Ln = La–Nd, Gd–Er) ions probably by four-center electrocyclic elimination of acetone, and also the $LnO(OC_3H_6)_2{}^+$ (Ln = Ho, Er) ions probably by six-center electrocyclic elimination of dihydrogen. The reaction efficiencies $k/k_{ADO}$ for the $LnO(OC_3H_6)^+$ ions [Ln = La (0.65), Pr (0.60)] were higher than the corresponding values for $LnO^+$, but in the case of $LnO(OC_3H_6)^+$ [Ln = Tb (0.45), Ho (0.42)] were similar to $LnO^+$. The $LnO(OC_3H_6)_2{}^+$ ions gave $Ln(OH)(OC_3H_7)(OC_3H_6)^+$ (Ln = Ho, Er) probably by four-center electrocyclic elimination of acetone. The reaction efficiency $k/k_{ADO}$ calculated for the $HoO(OC_3H_6)_2{}^+$ ion (0.50) was similar to $HoO^+$ and $HoO(OC_3H_6)^+$. On the other hand, in the case of Lu it was reported [49] that $LuO(OC_3H_6)^+$ yielded the $Lu(OH)(OC_3H_7)^+$ and $LuO(OC_3H_6)_2{}^+$ ions and, the latter gave subsequently the ionic product $Lu(OH)(OC_3H_7)(OC_3H_6)^+$.

### 3.4.2. Reactions of $Ln(OC_3H_7)_2{}^+$ and $Ln(OC_3H_7)_2(OC_3H_6)^+$

The reactions of the bis-alkoxide $Ln(OC_3H_7)_2{}^+$ ions corresponded to adduct formation, yielding species of general formula $Ln(OC_3H_7)_2(C_3H_7OH)_n{}^+$ ($n = 1$–3) (Ln = La–Nd) and also the $Ln(OC_3H_7)_2(OC_3H_6)^+$ (Ln = Gd–Dy) ions, probably by a four-center mechanism, followed by six-center electrocyclic elimination of dihydrogen. Finally, the latter ions yielded adducts with the formulation $Ln(OC_3H_7)_2(OC_3H_6)(C_3H_7OH)_n{}^+$ ($n = 1$, 2) (Ln = Gd–Er). In the case of Lu, it was reported [49] the formation of $Ln(OC_3H_7)_2(OC_3H_6)(C_3H_7OH)_n{}^+$ ($n = 1$, 2) from $Ln(OC_3H_7)_2(OC_3H_6)^+$. The reaction efficiencies $k/k_{ADO}$ calculated for the $Ln(OC_3H_7)_2{}^+$ ions were 0.18 (La), 0.15 (Pr) and 0.40 (Tb), for $Ln(OC_3H_7)_2(C_3H_7OH)^+$ were 0.092 (La) and 0.079 (Pr), and for $Ln(OC_3H_7)_2(C_3H_7OH)_2{}^+$ were 0.004 (La) and 0.0005 (Pr). On the other hand, the reaction efficiencies $k/k_{ADO}$ for the $Ln(OC_3H_7)_2(OC_3H_6)^+$ ions were 0.093 (Tb) and 0.35 (Ho), and for $Ln(OC_3H_7)_2(OC_3H_6)(C_3H_7OH)^+$ ions were 0.003 (Tb) and 0.007 (Ho). For these examples a decrease in the reaction efficiencies $k/k_{ADO}$ was observed as the number of ligands around the metal increased.

## 3.5. Reactions with methanol

The primary products formed in the reactions of lanthanide cations with $CH_3OH$ participated in subsequent reactions yielding in general the basic sequence: $Ln(OH)(OCH_3)^+$, $Ln(OCH_3)_2{}^+$ and $Ln(OCH_3)_2(CH_3OH)_n{}^+$ ($n = 1$–3) (Ln = La–Sm, Gd–Lu). The exception was obtained with Eu due to the tendency of this metal to attain the formal oxidation 2+, and therefore the sequence was: $LnOCH_3{}^+$, $Ln(OCH_3)(CH_3OH)_n{}^+$ ($n = 1$–3).

The primary product $LnO^+$ probably reacted with methanol yielding the ionic products $LnO(OCH_2)^+$ (Ln = Gd, Tb) and $Ln(OH)(OCH_3)^+$ (Ln = La–Sm, Gd–Er, Lu). The formation of $LnOCH_3{}^+$ (Ln = La–Tb, Lu) and $Ln(OH)_2{}^+$ (Ln = Gd, Tb, Lu) ions could be obtained from $LnOH^+$. The $LnOCH_2{}^+$ ion could be responsible for the formation of $Ln(OH)(CH_3)^+$ (Ln = La–Pr, Gd, Tb, Ho, Er), $LnO(OCH_2)^+$ (Ln = Gd, Tb) and $Ln(OCH_3)_2{}^+$ (Ln = La–Nd, Gd, Tb, Ho, Er). The $LnOCH_3{}^+$ ion was probably the origin of the ionic products $LnOOCH_3{}^+$ (Ln = Ce), $Ln(OH)(OCH_3)^+$ (Ln = La–Sm, Gd–Dy, Lu) and $Ln(OCH_3)_2{}^+$ (Ln = La–Sm, Gd–Dy, Lu). $EuOCH_3{}^+$ only formed the adducts $Eu(OCH_3)(CH_3OH)_n{}^+$ ($n = 1$–3).

The ionic products that presumably contained the hydroxo ligand probably participated in the following subsequent reactions with methanol: $Ln(OH)_2{}^+$ (Ln = Gd, Tb, Lu) yielded $Ln(OH)(CH_3)^+$; $Ln(OH)(CH_3)^+$ (Ln = La–Pr, Gd, Tb, Ho, Er) gave $Ln(OH)(OCH_3)^+$; $Ln(OH)(OCH_3)^+$ (Ln = La–Sm, Gd–Lu) originated $Ln(OCH_3)_2{}^+$. The $LnO(OCH_2)^+$ (Ln = Gd, Tb) and $LnO(OCH_3)^+$ (Ln = Ce) ions were probably the origin of the same ionic product: $Ln(OH)(OCH_3)^+$. Finally, the bis-methoxide ions $Ln(OCH_3)_2{}^+$ reacted with methanol yielding the adducts $Ln(OCH_3)_2(CH_3OH)_n{}^+$ ($n = 1$–3) (Ln = La–Sm, Gd–Lu).

## 3.6. Reactions with ethanol

The primary products formed in the reactions of lanthanide cations with $C_2H_5OH$ participated in subsequent reactions yielding the series $Ln(OH)(OC_2H_5)^+$, $Ln(OC_2H_5)_2{}^+$ and $Ln(OC_2H_5)_2(C_2H_5OH)^+$ ($n = 1$–3) (Ln = La–Sm, Gd–Lu). However, in the case of metals with the formal oxidation 2+ more accessible like Sm and Eu was also observed the sequence $Ln(OC_2H_5)^+$, $Ln(OC_2H_5)(C_2H_5OH)_n{}^+$ ($n = 1$–3). Also important was the presence of species containing presumably the aldehyde function as in the series: $LnO(OC_2H_4)^+$, $Ln(OC_2H_5)_2(OC_2H_4)(C_2H_5OH)_n{}^+$ ($n = 1$–2).

The primary product $LnO^+$ probably reacted with ethanol yielding the ionic products $Ln(OH)(CH_3)^+$ (Ln = Gd, Tb, Ho, Er), $LnO(OC_2H_4)^+$ (Ln = Gd, Tb, Ho, Er, Lu) and $Ln(OH)(OC_2H_5)^+$ (Ln = La–Sm, Lu). The formation of $Ln(OH)_2{}^+$ (Ln = La, Ce, Gd, Tb, Ho, Er, Lu), $LnOC_2H_5{}^+$ (Ln = La–Dy, Lu) and $Ln(OH)(OC_2H_5)^+$ (Ln = La, Ce) ions could be obtained from $LnOH^+$. The $LnOH_2{}^+$ ion could be responsible for the formation of $Ln(OH)_2{}^+$ (Ln = Lu), $LnO(OC_2H_4)^+$ (Ln = Lu) and $Ln(OH)(OC_2H_5)^+$ (Ln = Lu). $LnOCH_3{}^+$ could be the origin of $Ln(OH)(OCH_3)^+$ (Ln = Gd, Tb, Lu) and $Ln(OCH_3)(OC_2H_5)^+$ (Ln = Gd, Tb). Finally, the ionic products $Ln(OH)(OC_2H_5)^+$ (Ln = La–Sm, Gd–Dy, Lu) and $Ln(OC_2H_5)_2{}^+$ (Ln = La–Sm, Gd–Dy) were probably obtained from $LnOC_2H_5{}^+$. The formation of $Ln(OC_2H_5)(C_2H_5OH)^+$ (Ln = Sm, Eu) was also suggested from $LnOC_2H_5{}^+$.

The ionic products that presumably contained the hydroxo ligand probably participated in the following subsequent reactions with ethanol: $Ln(OH)_2{}^+$ (Ln = La, Ce, Gd, Tb, Ho, Er, Lu) yielded $Ln(OH)(OC_2H_5)^+$; $Ln(OH)(CH_3)^+$ (Ln = Gd, Tb, Ho, Er) gave $Ln(OH)_2{}^+$

and $Ln(OH)(OC_2H_5)^+$; $Ln(OH)(OCH_3)^+$ (Ln = Gd, Tb) originated $Ln(OCH_3)(OC_2H_5)^+$; $Ln(OH)(OCH_3)^+$ (Ln = Lu) yielded $Ln(OH)(OC_2H_5)^+$; $Ln(OH)(OC_2H_5)^+$ (Ln = La–Sm, Gd–Er, Lu) gave $Ln(OC_2H_5)^+$. The $LnO(OC_2H_4)^+$ (Ln = Gd, Tb, Ho, Er, Lu) ions were probably the origin of $Ln(OH)(OC_2H_5)^+$. The reactions of the bis-alkoxide $Ln(OC_2H_5)_2^+$ ions corresponded to adduct formation, yielding species of general formula $Ln(OC_2H_5)_2(C_2H_5OH)_n^+$ ($n$ = 1–3) (Ln = La–Sm, Gd–Lu), and also the $Ln(OC_2H_5)_2(OC_2H_4)^+$ (Ln = Ho, Er, Lu) ions. Finally, the latter species yielded adducts with the formulation $Ln(OC_2H_5)_2(OC_2H_4)(C_2H_5OH)_n^+$ ($n$ = 1, 2) (Ln = Ho, Er, Lu).

## 4. Conclusions

This work showed the existence of important differences in the relative reactivity of the lanthanide series cations with aliphatic alcohols, in agreement with the known data on the reactivity of these metal ions with other organic molecules. The results obtained for most of the members of the series showed close similarities with those obtained by Géribaldi and co-workers with group 3 metal cations and can be related to factors like the electron configurations of the metal ions, their oxophilicity and the second ionization energies of the metals.

All the lanthanide metal cations studied except $Tm^+$ and $Yb^+$ were observed to react with methanol, ethanol and 2-propanol with formation of $LnO^+$ and $LnOH^+$ as main primary products. The primary ions $LnOH_2^+$, $LnOCH_2^+$ and $LnOR^+$ (R = $CH_3$, $C_2H_5$, $C_3H_7$) were also obtained. These ions participated in subsequent reactions with the alcohols yielding species such as $Ln(OH)(OR)^+$, $Ln(OR)_2^+$ and $Ln(OR)_2(ROH)_n^+$ ($n$ = 1–3) (R = $CH_3$, $C_2H_5$, $C_3H_7$). With ethanol it was also observed the formation of several species containing presumably the aldehyde function: $LnO(OC_2H_4)^+$ and $Ln(OR)_2(OC_2H_4)(ROH)_n^+$ ($n$ = 1, 2) (R = $C_2H_5$). In the case of 2-propanol the presence of species containing presumably the ketone function was also observed: $LnO(OC_3H_6)^+$, $Ln(OH)(OR)(OC_3H_6)^+$, $Ln(OR)_2(OC_3H_6)^+$ and $Ln(OR)_2(OC_3H_6)(ROH)_n^+$ (R = $C_3H_7$). Formation of $Ln(OR)(ROH)_n^+$ ($n$ = 1–3) (R = $CH_3$, $C_2H_5$, $C_3H_7$) was also identified in the case of the metals, like Eu and Sm, that have high stabilities of the formal oxidation state 2+.

As a final comment on these experiments, it can be pointed out the prevalence of species which correspond to 3+ formal oxidation states of the metals; Eu was an exception in that it never went beyond the 2+ formal oxidation state. This observation draws a parallel with condensed-phase lanthanide alkoxide experiments where the 2+ formal oxidation state of Eu dominates. The formation of oxo and hydroxo containing species is also a common feature of gas-phase and condensed-phase lanthanide alkoxide chemistry.

## References

[1] D.C. Bradley, Chem. Rev. 89 (1989) 1317.
[2] R.C. Mehrotra, A. Singh, U.M. Tripathi, Chem. Rev. 91 (1991) 1287.
[3] L. Hubert-Pfalzgraf, New J. Chem. 19 (1995) 727.
[4] W.A. Herrmann, N.W. Huber, O. Runte, Angew. Chem. Int. Ed. Engl. 34 (1995) 2187.
[5] R.C. Mehrotra, A. Singh, Chem. Soc. Rev. (1996) 1.
[6] R. Anwander, Top. Curr. Chem. 179 (1996) 149.
[7] L. Hubert-Pfalzgraf, Coord. Chem. Rev. 178–180 (1998) 967.
[8] J.M. Carretas, A. Pires de Matos, Mater. Chem. Phys. 31 (1992) 123.
[9] J.M. Carretas, J. Branco, J. Marçalo, J.C. Waerenborgh, N. Marques, A. Pires de Matos, J. Alloys Comp. 275–277 (1998) 841.
[10] J.M. Carretas, J. Branco, J. Marçalo, P.C. Isolani, A. Domingos, A. Pires de Matos, J. Alloys Comp. 323–324 (2001) 169.
[11] J.M. Carretas, J. Branco, J. Marçalo, A. Domingos, A. Pires de Matos, Polyhedron 22 (2003) 1425.
[12] J.M. Carretas, J. Branco, J. Marçalo, N. Valente, J.C. Waerenborgh, A. Carvalho, N. Marques, A. Domingos, A. Pires de Matos, J. Alloys Comp., in press.
[13] K. Eller, H. Schwarz, Chem. Rev. 91 (1991) 1121.
[14] J.C. Weisshaar, Acc. Chem. Res. 26 (1993) 213.
[15] B.S. Freiser, Acc. Chem. Res. 27 (1994) 353.
[16] B.S. Freiser, J. Mass Spectrom. 31 (1996) 703.
[17] J.M. Carretas, A. Pires de Matos, J. Marçalo, M. Pissavini, M. Decouzon, S. Géribaldi, J. Am. Soc. Mass Spectrom. 9 (1998) 1035.
[18] N. Marchandé, S. Breton, S. Géribaldi, J.M. Carretas, A. Pires de Matos, J. Marçalo, Int. J. Mass Spectrom. 195–196 (2000) 139.
[19] S. Géribaldi, S. Breton, M. Decouzon, M. Azzaro, New J. Chem. 19 (1995) 887.
[20] A.G. Marshall, C.L. Hendrickson, G.S. Jackson, Mass Spectrom. Rev. 17 (1998) 1.
[21] B.S. Freiser, in: J.M. Farrar, W.H. Saunders Jr. (Eds.), Techniques for the Study of Ion-Molecule Reactions, Wiley, New York, 1988, p. 61.
[22] I.J. Amster, J. Mass Spectrom. 31 (1996) 1325.
[23] M. Azzaro, S. Breton, M. Decouzon, S. Géribaldi, Int. J. Mass Spectrom. Ion Processes 128 (1993) 1.
[24] S. Géribaldi, S. Breton, M. Decouzon, M. Azzaro, J. Am. Soc. Mass Spectrom. 7 (1996) 1151.
[25] W. Lu, S. Yang, J. Phys Chem. A 102 (1998) 1954.
[26] Y. Huang, M.B. Wise, D.B. Jacobson, B.S. Freiser, Organometallics 6 (1987) 346.
[27] J.B. Schilling, J.L. Beauchamp, J. Am. Chem. Soc. 110 (1988) 15.
[28] L.S. Sunderlin, P.B. Armentrout, J. Am. Chem. Soc. 111 (1989) 3845.
[29] W.W. Yin, A.G. Marshall, J. Marçalo, A. Pires de Matos, J. Am. Chem. Soc. 116 (1994) 8666.
[30] J. Marçalo, A. Pires de Matos, W.J. Evans, Organometallics 16 (1997) 3845.
[31] H.H. Cornehl, C. Heinemann, D. Schröder, H. Schwarz, Organometallics 14 (1995) 992.
[32] H.H. Cornehl, G. Hornung, H. Schwarz, J. Am. Chem. Soc. 118 (1996) 9960.
[33] H.H. Cornehl, R. Wesendrup, J.N. Harvey, H. Schwarz, J. Chem. Soc., Perkin Trans. 2 (1997) 2283.
[34] J.K. Gibson, J. Fluorine Chem. 78 (1996) 65.
[35] J.K. Gibson, J. Phys. Chem. 100 (1996) 15688.
[36] J.K. Gibson, Organometallics 16 (1997) 4214.
[37] J. Marçalo, A. Pires de Matos, J. Organomet. Chem. 647 (2002) 216.
[38] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, third ed., Pergamon Press, Oxford, 1988.
[39] S. Guan, A.G. Marshall, Int. J. Mass Spectrom. Ion Processes 137–138 (1996) 5.
[40] J.E. Bruce, J.R. Eyler, J. Am. Soc. Mass Spectrom. 3 (1992) 727.
[41] Y. Lin, D.P. Ridge, B. Munson, Org. Mass Spectrom. 26 (1991) 550.
[42] J.E. Bartmess, R.M. Georgiadis, Vacuum 33 (1983) 149.

[43] D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, 75th ed., CRC Press, Boca Raton, 1994.

[44] T. Su, M.T. Bowers, in: M.T Bowers (Ed.), Gas Phase Ion Chemistry, Academic Press, New York, 1979 (Chapter 3).

[45] C. Heinemann, N. Goldberg, I.C. Tornieporth-Oetting, T.M. Klapötke, H. Schwarz, Angew. Chem. Int. Ed. Engl. 34 (1995) 213.

[46] W.C. Martin, R. Zalubas, L. Hagan, Atomic energy levels: the rare-earth elements, NSRDS-NBS 60, National Bureau of Standards (NIST), Washington, DC, 1978.

[47] Z.B. Goldschmidt, in: K.A. Gschneidner, L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 1, North-Holland, Amsterdam, 1978 (Chapter 1).

[48] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data 17 (Suppl.) (1988) 1.

[49] S. Breton, Ph.D. thesis, Université de Nice-Sophia Antipolis, 1995.

[50] D. Schröder, H. Schwarz, Angew. Chem. Int. Ed. Engl. 34 (1995) 1973.