Gas phase reactivity of rare earth metal cations with trialkylorthoformates: synthesis of neutral rare earth alkoxides

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Abstract

Gas phase reactions of the rare earth metal cations Y^+ and Ln^+ (Ln = La–Lu, except Pm) with trimethylorthoformate and of Y^+ and Lu^+ with triethyl and tripropyl orthoformates were studied by Fourier transform ion cyclotron resonance mass spectrometry. The results obtained were compared with previous observations made with the remaining rare earth cation Sc^+ and confirmed that, in the gas phase, trialkylorthoformates can be good alkoxy group suppliers, leading to dialkoxymetal ions, which subsequently react with the orthoesters to form a dialkoxymethyl cation and, presumably, a neutral metal trialkoxide. These reactions appear to be a possible route for the gas phase synthesis of rare earth metal alkoxides. (Int J Mass Spectrom 195/196 (2000) 139–148) © 2000 Elsevier Science B.V.

Keywords: Rare earth alkoxides; Rare earth metal ions; Trialkylorthoformates; Gas phase; FTICR/MS

1. Introduction

The chemistry of rare earth (scandium, yttrium, and lanthanide) alkoxides has received considerable attention in recent years, particularly due to the use of these compounds as precursors for the synthesis of new materials [1–5]. One of the main synthetic methods used, metalorganic chemical vapor deposition (MOCVD), involves gas phase procedures and efforts continue to be made to prepare rare earth alkoxides that meet the requirements of the method, particularly in terms of volatility [1–3].

In a previous work [6], we have used Fourier transform ion cyclotron resonance mass spectrometry (FTICR/MS) [7–9] to demonstrate that the reaction between the Sc^+ cation and trialkylorthoformates is a possible route for the gas phase synthesis of rare earth metal alkoxides. The idea for the use of this type of reaction was based on the knowledge that rare earth metal cations M^+ react efficiently with methanol and other alcohols ROH leading to dialkoxy metal species $M(OR)_2^+$ [10–14], and that trialkylorthoformates $HC(OR)_3$ easily lose an alkoxy group under electron impact or chemical ionisation, leading to the electronically stabilised ion $HC(OR)_2^+$ [15]. Under the as-

sumption that the reaction of M^+ with $HC(OR)_3$ would also lead to $M(OR)_2^+$ species and that these dialkoxy metal ions could then act as chemical ionisation reagents toward $HC(OR)_3$, leading to $HC(OR)_2^+$ and neutral $M(OR)_3$, we were able to confirm the proposed concept in the case of Sc^+ and of trimethyl, triethyl and tripropyl orthoformates [6].

The aim of the present work is to test this method for the remaining of the rare earth metal cations and, therefore, we report the results of a FTICR/MS study of the gas phase reactivity of Y^+ and Ln^+ (Ln = La–Lu, except Pm) cations with trimethylorthoformate and of Y^+ and Lu^+ ions with triethyl and tripropyl orthoformates. This study can also be considered as a complement to the several recent studies of the gas phase reactivity of lanthanide cations with different classes of organic molecules [10–13,16–28] and the interpretation of some of the observations that we report should be considered in the context of these previous studies.
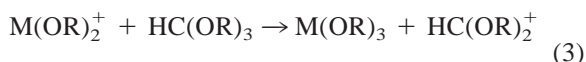
2. Experimental

All experiments in Nice were performed in a homebuilt FTICR mass spectrometer equipped with a 15 in. electromagnet giving a maximum magnetic field of 1.6 T, a Bruker data system and a Laser Science VSL 337ND pulsed nitrogen laser. All experiments in Sacavém were conducted in a Finnigan FT/MS 2001-DT FTICR mass spectrometer equipped with a 3 T superconducting magnet, a Nicolet 1280 data station recently replaced by a Finnigan Venus Odyssey data system, and a Spectra-Physics Quanta-Ray GCR-11 Nd:YAG laser operated at the fundamental wavelength (1064 nm). In both laboratories, the rare earth cations were produced by direct laser desorption/ionisation (LDI) of pure metal pieces. The trimethyl, triethyl, and tripropyl orthoformates, purified by distillation over sodium and degassed prior to use, were introduced in the spectrometers through leak valves. Neutral pressures were measured by Bayard-Albert type ionisation gauges. The detailed experimental procedures used in the two laboratories concerning pressure calibration and thermalization of

reactant ions have been described previously (Nice [10,11], Sacavém [18]). Studies with three common rare earth cations were performed in both laboratories in order to be able to compare the product distributions and the rate constants for the different metal ions. Reaction sequences were identified by means of double-resonance and MS/MS techniques. 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. When consecutive and/or concomitant reactions were involved, the reaction sequences, product distributions and rate constants were verified by fitting of data to kinetic models [29] using computer programs [30,31]. The rate constants are reported as reaction efficiencies, that is, as fractions of the average dipole orientation (ADO) theory collisional rates [32], calculated using an estimated dipole moment [33] of 1.5 D for the three trialkylorthoformates and estimated molecular polarizabilities [34] of 10.02, 15.48, and 20.97 $Å^3$ for trimethyl, triethyl, and tripropyl orthoformates, respectively. For the two laboratories, 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. Uncertainties in the pressure calibration procedures 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

We have recently reported the results of a FTICR/MS study of the gas phase reactivity of Sc^+ cations with trimethyl, triethyl, and tripropyl orthoformates, which indicated that this system could probably be used in the gas phase preparation of

neutral scandium trialkoxides [6]. The reactions described by

$$M^+ + HC(OR)_3 \rightarrow MOR + HC(OR)_2^+ \qquad (1)$$

$$M^+ + HC(OR)_3$$
$$\rightarrow M(OR)_2^+ + (RCHO \text{ or } RH + CO) \qquad (2)$$

$$M(OR)_2^+ + HC(OR)_3 \rightarrow M(OR)_3 + HC(OR)_2^+ \qquad (3)$$

were observed (R = Me, Et, Pr; M = Sc), showing that through reactions (2) and (3) scandium trialkoxide was presumably formed. In the present work, we have also used FTICR/MS to study the gas phase reactivity of Y^+ and Ln^+ (Ln = La–Lu, except Pm) cations with trimethylorthoformate and of Y^+ and Lu^+ ions with triethyl and tripropyl orthoformates, and test the initial idea for the remaining of the rare earth metal cations.
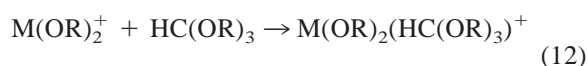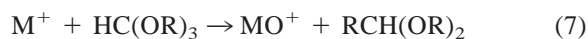
3.1. Reactivity of rare earth metal cations with trimethylorthoformate

We observed that the reactivity of the rare earth metal cations with trimethylorthoformate was rather varied, with noticeable differences along the lanthanide series, but included as main reaction pathways besides reactions (1)–(3) the reactions in the following (R = Me):

$$M^+ + HC(OR)_3 \rightarrow MOR^+ + HC(OR)_2 \qquad (4)$$

$$MOR^+ + HC(OR)_3 \rightarrow M(OR)_2 + HC(OR)_2^+ \qquad (5)$$

$$MOR^+ + HC(OR)_3 \rightarrow M(OR)_2^+ + HC(OR)_2 \qquad (6)$$

We should remark at this point that the sequence constituted by reactions (4), (6), and (3) is also a possible route leading to neutral rare earth trisalkoxides, whereas reactions (4) and (5) could lead to bisalkoxides, which could be favoured for some of the rare earth metals with more stable 2+ formal oxidation states.

Other reaction pathways were observed in the case of some of the lanthanide metal cations, and these are indicated in (R = Me)

$$M^+ + HC(OR)_3 \rightarrow MO^+ + RCH(OR)_2 \qquad (7)$$

$$M^+ + HC(OR)_3 \rightarrow MOCH(OR)_2^+ + R \qquad (8)$$

$$MOR^+ + HC(OR)_3$$
$$\rightarrow M(OR)(RC(O)OR)^+ + ROH \qquad (9)$$

$$MOR^+ + HC(OR)_3 \rightarrow M(OR)(HC(OR)_3)^+ \qquad (10)$$

$$M(OR)_2^+ + HC(OR)_3$$
$$\rightarrow M(OR)_2(RC(O)OR)^+ + ROH \qquad (11)$$

$$M(OR)_2^+ + HC(OR)_3 \rightarrow M(OR)_2(HC(OR)_3)^+ \qquad (12)$$

In Table 1 we list the products formed in the primary reactions of the different rare earth metal cations with methylorthoformate [Eqs. (1), (2), (4), (7), and (8)] and we include the corresponding reaction efficiencies k/k_{ADO}.

Previous gas phase reactivity studies of lanthanide metal cations [10–13,16–28] 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 $4f^n 6s^1$, to configurations with two unpaired non-f electrons, like $4f^{n-1} 6s^1 5d^1$ [35,36], that are a necessary condition if two single bonds are to be formed between a metal ion and two organic moieties. The group 3 metal ions Sc^+ and Y^+ are very reactive with organic molecules [10–12,14,16–19,21,37] and have $4s^1 3d^1$ and $5s^2$ ground state electron configurations, respectively, with Y^+ possessing an easily accessible $4d^1 5s^1$ configuration [21]. In Table 1 we list these excitation energies E_{exc} from the ground state configurations to the $4f^{n-1} 6s^1 5d^1$ configurations of the lanthanide ions or the $ns^1(n - 1)d^1$ of Sc^+ and Y^+.

In Table 1 we can see that the bismethoxide ion is formed for all the rare earths cations except Eu^+ and Yb^+, precisely the ones that have the largest excitation energies and, consequently, stable 2+ formal oxidation states.

Eu^+ and Yb^+ are also the only metal ions for which reaction (8) is observed, along with formation of the monomethoxide metal ion, reaction (4). We can

Table 1
Primary product distributions (%) and efficiencies k/k_{ADO} of the reactions of rare earth cations with trimethylorthoformate, and excitation energies E_{exc} (eV) ground state $\rightarrow d^1s^1$ state of the rare earth cations M^+

M^+	Primary product distributions[a]					k/k_{ADO}	E_{exc}[b]
	$HC(OMe)_2^+$	MO^+	$M(OMe)^+$	$M(OMe)_2^+$	$M(OC)(H)(OMe)_2^+$		
Sc^+	40	0	0	60	0	1.17	0
Y^+	10	0	35	55	0	1.12	0.15
La^+	0	10	25	65	0	1.03	0.19
Ce^+	0	15	30	55	0	0.96	0.30
Pr^+	0	0	25	75	0	0.72	1.02
Nd^+	0	0	25	75	0	0.65	1.40
Sm^+	0	0	55	45	0	0.59	2.43
Eu^+	0	0	90	0	10	0.55	3.60
Gd^+	10	0	30	60	0	0.81	0
Tb^+	10	0	10	80	0	0.67	0.42
Dy^+	0	0	0	100	0	0.53	1.31
Ho^+	0	0	0	100	0	0.50	1.44
Er^+	0	0	0	100	0	0.51	1.31
Tm^+	0	0	25	75	0	0.49	2.05
Yb^+	0	0	40	0	60	0.47	3.32
Lu^+	65	0	15	20	0	0.92	1.63

[a] Product distribution and k/k_{ADO} for Sc^+ from [6].
[b] E_{exc} values from [21] and [36].

consider that initial coordination of the metal cation to one of oxygen atoms of the methylorthoformate (that we can write as the ether MeOR′) can be followed by electron density transfer from the metal cation to either the methoxo or the OR′ group, homolytic cleavage of the C–O bond and elimination of bismethoxymethyl or methyl radicals, respectively.

The formation of the bismethoxide metal ions [reaction (2)] for the majority of the rare earth metal cations could be facilitated by the presumable confor-

Table 2
Primary product distributions (%) of the reactions of rare earth methoxide metal ions $M(OMe)^+$ with trimethylorthoformate

M	Primary product distributions[a]			
	$HC(OMe)_2^+$	$M(OMe)_2^+$	$M(OMe)(MeC(O)OMe)^+$	$M(OMe)(HC(OMe)_3)^+$
Sc	...	...	...	...
Y	35	65	0	0
La	0	100	0	0
Ce	0	100	0	0
Pr	15	85	0	0
Nd	25	75	0	0
Sm	10	40	30	20
Eu	0	0	45	55
Gd	35	65	0	0
Tb	30	70	0	0
Dy	...	...	...	...
Ho	...	...	...	...
Er	...	...	...	...
Tm	30	60	5	5
Yb	20	0	40	40
Lu	50	50	0	0

[a] Product distribution for Sc from [6].

Table 3
Primary product distributions (%) of the reactions of rare earth bismethoxide metal ions $M(OMe)_2^+$ with trimethylorthoformate

M	Primary product distributions[a]		
	$HC(OMe)_2^+$	$M(OMe)_2(MeC(O)OMe)^+$	$M(OMe)_2(HC(OMe)_3)^+$
Sc	100	0	0
Y	100	0	0
La	10	65	25
Ce	10	45	45
Pr	30	35	35
Nd	30	50	20
Sm	30	60	10
Eu	...	...	...
Gd	50	20	30
Tb	50	30	20
Dy	75	15	10
Ho	80	10	10
Er	90	5	5
Tm	90	5	5
Yb	...	...	...
Lu	100	0	0

[a] Product distribution for Sc from [6].

mation of the methylorthoformate molecule, which should have at least two oxygen atoms available for coordination to the metal ion. If such a strongly bound ion–neutral complex is sufficiently long lived, rearrangements could occur leading to the elimination of stable neutral species like acetaldehyde or methane plus carbon monoxide and the formation of two strong metal cation–methoxide bonds. For the case of the formation of the monomethoxide metal ions [reaction (4)], in which the electronically stabilised bismethoxymethyl radical is formed, similar considerations can be made. These processes could both include a C–O bond insertion step, which could be favoured in the case of the rare earth metal cations with excitation energies E_{exc} lower than the ones of Eu^+ and Yb^+.

We can calculate from the available thermochemical data [38] that the occurrence of reaction (2) (considering that acetaldehyde is formed) requires the average M^+–OMe bond dissociation enthalpy in $M(OMe)_2^+$ to be equal to or larger than 371 ± 5 kJ/mol. The occurrence of reaction (4) requires $D(M^+$–OMe) to be equal to or larger than 351 ± 12 kJ/mol, if we consider that the carbon–methoxy bond dissociation enthalpy in trimethylorthoformate (i.e. trismethoxymethane) equals the one in bismethoxymethane [38].

The thermochemical data available for rare earth metal ion–alkoxide systems are limited to the Sc^+–alkoxide bond strengths very recently reported by Crellin et al. (in a collaboration with one of us) [14], and we can compare the values above with $D(CD_3OSc^+$–$OCD_3)$ and $D(HOSc^+$–$OCD_3)$ which are both equal to 481 ± 9 kJ/mol. We can make comparisons with $D(Sc^+$–OH) = 499 ± 9 kJ/mol, determined by Clemmer et al. [39], and with a lower limit for $D(M^+$–OMe) of 435 ± 3 kJ/mol, determined by us from observation of the methoxide metal ion in reactions of rare earth metal cations with methanol [10,11,13].

The available thermochemical data [38,39] tell us that the formation of the MO^+ ion [reaction (7)] should be exothermic for all the rare earth cations except Eu^+ and Yb^+. Its observation only in the case of La^+ and Ce^+ is probably a consequence of the fact that these two rare earth ions are the ones that have the largest M^+–O bond dissociation enthalpies [38–40]. If we consider as previously mentioned that there is an initial C–O bond insertion step, the strong thermodynamic driving force for the formation of MO^+ in the case of these two metal cations could facilitate a rearrangement leading to the stable neutral bismethoxyethane.

Table 4

Product distributions (%) and efficiencies k/k_{ADO} of the reactions of scandium, yttrium, and lutetium metal ions M^+, ethoxide metal ions $M(OEt)^+$, and bisethoxide metal ions $M(OEt)_2^+$ with triethylorthoformate

M^+	Primary product distributions[a]			k/k_{ADO}
	$HC(OEt)_2^{+\ b}$	$M(OEt)^+$	$M(OEt)_2^+$	
Sc	60	0	40	1.1
Y	15	25	60	1.3
Lu	65	0	35	1.1

$M(OEt)^+$	Primary product distributions[a]		k/k_{ADO}
	$HC(OEt)_2^{+\ b}$	$M(OEt)_2^+$	
Sc	. . .	. . .	
Y	35	65	1.2
Lu	. . .	. . .	

$M(OEt)_2^+$	Primary product distributions[a]	k/k_{ADO}
	$HC(OEt)_2^{+\ b}$	
Sc	100	1.2
Y	100	1.0
Lu	100	1.1

[a] Product distributions and k/k_{ADO} for Sc^+ from [6].
[b] Includes fragment ion $HC(OH)(OEt)^+$ with $\sim$2/10 abundance.

In reaction (1), which is only observed for Y^+, Gd^+, Tb^+, and Lu^+ ions (and also for Sc^+), the stable bismethoxymethyl cation is formed together with the presumed neutral metal methoxide. Using again the available thermochemical data and the same assumption as before that the carbon–methoxy bond dissociation enthalpy in trimethylorthoformate is the same as in bismethoxymethane [38], we can arrive at two relations that indicate that the sums $D(M^+–OMe) + IE(MOMe)$ or $D(M–OMe) + IE(M)$ should be equal to or larger than 966 ± 5 kJ/mol. For the second relation, we find lower limits for $D(M–OMe)$ in the range 335–443 kJ/mol using the available rare earth metal ionisation energies [38]. If we consider that in the case of Sc^+ $D(M^+–OMe)$ is close to $D(CD_3OSc^+–OCD_3) = 481 \pm 9$ kJ/mol [14], the first relation leads to a lower limit for $IE(MOMe)$ of 485 ± 14 kJ/mol; although $IE(MOMe)$ is unknown for $M = Sc$ (as well as for all the other rare earth metals), one might reasonably expect its value to be larger than $IE(M) = 631$ kJ/mol [38]. These considerations appear to indicate that, on thermodynamic grounds, reaction (1) should occur for all the rare

earth metal cations, although it could be favoured in the case of the metal ions with larger ionisation energies (like Sc and Y).

The reaction efficiencies k/k_{ADO} determined for the different rare earth metal ions and depicted in Table 1 seem to correlate with the excitation energies E_{exc} also presented in Table 1. This agreement has been observed before in several gas phase reactivity studies of rare earth metal cations with different organic molecules [10–13,17,18,23–26]. We conclude here our discussion of the primary reactions of the rare earth metal cations with methylorthoformate [Eqs. (1), (2), (4), (7), and (8)] and we proceed now to the main secondary reactions, that is the ones of the mono- and bismethoxide metal ions [Eqs. (3), (5), (6), and (9)–(12)].

In Tables 2 and 3 we list the product distributions of the reactions of the methoxide metal ions $M(OMe)^+$ and of the bismethoxide metal ions $M(OMe)_2^+$ with trimethylorthoformate, respectively.

One of the salient features of the data in Table 2 is the absence of reaction channel (6), formation of the bismethoxide metal ion, in the case of Eu and Yb. We

Table 5

Product distributions (%) and efficiencies k/k_{ADO} of the reactions of scandium, yttrium, and lutetium metal ions M^+, propoxide metal ions $M(OPr)^+$, and bispropoxide metal ions $M(OPr)_2^+$ with tripropylorthoformate

M^+	Primary product distributions[a]			
	$HC(OPr)_2^{+}$ [b]	$M(OPr)^+$	$M(OPr)_2^+$	k/k_{ADO}
Sc	50	0	50	2.8
Y	35	15	50	1.3
Lu	75	0	25	1.2

$M(OPr)^+$	Primary product distributions[a]		k/k_{ADO}
	$HC(OPr)_2^{+}$ [b]	$M(OPr)_2^+$	
Sc	. . .	. . .	
Y	70	30	1.5
Lu	. . .	. . .	

$M(OPr)_2^+$	Primary product distributions[a]	k/k_{ADO}
	$HC(OPr)_2^{+}$ [b]	
Sc	100	1.7
Y	100	1.5
Lu	100	1.3

[a] Product distributions and k/k_{ADO} for Sc^+ from [6].
[b] Includes fragment ion $HC(OH)(OPr)^+$ with ~4/10 abundance.

recall that these two metals are the ones that have the more stable 2+ formal oxidation states. These two metals, along with Sm and Tm which are the following metals in terms of stability of a 2+ formal oxidation state, also yield other species in which the formally neutral ligands methylorthoformate [reaction (10)] and presumably methyl acetate [reaction (9), see below CID evidence for the proposed formulation] add to the metal centre, in this way preserving the 2+ oxidation state.

Another feature of the data in Table 2 is the absence of formation of the bismethoxymethyl cation through reaction (5) in the case of La, Ce, and Eu. This absence is particularly puzzling in the case of Eu which, due to the stability of the 2+ oxidation state, could be expected to form neutral $Eu(OMe)_2$ with a certain ease, specially if compared with Yb for which reaction channel (5) is present.

From the occurrence of reaction (6) and the available thermochemical data [38] we can calculate, as before for reaction (4) and $D(M^+–OMe)$, a lower limit for the second methoxo–metal cation bond dissociation enthalpy $D[(MeO)M^+–OMe]$ of 351 ±

12 kJ/mol, that we can compare with $D(CD_3OSc^+–OCD_3) = 481 ± 9$ kJ/mol, recently determined by Crellin et al. [14].

The reactivity of the different bismethoxide metal ions, as shown in Table 3, is dominated by the formation of the bismethoxymethyl cation [reaction (3)] and by the formation of two other species in which the formally neutral ligands methylorthoformate [reaction (12)] and presumably methyl acetate [reaction (11)] add to the metal centre, preserving the 3+ oxidation state. These last two species are not observed in the case of Y and Lu (and of Sc [6]).

Collision-induced dissociation (CID) experiments, where argon was used as a collision gas and the ions in question were excited to lab-frame energies of ~10–80 eV, were carried out in the case of La, with the goal of probing the formulations of the ions formed in reactions (11) and (12), $M(OMe)_2$-$(MeC(O)OMe)^+$ and $M(OMe)_2(HC(OMe)_3)^+$, respectively. Both ions fragmented to give the $M(OMe)_2^+$ ion at low energies, losing the presumed neutral ligands methylacetate and methylorthoformate, respectively. At higher energies, the formation

Table 6
Calculated yield (%) of the presumed rare earth metal trismethoxide $M(OMe)_3$ formed through reactions (2) + (3) and reactions (4) + (6) + (3)

M^+	Yield	M^+	Yield	M^+	Yield	M^+	Yield
Sc^+	60	Pr^+	29	Gd^+	40	Er^+	90
Y^+	78	Nd^+	28	Tb^+	44	Tm^+	81
La^+	9	Sm^+	20	Dy^+	75	Yb^+	0
Ce^+	9	Eu^+	0	Ho^+	80	Lu^+	28

of $M(H)(OMe)^+$ and of $MOCH_2^+$ ions was also observed, corresponding to the losses of formaldehyde and methanol, respectively. Experiments with the precursor ion $M(OMe)_2^+$ were also performed for comparison and showed the formation of $M(H)(OMe)^+$ and of $MOCH_2^+$ ions.

From Table 3 it is apparent that the relative yield of reaction channel (3) increases along the lanthanide series, from La to Lu. This observation could be related to the known increase in the IE(M) values along the Ln series [38] which could be reflected in $IE(M(OMe)_3)$, quantity that plays a role in the thermodynamic driving force for reaction (3). There are no thermochemical data available for the rare earth trisalkoxides but from the literature data [38] we can arrive at a relation that indicates the sum $D[(OMe)_2M^+–OMe) + IE(M(OMe)_3]$ to be equal to or larger than 966 ± 5 kJ/mol. The value of $D[(OMe)_2M^+–OMe]$ is probably rather low due to the formal 4+ oxidation state of the metal in the trismethoxide metal cation and, in the limit, we could consider it close to zero, turning the above relation into a lower limit of 966 ± 5 kJ/mol for the ionisation energy of the metal trismethoxides. In the absence of data for the alkoxide systems, we may roughly compare the value above with the available values of $IE(LaCl_3) = 1023 \pm 48$ kJ/mol and of $IE(LuCl_3) = 1110 \pm 48$ kJ/mol [38].

The efficiencies k/k_{ADO} of the reactions of $M(OMe)^+$ ions for M = Y, Lu were 0.92 and 0.71, respectively, and 0.82 and 0.89 in the case of the reactions of $M(OMe)_2^+$ ions (k/k_{ADO} for Sc from the data in [6] is 0.83). The reaction efficiencies in the case of the lanthanide series metals were all in the range of 0.5–0.7, either for $M(OMe)^+$ ions or $M(OMe)_2^+$ ions, and we were unable to see any particular trend relating the various k/k_{ADO} values.

We should also mention that the MO^+ ions formed in the case of La and Ce react with trimethylorthoformate to give the bismethoxide metal ions, presumably with elimination of methyl formate.

3.2. Reactivity of Y^+ and Lu^+ metal cations with triethyl and tripropyl orthoformates

With triethyl and tripropyl orthoformates reactions (1)–(6) were observed in the case of Y^+, whereas in the case of Lu^+ only reactions (1)–(3) occurred (R = Et, Pr). In Tables 4 and 5 we summarize the product distributions as well as the efficiencies k/k_{ADO} for these reactions. We also list the corresponding Sc^+ data from [6] for comparison.

The reactivity of Y^+ and Lu^+ with the larger alkylorthoformates is basically similar to the one with trimethylorthoformate and we believe that a discussion along the lines developed before would be repetitive. One minor difference found for triethyl and tripropyl with respect to trimethyorthoformate is the fact that the bisethoxymethyl and bispropoxymethyl cations are formed in reactions (1), (3), and (5) with

Table 7
Calculated yield (%) of the presumed rare earth metal trisethoxide $M(OEt)_3$ and trispropoxide $M(OPr)_3$ formed through reactions (2) + (3) and reactions (4) + (6) + (3)

M^+ (R = Et)	Yield	M^+ (R = Pr)	Yield
Sc^+	40	Sc^+	50
Y^+	76	Y^+	55
Lu^+	35	Lu^+	25

excess energies and fragment to the hydroxy–alkoxymethyl cations, with elimination of the corresponding neutral alkenes. These fragment ions were taken into account in the determination of the data presented in Tables 4 and 5.

One last comment should be made concerning the rather large values of the reaction efficiencies in Tables 4 and 5, that indicate that the experimental rate constants k largely exceed the collisional rates k_{ADO}, particularly in the case of the reactions with tripropylorthoformate. Apart from uncertainties in the pressure calibration procedures or ineffective thermalization of the reagent ions, we should refer the limitations of the ADO model used [32], which for instance does not take into account the polarizability anisotropy of the neutral reagents [41,42]. Relevant to this problem are some recent papers on the limitations of polarization models of ion/molecule collisions [43–46].

4. Conclusions

In this work, we were able to confirm for the whole of the rare earth metal ions the results previously obtained in the case of Sc^+ that, in the gas phase, trialkylorthoformates can be good alkoxy group suppliers, leading to dialkoxymetal ions which subsequently react with the orthoesters to form a dialkoxymethyl cation and, presumably, a neutral metal trialkoxide. The present work appears to corroborate our previous suggestion to use this type of reactions as a new route for the gas phase synthesis of rare earth metal alkoxides.

As a final exercise, let us calculate the yield of neutral metal trisalkoxides $M(OR)_3$ for the different rare earth metal cations using the appropriate entries in Tables 1–5. The values obtained are listed in Tables 6 and 7 and show that Sc^+, Y^+, and the later part of the lanthanide series ions $Dy^+–Tm^+$ could be better candidates for any attempt to test an hypothetical technique based on the proposed concept.

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