Journal of Organometallic Chemistry 647 (2002) 216–224

www.elsevier.com/locate/jorganchem

Organolanthanide chemistry in the gas phase

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Received 4 October 2001; received in revised form 30 October 2001

Abstract

Gas-phase ion chemistry studies of lanthanide organometallic species have been performed, seeking differences and similarities with equivalent condensed-phase systems. Several examples of the work done are given, namely investigations of lanthanide–arene complexes, lanthanocenes, lanthanide alkoxides and aryloxides, and complexes with lanthanide–transition metal bonds. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Lanthanide ions; Arene complexes; Metallocenes; Alkoxides; Metal–metal bonds; Gas phase; FT-ICR/MS

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1. Introduction

We have been using mass spectrometry to study the gas-phase reactivity of the lanthanide (Ln) series cations with different organic molecules, by examining pathways, kinetics and energetics of the reactions. The main purpose has been to try to understand the reactivity patterns of the 4f metal ions, through their relationship with electronic structure [1–6]; other research groups have made important contributions to this endeavour with concurrent results [7–21]. Simultaneously, we have been probing new lanthanide organometallic species, looking for differences and similarities with equivalent condensed-phase systems and eventually hints for condensed-phase syntheses.

The mass spectrometric technique that we have been using, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR/MS) [22,23], is specially suited to the study of ion/molecule reactions, due to its ability to perform complex sequences of ion manipulation. Briefly, FT-ICR/MS uses crossed magnetic and electrical fields to trap ions in a finite region of space. Ions generated by any ionisation technique (for instance laser desorption/ionisation in the case of metal ions) are injected and confined in the so-called ICR cell, where they can be selected, collided with neutral species, and any reactions that occur can be monitored with time, being the ionic species detected.

Gas-phase metal ion chemistry has been the subject of several excellent reviews which also address general aspects of gas-phase ion/molecule reactivity as compared to condensed phase [24–28]. In a somewhat simplified way, we can say that in the gas phase, particularly in the low-pressure setting of a mass spectrometer, the physical and chemical properties of ionic species can be studied in the absence of disturbing factors, while in condensed phases, solution or solid, the dense environments formed by solvent or lattice have an important contribution to the chemical processes. In solution, due to the effect of solvation, for any ion/molecule reaction to proceed there will be an initial activation barrier to surpass. In the gas phase, in the absence of solvent, a long-range attractive force is established between an ion and a neutral molecule, due to an ion-induced dipole interaction and, depending on the cases, ion-permanent dipole and/or ion-quadrupole interactions. This attractive force originates an initial well in the potential energy surface which may confer to the ion-neutral complex that forms enough energy to overcome any barriers present and proceed to reaction products. Therefore, ion/molecule reactions in the gas phase can be up to two orders of magnitude faster than in solution. Due to the low-pressure environment, ion/molecule reactions in the gas phase are sequential bimolecular processes. Owing to the large excess of neutral molecules relative to ions, the reactions follow

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0022-328X/02/$ - see front matter
PII: S0022-328X(01)01409-7

pseudo-first-order kinetics. The rate constants k that can be obtained are normally compared with theoretical collisional rate constants k_L (Langevin) or k_{ADO} ("average dipole orientation"), depending on the type of ion-neutral interactions present [29]. A reaction efficiency k/k_L or k/k_{ADO} can then be defined, representing the fraction of ion/neutral collisions which are effective in the formation of reaction products.

The gas-phase lanthanide ion chemistry studies performed to date have shown that the reactivity of Ln^+ metal cations with organic molecules varies markedly along the 4f series, both in terms of the ionic products formed and of the reaction efficiencies [1,3,4,8,12,14,16,18,21]. These reactivity differences have been related to the accessibility of excited electronic configurations with two unpaired non-f electrons, that is, to the excitation energies from the ground states of the Ln^+ ions, typically of the type $4f^n6s^1$, to $4f^{n-1}5d^16s^1$ states [30,31]. In Fig. 1 we present a plot of the excitation energies as a function of the lanthanide metal cation. Like in condensed-phase lanthanide chemistry, the contracted nature of the 4f orbitals precludes the direct participation of the 4f electrons in the bonding [32]. The requirement of availability of two non-f electrons in the reactions of Ln^+ metal cations with organic molecules presupposes that a bond insertion mechanism is occurring. In some cases, evidence could be obtained for other types of mechanisms, depending on the neutral reagent and on the specific Ln^+ ion [4,6,14,17].

Besides unravelling periodic trends in the reactivity of Ln^+ ions with organic molecules, gas-phase studies have given access to numerous species that have been of elusive nature in condensed-phase lanthanide chemistry. A first example is the LnO^+ species, which can be easily obtained for all the lanthanides by reaction of Ln^+ with O_2 or N_2O [16], while there is no example of a discrete organolanthanide complex with a terminal oxo ligand [33,34]. Another example is the $LnCH_2^+$ species, a Schrock-type carbene, which can be obtained by reaction of La^+ and Ce^+ with cyclopropane or propene [12], and has no counterpart in condensed-phase lanthanide organometallic chemistry [33,34].

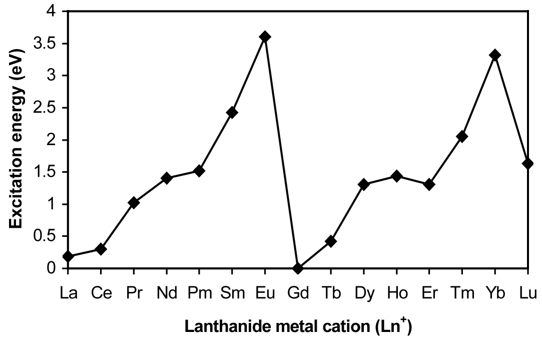

Fig. 1. Excitation energies ground state → $4f^n5d^16s^1$ state of the lanthanide metal cations Ln^+ (values from Refs. [30,31]); ground states are: La^+ $5d^2$, Ce^+ $4f^15d^2$, Pr^+–Eu^+ $4f^36s^1$–$4f^76s^1$, Gd^+ $4f^75d^16s^1$, Tb^+–Yb^+ $4f^96s^1$–$4f^{14}6s^1$, Lu^+ $4f^{14}6s^2$.

In this brief review of our work, we will focus on the formation of several organolanthanide ionic species and we will try to establish some parallels with condensed-phase organolanthanide chemistry. The examples to be described include lanthanide–arene complexes, lanthanocenes, lanthanide alkoxides and aryloxides, and complexes with lanthanide–transition metal bonds.

2. Lanthanide–arene complexes

In 1987, Cloke et al. reported on the synthesis and characterisation of the first authentic examples of zero oxidation state lanthanide complexes, the bis(arene) "sandwich" complexes Ln(1,3,5-tri-*t*-butylbenzene)$_2$, using the metal vapour synthesis (MVS) technique [35,36]. Different stabilities among members of the lanthanide series were observed, that were explained by a simple bonding model in which a $5d^16s^2$ configuration was required either in the ground state or in an easily accessible excited state of the lanthanide atom [36]. Thus, for Sm, Eu, Tm and Yb, which have $4f^n6s^2$ ground-state configurations and high $4f^n6s^2 \rightarrow 4f^{n-1}5d^16s^2$ excitation energies, no stable compounds were obtained. These stability trends were later corroborated by the determination of the bond dissociation enthalpies for selected complexes [37] and by theoretical studies [38].

These results encouraged us to study the gas-phase reactions of Ln^+ metal cations with 1,3,5-tri-*t*-butylbenzene (L), in what became the first systematic study of the reactivity of all the lanthanide series cations (except Pm^+) with an organic molecule [1,39]. While looking for stable LnL_2^+ species, we observed two types of reaction sequences:

$$Ln^+ \xrightarrow{L} LnL^+ \xrightarrow{L} LnL_2^+ \qquad (1)$$

Ln = Sm, Eu, Tm, Yb

$$Ln^+ \xrightarrow{L} Ln(L\text{-}H_2)^+ + Ln(L\text{-}CH_4)^+ + \ldots \xrightarrow{L} LnL(L\text{-}H_2)^+ + LnL(L\text{-}CH_4)^+ + \ldots \qquad (2)$$

Ln = La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Lu

These results showed that high yields of the bis(arene) species could only be obtained when the $4f^n6s^1 \rightarrow 4f^{n-1}5d^16s^1$ excitation energies were too high to permit facile C–C and/or C–H bond activation of the *t*-butyl group, namely for Sm^+, Eu^+, Tm^+ and Yb^+. As in the case of the neutral metal atoms, the stability of bis(arene) species could be explained by a simple bonding model.

This work was extended through the study of the reactivity of the lanthanide ions toward other arenes, namely benzene, naphthalene, toluene, mesitylene and hexamethylbenzene [40]. Again, different yields of bis(arene) species were obtained depending on the $4f^n6s^1 \rightarrow 4f^{n-1}5d^16s^1$ excitation energies and also on the strength of the C–H bonds that were present in the different arenes (strong aromatic C–H bonds in benzene and naphthalene and weak C–H bonds of the methyl substituents in toluene, mesitylene and hexamethylbenzene). The reaction sequences observed were the following (L = arene):

$$Ln^+ \xrightarrow{L} LnL^+ \xrightarrow{L} LnL_2^+ \tag{3}$$

$$Ln^+ \xrightarrow{L} LnL^+ \xrightarrow{L} LnL(L\text{-}H_2)^+ \tag{4}$$

$$Ln^+ \xrightarrow{L} Ln(L\text{-}H_2)^+ \xrightarrow{L} LnL(L\text{-}H_2)^+ \tag{5}$$

$$Ln^+ \xrightarrow{L} Ln(L\text{-}H_2)^+ \xrightarrow{L} Ln(L\text{-}H_2)_2^+ \tag{6}$$

In the case of benzene and naphthalene, only sequences 3 and 5 were observed, while for the methyl-substituted arenes all sequences took place. The formation of bis(arene) species (sequence 3) was verified from Pr^+ to Lu^+ in the case of benzene, for all the Ln^+ ions in the case of naphthalene, for Pr^+, Nd^+, Sm^+, Eu^+, Tm^+ and Yb^+ in the case of toluene, and for Sm^+, Eu^+ and Yb^+ in the case of both mesitylene and hexamethylbenzene. Another aspect that can be emphasised is the occurrence of sequence 4, that corresponds to an enhancement of the reactivity of some of the lanthanide metal ions after addition of one arene, probably due to changes in the electronic configuration of the metal ion after bonding of the arene ligand. It can also be noticed that, in the case of benzene, the first step in sequence 5 corresponds to the formation of $Ln(benzyne)^+$ species, a type of ligand which has not been observed yet in condensed-phase organolanthanide chemistry [33,34].

3. Lanthanide metallocenes

3.1. Pentamethylcyclopentadienyl

The extensive chemistry that has developed in the last decades for organolanthanide compounds involving the pentamethylcyclopentadienyl ligand, C_5Me_5, particularly in the case of the complex $Sm(C_5Me_5)_2$ [33,34,41], motivated us to study the Sm/C_5Me_5 system, in what became the first gas-phase ion chemistry experiments involving a lanthanide metallocene [2]. Since $Sm(C_5Me_5)_2$ is volatile, the gas-phase studies could be conducted starting from the molecular precursor, as well as from the combination of metal-derived Sm^+ with pentamethylcyclopentadiene.

The studies involving the $Sm(C_5Me_5)_2$ complex revealed that, after electron ionisation, the evolution in time of the relative abundances of the major ionic species formed, $Sm(C_5Me_5)_2^+$, $Sm(C_5Me_5)^+$ and Sm^+, corresponded to the superposition of several processes, namely the charge exchange reactions of the above ions with the neutral metallocene and the condensation reaction of $Sm(C_5Me_5)^+$ with neutral $Sm(C_5Me_5)_2$ to yield the $Sm_2(C_5Me_5)_3^+$ ion, presumably a "triple-decker sandwich" species. This behaviour of $Sm(C_5Me_5)_2$ was remarkably similar to the behaviour of d-transition element metallocenes in the gas phase [42–46], despite the differences in bonding thought to exist between metallocenes of transition metals and lanthanides.

The metallocene ion $Sm(C_5Me_5)_2^+$ could also be obtained by reaction of Sm^+ cations with C_5Me_5H in a two-step sequence involving the intermediacy of a tetramethylfulvenide species, $Sm(C_5Me_4CH_2)^+$, as shown in Eq. (7).

$$Sm^+ \xrightarrow{C_5Me_5H} Sm(C_5Me_4CH_2)^+ \xrightarrow{C_5Me_5H} Sm(C_5Me_5)_2^+ \tag{7}$$

It should be noted at this point that fulvenes have been used in condensed-phase lanthanide organometallic chemistry as reagents for the synthesis of metallocenes [33,34].

Formation of other cyclopentadienyl species, formally Sm(II) species, was also observed, as indicated in Eqs. (8) and (9).

$$Sm^+ \xrightarrow{C_5Me_5H} Sm(C_5Me_4H)^+ \xrightarrow{C_5Me_5H} Sm(C_5Me_5)^+ \tag{8}$$

$$Sm^+ \xrightarrow{C_5Me_5H} Sm(C_5Me_5)^+ \xrightarrow{C_5Me_5H} Sm(C_5Me_5)(C_5Me_5H)^+ \tag{9}$$

This work with Sm was later extended to the remaining lanthanide series cations and complemented by studies of related Group 2 (Ca^+, Sr^+ and Ba^+) and Group 3 (Sc^+ and Y^+) metal ions [3]. The reactivity of Eu^+, Tm^+, Yb^+ and the alkaline earth metal ions was similar to that observed previously for Sm^+, namely formation of the fulvenide ion $M(C_5Me_4CH_2)^+$ as main primary product and of the metallocene ion $M(C_5Me_5)_2^+$ as main secondary product. With Sc^+, Y^+ and the remaining lanthanide series ions, the above reaction sequence was only a minor channel, as several other species were observed in the primary reactions, such as $M(C_5Me_5H\text{–}2H_2)^+$, $M(C_5Me_5H\text{–}3H_2)^+$, $M(C_5Me_5H\text{–}CH_4)^+$, $M(C_5Me_5H\text{–}CH_4,H_2)^+$ and $M(C_5Me_5H\text{–}C_2H_6)^+$, corresponding to single and multiple losses of small neutral molecules. In the secondary reactions, addition of C_5Me_5H was observed for all these ions, leading in the case of the first, third and fifth ions to species that were tentatively formulated as $M(C_5Me_4CH_2)_2^+$, $M(C_5Me_4H)(C_5Me_5)^+$ and $M(C_5Me_4H)_2^+$, respectively, while in the case of the two remaining ions, the species formed could not be assigned. The differences in reactivity were correlated with the accessibility of reactive excited state electron configurations of the metal ions through the corresponding excitation energies.

In the same work, the reactivity of the monoxide ions MO^+ with C_5Me_5H was also studied, with the reactivity appearing to be determined by the strength of the M^+–O bonds [47,48]. The ions with the strongest bonds, LaO^+, CeO^+, PrO^+ and NdO^+ formed $M(C_5Me_5)(OH)^+$ as sole primary product, which reacted further, eliminating water, to give the metallocene ion $M(C_5Me_5)_2^+$. ScO^+, YO^+, and the lanthanide series ions SmO^+, GdO^+ to TmO^+, and LuO^+ yielded $MO(C_5Me_4CH_2)^+$ and $M(C_5Me_4CH_2)^+$ as primary products in addition to $M(C_5Me_5)(OH)^+$, and $M(C_5Me_4CH_2)_2^+$ and $M(C_5Me_5)_2^+$ as secondary products. The ions with the weakest M^+–O bonds, EuO^+, YbO^+, CaO^+, SrO^+, and BaO^+, formed MOH^+ as a primary product and $M(C_5Me_5H)^+$ as a secondary product. These reaction sequences are summarised in the following equations:

$$MO^+ \xrightarrow{C_5Me_5H} M(OH)(C_5Me_5)^+ \xrightarrow{C_5Me_5H} M(C_5Me_5)_2^+ \tag{10}$$

M = Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb,
Dy, Ho, Er, Tm, Lu

$$MO^+ \xrightarrow{C_5Me_5H} MO(C_5Me_4CH_2)^+ \xrightarrow{C_5Me_5H} M(C_5Me_4CH_2)_2^+ \tag{11}$$

M = Sc, Y, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu

$$MO^+ \xrightarrow{C_5Me_5H} M(C_5Me_4CH_2)^+ \xrightarrow{C_5Me_5H} M(C_5Me_5)_2^+ \tag{12}$$

M = Sc, Y, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu

$$MO^+ \xrightarrow{C_5Me_5H} MOH^+ \xrightarrow{C_5Me_5H} M(C_5Me_5H)^+ \tag{13}$$

M = Ca, Sr, Ba, Eu, Yb

This study showed that starting from either the metal cation M^+ or from the corresponding monoxide ion MO^+, easy access to lanthanide and related Group 2 and Group 3 metallocenes could be obtained. It should be remarked that the process starting from the oxide species constitutes an unusual way to synthesise a metallocene in terms of condensed-phase organolanthanide chemistry. Another interesting observation in this study is the similarity of Eu and Yb, the lanthanide elements with the more stable 2+ oxidation state, to the alkaline-earth metals; this similarity has also been noticed by other authors for the case of Eu [49].

3.2. Indenyl

A further extension of these gas-phase studies of lanthanide metallocenes was performed, involving Ln^+ cations and indene, C_9H_8 [50]. Although less used as a ligand then pentamethylcyclopentadienyl in condensed-phase organolanthanide chemistry, there are several examples of Ln(II) and Ln(III) indenyl compounds [33,34].

The results obtained in these reactivity studies are summarised in the following equations:

$$Ln^+ \xrightarrow{C_9H_8} Ln(C_9H_8)^+ \xrightarrow{C_9H_8} Ln(C_9H_7)_2^+ \tag{14}$$

Ln = Pr, Nd, Tb, Dy, Ho, Er, Tm, Yb, Lu

$$Ln^+ \xrightarrow{C_9H_8} Ln(C_9H_7)^+ \xrightarrow{C_9H_8} Ln(C_9H_7)_2^+ \tag{15}$$

Ln = La, Ce, Pr, Nd, Gd, Tb

$$Ln^+ \xrightarrow{C_9H_8} Ln(C_9H_7)^+ \xrightarrow{C_9H_8} Ln(C_9H_7)(C_9H_8)^+ \tag{16}$$

Ln = Nd, Sm, Eu

$$Ln^+ \xrightarrow{C_9H_8} Ln(C_9H_6)^+ \xrightarrow{C_9H_8} Ln(C_9H_7)_2^+ \tag{17}$$

Ln = La, Ce, Pr, Gd, Tb

It should be noted that in the case of Sm^+ and Eu^+, no bis(indenyl) species $Ln(C_9H_7)_2^+$ could be obtained and only the formally Ln(II) ion $Ln(C_9H_7)(C_9H_8)^+$ formed, as indicated in sequence 16. Another noticeable result was that for the metal ions of the second half of the lanthanide series Dy^+ to Lu^+ (including Yb^+), sequence 14 was the only one observed, with formation of the adduct ion $Ln(C_9H_8)^+$ as the primary reaction channel and with this species then reacting with indene to form the bis(indenyl) ion $Ln(C_9H_7)_2^+$, eliminating H_2.

Although, as before with pentamethylcyclopentadiene, the major differences in the product distributions and in the kinetics along the lanthanide series were related to the accessibility of reactive excited state electron configurations of the metal cations with two unpaired non-f electrons, $4f^{n-1}6s^15d^1$, other factors may also play a role in the observed reactivity. Further studies may be needed to try to understand the different behaviour of the less reactive metal cations of the first and the second halves of the lanthanide series, and the effect of the ligation of a neutral indene molecule, that was observed to lead to a significant increase in the reactivity as compared to the bare metal ions, particularly in the case of the less reactive metal ions of the second half of the lanthanide series, Dy^+ to Lu^+. This effect of ligation on the reactivity was also observed in the case of the Ln^+/arene systems, as referred to in Section 2.

3.3. Cyclooctatetraenyl

The use of the cyclooctatetraenyl ligand, C_8H_8, in condensed-phase organolanthanide chemistry has received a renewed interest in recent years, both as an alternative and as a complement to the widely used substituted cyclopentadienyl ligands [33,34,51,52]. As a logical extension of our work on the lanthanide metallocenes, we examined the gas-phase reactions of Ln^+ metal cations with C_8H_8 [53]. Other gas-phase studies involving the Ln/C_8H_8 system have recently been reported [19,54].

In our experiments, two main types of behaviour of the lanthanide cations were observed, with the more reactive Ln^+ ions activating cyclooctatetraene to yield $LnC_8H_6^+$, $LnC_6H_6^+$ and $LnC_5H_5^+$ species, together with minor formation of the adduct ion $LnC_8H_8^+$. The less reactive Sm^+, Eu^+ and Yb^+ ions only formed the adduct ion. The $LnC_8H_6^+$, $LnC_6H_6^+$ and $LnC_5H_5^+$ ions react very efficiently with new cyclooctatetraene molecules to give the ion $LnC_8H_8^+$. In all cases, slow reactions of the $LnC_8H_8^+$ ions with C_8H_8 yield the bis(cyclooctatetraenyl) species $Ln(C_8H_8)_2^+$. These reaction sequences are summarised in the following equations:

$$Ln^+ \xrightarrow{C_8H_8} Ln(C_8H_6)^+,\ Ln(C_6H_6)^+,\ Ln(C_5H_5)^+ \xrightarrow{C_8H_8} Ln(C_8H_8)^+ \xrightarrow{C_8H_8} Ln(C_8H_8)_2^+ \qquad (18)$$

$Ln = La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Lu$

$$Ln^+ \xrightarrow{C_8H_8} Ln(C_8H_8)^+ \xrightarrow{C_8H_8} Ln(C_8H_8)_2^+ \qquad (19)$$

$Ln = La–Lu$

The different ability of the Ln^+ metal cations to activate the C–H and/or C–C bonds of cyclooctatetraene and the different reaction efficiencies along the lanthanide series could be related, as in the case of the reactions with substituted cyclopentadienes and other hydrocarbons, to the excitation energies ground state → $4f^{n-1}5d^16s^1$ state.

This study showed that easy access to lanthanide mono and bis(cyclooctatetraenyl) cationic species in the gas-phase can be obtained. Some questions remain unanswered, namely what are the formal oxidation states of the different lanthanide cations in $LnC_8H_8^+$ and $Ln(C_8H_8)_2^+$ species, and what is the form of the C_8H_8 ligand in these species, dianion, radical anion or neutral. Recent experimental [54,55] and theoretical [56] studies of lanthanide–cyclooctatetraenyl systems can be helpful for discussing the bonding in these mono and bis(cyclooctatetraenyl) lanthanide species.

4. Lanthanide alkoxides and aryloxides

The condensed-phase chemistry of rare earth (scandium, yttrium and lanthanide) alkoxides has received considerable attention in recent years, mainly due to the use of these compounds as precursors for the synthesis of new materials [57–62]. One of the main synthetic methods used, MOCVD, involves gas-phase procedures and efforts continue to be made to prepare lanthanide alkoxides that meet the requirements of the method, particularly in terms of volatility. One of the features of rare earth alkoxides is the formation of oligomeric compounds for small aliphatic alcohols, with the presence of oxo or hydroxo ligands in some cases. Only for bulky or functionalised alcohols can discrete monomeric rare earth alkoxides be prepared.

4.1. Ionic alkoxides and aryloxides

With the above considerations in mind, we decided to study the gas-phase reactions of Ln^+ cations with simple alcohols [63]. In the case of the small aliphatic alcohols, methanol, ethanol and isopropanol, we observed that all the lanthanide ions reacted to form LnO^+ and $LnOH^+$ ions as main primary products, showing strong similarities with the results obtained by Géribaldi and co-workers with group 3 metal cations (Sc^+, Y^+ and Lu^+) and the same alcohols [10,11]. For some of the cations of the second half of the lanthanide series, especially Tm^+ and Yb^+, the primary reactions were rather inefficient and slower than subsequent reactions.

The primary product ions participated in subsequent reactions, with rather high kinetic efficiencies, which, through the intermediacy of species such as $M(OH)_2^+$ and $M(OH)(OR)^+$, yielded mainly to $M(OR)_2(HOR)_n^+$ ions, where $n = 0–3$. Eu^+ constituted an exception as, due to the stability of its formal oxidation state $2+$, it only formed $M(OR)(HOR)_n^+$ species. For several lanthanide cations, the presence of aldehyde or ketone ligands in some of the intermediate ions could be observed.

As an example, we present below the reaction sequences observed for the case of Pr^+ and isopropanol:

$$Pr^+ \xrightarrow{HOC_3H_7} PrO^+ \xrightarrow{HOC_3H_7} Pr(OH)(OC_3H_7)^+ \xrightarrow{HOC_3H_7} Pr(OC_3H_7)_2^+ \xrightarrow{HOC_3H_7} Pr(OC_3H_7)_2(HOC_3H_7)^+ \xrightarrow{HOC_3H_7} \ldots \qquad (20)$$

$$Pr^+ \xrightarrow{HOC_3H_7} PrO^+ \xrightarrow{HOC_3H_7} PrO(OC_3H_6)^+ \xrightarrow{HOC_3H_7} Pr(OH)(OC_3H_7)^+ \xrightarrow{HOC_3H_7} Pr(OC_3H_7)_2^+ \xrightarrow{HOC_3H_7} \ldots \qquad (21)$$

$$Pr^+ \xrightarrow{HOC_3H_7} PrOH^+ \xrightarrow{HOC_3H_7} Pr(OC_3H_7)^+ \xrightarrow{HOC_3H_7} Pr(OH)(OC_3H_7)^+ \xrightarrow{HOC_3H_7} Pr(OC_3H_7)_2^+ \xrightarrow{HOC_3H_7} \ldots \qquad (22)$$

In a joint work with the group of Géribaldi, we then studied the gas-phase reactions of Sc^+, Y^+, and Ln^+ ($Ln = La–Lu$, except Pm) ions with phenol [4,64]. All the ions except Yb^+ were observed to react with the organic substrate, activating O–H, C–O, and/or C–H bonds, with formation of MO^+, MOH^+, and/or $MOC_6H_4^+$ ions as primary products.

The primary product ions participated in subsequent reactions, yielding species such as $M(OH)(OC_6H_5)^+$, which led mainly to $M(OC_6H_5)_2(HOC_6H_5)_n^+$ ions, where $n = 0–2$. Formation of $M(OC_6H_5)(HOC_6H_5)_n^+$ species was observed in the case of the metals which have high stabilities of the formal oxidation state $2+$, Sm and Eu.

As an example, we show below the reaction sequence observed for the case of Pr^+:

$$Pr^+ \xrightarrow{HOC_6H_5} PrO^+ \xrightarrow{HOC_6H_5} Pr(OH)(OC_6H_5)^+ \xrightarrow{HOC_6H_5} Pr(OC_6H_5)_2^+ \xrightarrow{HOC_6H_5} Pr(OC_6H_5)_2(HOC_6H_5)^+ \xrightarrow{HOC_6H_5} \ldots \quad (23)$$

The study of the rare earth cation/phenol system was complemented by reactivity studies with 2,4,6-trimethylphenol, and the results were similar [64].

The product distributions and reaction efficiencies obtained in the reactions of lanthanide or rare earth cations towards alcohols and phenols showed the existence of important differences in the relative reactivity of the metal cations, which were discussed in terms of the electron configurations of the metal ions, their oxophilicity and the second ionisation energies of the metals.

As a final comment on these experiments, it can be pointed out the prevalence of MO^+, MOH^+, $M(OH)(OR)^+$ and particularly $M(OR)_2^+$ 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. The formation of oxo and hydroxo containing ions draws a parallel with the presence of oxo and hydroxo ligands in condensed-phase rare earth alkoxides.

4.2. Gas-phase synthesis of neutral rare earth alkoxides

Géribaldi and co-workers used FT-ICR/MS to demonstrate that the reaction between the Sc^+ cation and trialkylorthoformates was a possible route for the gas-phase synthesis of rare earth metal alkoxides [65]. The idea for the use of this type of reaction was based on the knowledge that rare earth metal cations M^+ react efficiently with alcohols and phenols, ROH, leading to dialkoxy metal species $M(OR)_2^+$, as described in Section 4.1, and that trialkylorthoformates $HC(OR)_3$ easily lose an alkoxy group under electron impact or chemical ionisation, leading to the electronically stabilised ion $HC(OR)_2^+$ [66]. The assumption was 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 $M(OR)_3$.

In a joint effort with the group of Géribaldi, we decided to test the above method for the remaining of the rare earth metal cations [5]. Thus, the gas-phase reactivity of Y^+ and Ln^+ (Ln = La–Lu, except Pm) cations with trimethylorthoformate, $HC(OCH_3)_3$, and of Y^+ and Lu^+ ions with triethyl and tripropyl orthoformates, $HC(OC_2H_5)_3$ and $HC(OC_3H_7)_3$, was studied.

The main reaction sequences observed in the case of $HC(OCH_3)_3$ are indicated in Eqs. (24) and (25), showing two ways of reaching the presumed neutral rare earth trismethoxide.

$$M^+ \xrightarrow{HC(OCH_3)_3} M(OCH_3)_2^+ \xrightarrow{HC(OCH_3)_3} M(OCH_3)_3 + HC(OCH_3)_2^+ \quad (24)$$

$$M^+ \xrightarrow{HC(OCH_3)_3} MOCH_3^+ \xrightarrow{HC(OCH_3)_3} M(OCH_3)_2^+ \longrightarrow M(OCH_3)_3 + HC(OCH_3)_2^+ \quad (25)$$

The yield of $M(OCH_3)_3$ for the different rare earth metal cations showed substantial variations. Sc^+, Y^+ and the later part of the lanthanide series ions, from Dy^+ to Tm^+, appeared to be the best candidates for any attempt to test a hypothetical technique based on the proposed concept.

5. Complexes with lanthanide–transition metal bonds

In condensed-phase organolanthanide chemistry there were several attempts to prepare compounds with direct lanthanide to transition metal bonds [33,34]. The synthetic strategies typically involved the use of nucleophilic transition metal carbonyl or mixed carbonyl–cyclopentadienyl complexes, but the oxophilic nature of the lanthanide metal centres frequently favoured the formation of complexes with isocarbonyl linkages, and only in a few cases could complexes with direct, unsupported, metal–metal bonds be prepared [67,68].

In the gas phase, transition metal cations and metal–carbonyl fragment cations react readily with neutral metal carbonyls to form cluster species [69,70] and access to "naked" bimetallic species can be obtained by stripping of the bonded carbonyls in the cluster ions by collision induced dissociation (CID) [71–73]. Transition metal cations react with neutral metallocenes by charge transfer or by metal switching, while metal–cyclopentadienyl fragment cations, besides charge transfer, also give rise to bimetallic species [42–46,74]. As indicated in Section 3, the gas-phase ion chemistry of $Sm(C_5Me_5)_2$ showed remarkable similarities with that of transition element metallocenes.

With this background, we decided to extend our investigation of lanthanide organometallic species in the gas phase to the formation of bimetallic species with transition metals, and, therefore, we examined the reactions of lanthanide ($Ln^+ = La^+–Lu^+$, except Pm^+) cations with the archetypal, volatile, complexes iron pentacarbonyl, $Fe(CO)_5$, and ferrocene, $Fe(C_5H_5)_2$ [6,75].

In the case of $Fe(CO)_5$, the observed primary products were of the type $LnFe(CO)_x^+$, as indicated in the following equations:

$$Ln^+ \xrightarrow{Fe(CO)_5} LnFe(CO)_3^+ \quad (26)$$

Ln = La, Ce, Pr, Nd, Gd, Tb, Ho, Er, Lu

$$Ln^+ \xrightarrow{Fe(CO)_5} LnFe(CO)_4^+ \quad (27)$$

Ln = Sm, Eu, Dy, Ho, Er, Tm, Yb, Lu

Evidence was obtained for the presence of direct Ln–Fe bonds in these species by means of CID experiments:

$$\mathrm{LnFe(CO)}_x^+ \xrightarrow{\mathrm{CID/[Ar]}} \mathrm{LnFe(CO)}_{x-1}^+ + \mathrm{CO} \rightarrow \ldots$$
$$\rightarrow \mathrm{LnFe}^+ + x\mathrm{CO} \qquad (28)$$

The emergence of polymetallic species, up to $\mathrm{LnFe}_5\mathrm{(CO)}_{20}^+$ ions, in reactions of $\mathrm{LnFe(CO)}_x^+$ with neutral $\mathrm{Fe(CO)}_5$ and in subsequent ones, apparently corresponded to the formation of cluster species involving Fe–Fe bonds, as described in gas-phase ion chemistry studies of iron and other transition metal carbonyls [69,70].

With $\mathrm{Fe(C_5H_5)_2}$ the majority of the Ln^+ cations reacted by metal exchange, yielding Ln bis(cyclopentadienyl) ions $\mathrm{Ln(C_5H_5)_2^+}$, while the less reactive Ln^+ cations formed the "adduct" ions $\mathrm{LnFe(C_5H_5)_2^+}$, as shown in the following equations:

$$\mathrm{Ln}^+ \xrightarrow{\mathrm{Fe(C_5H_5)_2}} \mathrm{Ln(C_5H_5)_2^+} \qquad (29)$$

Ln = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy,
Ho, Er, Tm, Lu

$$\mathrm{Ln}^+ \xrightarrow{\mathrm{Fe(C_5H_5)_2}} \mathrm{LnFe(C_5H_5)_2^+} \qquad (30)$$

Ln = Sm, Eu, Tm, Yb

CID experiments gave no evidence for the presence of Ln–Fe bonds in the $\mathrm{LnFe(C_5H_5)_2^+}$ ions:

$$\mathrm{LnFe(C_5H_5)_2^+} \xrightarrow{\mathrm{CID/[Ar]}} \mathrm{Ln}^+ + \mathrm{Fe(C_5H_5)_2} \qquad (31)$$

Ln = Sm, Eu, Tm, Yb

$$\mathrm{LnFe(C_5H_5)_2^+} \xrightarrow{\mathrm{CID/[Ar]}} \mathrm{Ln(C_5H_5)_2^+} + \mathrm{Fe} \qquad (32)$$

Ln = Tm

The formation of Ln bis(cyclopentadienyl) ions $\mathrm{Ln(C_5H_5)_2^+}$ by the route just described, constitutes a new mode of gas-phase synthesis of lanthanide metallocenes (see Section 3).

The product ion distributions observed with the two organometallic reagents and the reaction efficiencies obtained in kinetics studies both revealed a close relation with the relative stability of the accessible formal oxidation states of the lanthanide metal cations, as measured by the third ionisation energies of the lanthanide metals [76].

6. Conclusions

We hope to have shown some of the merits of gas-phase ion chemistry studies in yielding information on the intrinsic reactivity of metal cations. In the case of the lanthanide series, periodic trends based on the electronic structure of the cations or on selected physical properties of the elements can be obtained. A few parallels can be drawn between gas-phase and equivalent condensed-phase systems. Further developments in this area will probably take advantage of the use of electrospray ionisation (ESI), to open up access to new lanthanide organometallic species and to the study of ion/molecule reactions which are progressively closer to condensed-phase processes [77,78].

Acknowledgements

The authors are grateful to the coworkers of ITN who participated in the work: João P. Leal, José M. Carretas and M. Conceição Vieira. Parts of the work profited from collaborations with the research groups of Professors Alan G. Marshall (Ohio State University and National High Magnetic Field Laboratory, FL), William J. Evans (University of California-Irvine) and Serge Géribaldi (Université de Nice-Sophia Antipolis). The work has benefited from the financial support of JNICT/FCT and JNICT/ICCTI (Portugal), NATO and the French Embassy in Portugal.

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