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Gas-phase reactivity of lanthanide and actinide cations with the archetypal organometallic complexes $Fe(CO)_5$ and $Fe(C_5H_5)_2$

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This paper is dedicated to Professor Alberto Romão Dias on the occasion of his 60th birthday. The authors acknowledge his invaluable contribution to the development of Organometallic Chemistry in Portugal.

Abstract

The gas-phase reactions of lanthanide ($Ln^+ = La^+–Lu^+$, except Pm^+) and actinide ($An^+ = Th^+$, U^+) cations with iron pentacarbonyl, $Fe(CO)_5$, and with ferrocene, $Fe(C_5H_5)_2$, were studied by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR/MS). In the case of $Fe(CO)_5$, the observed primary products were of the type $MFe(CO)_x^+$ (M = La, Ce, Pr, Nd, Gd, Tb: $x = 3$; M = Ho, Er, Lu: $x = 3$ and 4; M = Sm, Eu, Dy, Tm, Yb: $x = 4$; M = Th, U: $x = 2$ and 3) and evidence was obtained for the presence of direct Ln–Fe and An–Fe bonds in these species. With $Fe(C_5H_5)_2$ the An^+ cations and the majority of the Ln^+ cations reacted by metal exchange, yielding Ln and An biscyclopentadienyl ions $M(C_5H_5)_2^+$, while the less reactive Ln^+ cations formed the 'adduct' ions $LnFe(C_5H_5)_2^+$. 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 metal cations. A few thermochemical estimates pertaining to the different species formed in the reactions could also be made. Reactivity studies of Ln, Th and U oxide and hydroxide cations with the iron complexes are also reported.

Keywords: Lanthanide ions; Actinide ions; Iron complexes; Metal–metal bonds; Gas phase; FT-ICR/MS

1. Introduction

Organometallic chemistry in condensed phases, solution or solid, is clearly influenced by the dense environment formed by solvent or lattice. In the gas phase, particularly in the low pressure environment of a mass spectrometer, the intrinsic physical and chemical properties of organometallic ionic species can be studied in the absence of disturbing factors [1–5]. Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR/MS) [6], due to its ability to perform complex sequences of ion manipulation, is a technique that is specially suited to the study of ion-molecule systems at a fundamental level, yielding information on the structure of the ionic species and on the mechanisms, kinetics and energetics of the reactions [7].

In our laboratory, we have been using FT-ICR/MS to study the gas-phase reactivity of the f-block metal cations with different organic molecules, by examining reaction rates and reaction pathways [8–14]. The purpose has been to gain a better understanding of how reactivity varies in the lanthanide (Ln) and actinide (An) series and to relate it to the electronic configuration of the metal cations. These studies have become part of a recent interest in the previously unexplored gas-phase ion chemistry of lanthanides and actinides [15–35].

Simultaneously, we have been probing the gas-phase ion chemistry of new lanthanide and actinide organometallic species, trying to devise differences and similarities with equivalent condensed-phase systems and eventually to obtain guidance for condensed-phase syntheses. Examples of the work done include studies of lanthanide– and actinide–arene complexes [8,12], of lanthanide metallocenes [10,11] and of lanthanide alkoxides and aryloxides [13,14].

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In condensed-phase organometallic chemistry there were several attempts to prepare compounds with direct lanthanide or actinide to transition metal bonds [36]. The synthetic strategies typically involved the use of nucleophilic transition metal carbonyl or mixed carbonyl–cyclopentadienyl complexes, but the oxophilic nature of the lanthanide and actinide 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 [37–40].

In the gas phase, transition metal cations and metal-carbonyl fragment cations react readily with neutral metal carbonyls to form cluster species [41–45] and access to 'naked' bimetallic species can be obtained by stripping of the bonded carbonyls in the cluster ions by collision induced dissociation (CID) [46–52]. 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 [53–55]. The gas-phase ion chemistry of bis(pentamethylcyclopentadienyl)-samarium showed remarkable similarities with transition element metallocenes, in terms of electron transfer reactions and the formation of bimetallic species with presumed 'triple-decker sandwich' structures [10].

With this background, we decided to extend our investigation of lanthanide and actinide organometallic species in the gas phase to the formation of bimetallic species with transition metals, and, therefore, in this work, we examine by FT-ICR/MS the reactions of lanthanide ($Ln^+ = La^+–Lu^+$, except Pm^+) and actinide ($An^+ = Th^+, U^+$) cations with the archetypal, volatile, complexes iron pentacarbonyl, $Fe(CO)_5$, and ferrocene, $Fe(C_5H_5)_2$.

2. Experimental

The experiments were carried out using a Finnigan FT/MS 2001-DT FT-ICR mass spectrometer, equipped with a 3 T superconducting magnet, a Spectra-Physics Quanta-Ray GCR-11 Nd:YAG laser operated at the fundamental wavelength (1064 nm) and a Finnigan Venus Odyssey data system (recently replacing the original Nicolet 1280 data station).

The lanthanide and actinide metal ions were produced by direct laser desorption/ionisation (LDI) of pure metal pieces (obtained commercially or prepared in the Institute for Transuranium Elements — JRC Karlsruhe in the case of Th and U), mounted on the solids probe of the instrument. Metal oxide ions were produced by LDI of the oxide layer on the surface of the metal samples, or by use of a formation period prior to isolation, in which the oxophilic metal ions oxidised by reaction with background water or oxygen. The volatile reagent complexes $Fe(CO)_5$ (obtained commercially and degassed prior to use) and $Fe(C_5H_5)_2$ (incidentally, a generous gift from the Group of Professor Romão Dias) were introduced into the spectrometer through leak valves, on the 'source' side of the dual ion trap of the instrument.

Ion selection and excitation was achieved using single-frequency, frequency-sweep or SWIFT [56] excitation. Reaction sequences were identified by means of double-resonance and MS/MS techniques. The collision-induced dissociation (CID) experiments were carried out by excitation of the ions in question to lab-frame energies of 10–80 eV followed by collisions with argon, introduced in the vacuum chamber through a leak valve at constant pressures of ca. 5×10^{-7} Torr.

Neutral pressures were measured by a Bayard–Albert type ionisation gauge. Pressure calibration was achieved using standard reactions of methane [57] and acetone ions [58], and included corrections for the different ionisation efficiencies of the iron complexes, calculated according to Bartmess et al. [59] from estimated molecular polarisabilities. The polarisabilities of $Fe(CO)_5$ and $Fe(C_5H_5)_2$ were taken as the sums of the polarisabilities of the organic ligands bonded to Fe (from an experimental value in the case of CO [60] and a value estimated by the method of Miller in the case of C_5H_5 [61]), leading to values of 9.8 $Å^3$ for $Fe(CO)_5$ and 17.4 $Å^3$ for $Fe(C_5H_5)_2$.

Rate constants were determined from the pseudo-first order decay of the reactant ion relative signal magnitude as a function of time at constant reagent pressure and are reported as reaction efficiencies, that is, as fractions of the Langevin collisional rates, k_L [62], calculated using estimated molecular polarisabilities, as indicated above. Uncertainties in the pressure calibration procedure may lead to errors in the rate constants that we estimate to be $\pm 50\%$, but the relative magnitudes of the reaction efficiencies should have errors lower than 20%. Due to the oxophilicity of thorium, uranium and the early lanthanide metals, reactions of the metal ions and some of their reaction products with residual water and oxygen were observed and the formation of oxygenated products was taken into account in the kinetics calculations.

The reactant ions were thermalised by collisions with argon, introduced in the instrument through pulsed valves to pressures of ca. 10^{-5} Torr or through a leak valve with constant pressures of 5×10^{-7}–5×10^{-6} Torr. The reproducibility of the reaction kinetics as well as the linearity of the semilog plots of the normalised reactant ion intensities versus time were used as indications of the thermalisation 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 thermalisation effectiveness.

3. Results

3.1. Reactions with Fe(CO)$_5$

In Table 1 we show the primary product ion distributions obtained in the reactions of Ln^+ (Ln = La–Lu, except Pm) and An^+ (An = Th, U) ions with iron pentacarbonyl, $Fe(CO)_5$, as well as the corresponding reaction efficiencies k/k_L.

Table 1
Primary product distributions (%) and efficiencies (k/k_L) of the reactions of lanthanide and actinide metal cations with $Fe(CO)_5$

M^+	Primary product distributions (%)			k/k_L
	$MFe(CO)_2^+$	$MFe(CO)_3^+$	$MFe(CO)_4^+$	
La	0	100	0	1.27
Ce	0	100	0	1.29
Pr	0	100	0	1.07
Nd	0	100	0	1.01
Sm	0	0	100	0.92
Eu	0	0	100	0.84
Gd	0	100	0	1.21
Tb	0	100	0	1.13
Dy	0	0	100	0.73
Ho	0	20	80	0.69
Er	0	35	65	0.84
Tm	0	0	100	0.51
Yb	0	0	100	0.32
Lu	0	60	40	1.08
Th	80	20	0	1.43
U	45	55	0	1.31

Table 2
Primary product distributions (%) and efficiencies (k/k_L) of the reactions of lanthanide and actinide metal cations with $Fe(C_5H_5)_2$

M^+	Primary product distributions (%)		k/k_L
	$M(C_5H_5)_2^+$	$MFe(C_5H_5)_2^+$	
La	100	0	0.99
Ce	100	0	0.92
Pr	100	0	0.66
Nd	100	0	0.56
Sm	25	75	0.20
Eu	0	100	0.18
Gd	100	0	0.73
Tb	100	0	0.72
Dy	100	0	0.52
Ho	100	0	0.44
Er	100	0	0.47
Tm	90	10	0.30
Yb	0	100	0.15
Lu	100	0	0.68
Th	100	0	1.23
U	100	0	1.14

All the metal cations reacted with $Fe(CO)_5$ and the observed primary products were of the type $MFe(CO)_x^+$ (M = La, Ce, Pr, Nd, Gd, Tb: $x = 3$; M = Ho, Er, Lu: $x = 3$ and 4; M = Sm, Eu, Dy, Tm, Yb: $x = 4$; M = Th, U: $x = 2$ and 3), corresponding to neutral losses of $(5 - x)$CO groups.

The primary products' ions reacted with new $Fe(CO)_5$ molecules with loss of one or two neutral CO groups to give species of the type $MFe_2(CO)_{x+4}^+$ or $MFe_2(CO)_{x+3}^+$ (M and x as above). Further reactions of these and subsequent product ions were observed, again with loss of one or two CO groups, and products corresponding to $MFe_5(CO)_{20}^+$ could be identified.

The CID experiments were carried out with the $MFe(CO)_x^+$ ($x = 2$–4) ions formed in the primary reactions. With increasing excitation energy, consecutive losses of the carbonyl ligands were observed, until the formation of the bare intermetallic ions MFe^+.

Reactions of the product ions with background water were detected, in which one CO group was replaced by a water molecule.

The reactivity of thorium and uranium oxide cations, ThO^+, UO^+ and UO_2^+, with $Fe(CO)_5$ was also studied. ThO^+ formed $ThOFe(CO)_4^+$ (15%) and $ThOFe(CO)_3^+$ (85%) ions, with concomitant loss of one and two CO groups, respectively, UO^+ produced only the $UOFe(CO)_3^+$ ion, while UO_2^+ yielded the 'adduct' ion $UO_2Fe(CO)_5^+$. Reaction efficiencies k/k_L of 1.02 for ThO^+, 1.04 for UO^+ and 0.13 for UO_2^+ were determined.

Reactions of the $MOFe(CO)_3^+$ product ions and subsequent products were also observed, and proceeded, like in the case of the metal ions, with loss of one or two CO groups. In the case of the $UO_2Fe(CO)_5^+$ ion, subsequent reactions corresponded to additions of $Fe(CO)_5$.

3.2. Reactions with Fe(C$_5$H$_5$)$_2$

Table 2 shows the primary product ion distributions for the reactions of Ln^+ (Ln = La–Lu, except Pm) and An^+ (An = Th, U) cations with ferrocene, $Fe(C_5H_5)_2$, and the corresponding reaction efficiencies k/k_L.

For the An^+ cations and all the Ln^+ cations except Eu^+ and Yb^+ metal exchange reactions occurred, with the formation of the biscyclopentadienyl ions $M(C_5H_5)_2^+$ and elimination of neutral Fe. Formation of the 'adduct' ion $MFe(C_5H_5)_2^+$ was observed for Sm^+, Eu^+, Tm^+ and Yb^+.

Reactions of the $M(C_5H_5)_2^+$ ions with neutral $Fe(C_5H_5)_2$ gave the 'adduct' species $M(C_5H_5)_2Fe(C_5H_5)_2^+$. Efficiencies k/k_L of these secondary reactions were in the range of 0.3–0.5. The primary 'adduct' ions $MFe(C_5H_5)_2^+$ reacted with neutral $Fe(C_5H_5)_2$ to generate the bis-'adduct' ions $M[Fe(C_5H_5)_2]_2^+$, with efficiencies k/k_L around 0.05.

The CID experiments performed with the $LnFe(C_5H_5)_2^+$ ions (Ln = Sm, Eu, Tm, Yb) led to the formation of Ln^+ and also of $Ln(C_5H_5)_2^+$ in the case of Tm.

Coordination of water molecules from the background to the $M(C_5H_5)_2^+$ cations to form $M(C_5H_5)_2(H_2O)^+$ was observed.

Metal oxide and hydroxide ions, produced in reactions of the metal cations with background water and/or oxygen, also reacted with neutral $Fe(C_5H_5)_2$. In the case of the lanthanides, the LnO^+ and $LnOH^+$ cations yielded the respective 'adduct' species $LnOFe(C_5H_5)_2^+$ and $Ln(OH)Fe(C_5H_5)_2^+$. In the case of the actinides, ThO^+, $ThO(OH)^+$ and UO_2^+ formed the 'adduct' ions $ThOFe(C_5H_5)_2^+$, $ThO(OH)Fe(C_5H_5)_2^+$ and $UO_2Fe(C_5H_5)_2^+$, respectively, and the metal hydroxides $ThOH^+$ and UOH^+ gave rise to elimination of neutral Fe to form $Th(OH)(C_5H_5)_2^+$ and $U(OH)(C_5H_5)_2^+$ ions, respectively, while UO^+ led to both the 'adduct' ion $UOFe(C_5H_5)_2^+$ and the $UO(C_5H_5)_2^+$ ion. In all cases, subsequent reactions with neutral $Fe(C_5H_5)_2$ were of the addition type.

4. Discussion

The overall reactivity of the lanthanide and actinide cations with iron pentacarbonyl, with formation of $MFe(CO)_x^+$ ions as primary products, is in agreement with previous observations by Freiser and co-workers involving metal cations of the d and s blocks and $Fe(CO)_5$ [46–52], and by Fredeen and Russell in studying the ion chemistry of cobalt/iron and nickel/iron carbonyl systems [44]. The La^+ cation was studied before by Freiser et al. [49], who observed the formation of a single product, $LaFe(CO)_3^+$, in accord with our observations.

In the case of ferrocene, metal switching reactions, yielding $M(C_5H_5)_2^+$ ions, were dominant. This type of reaction was previously observed by Freiser and co-workers in systems involving d-transition metal cations [55], but the formation of 'adduct' ions $MM'(C_5H_5)_2^+$ was not observed. Instead, these authors observed charge exchange reactions in the cases where the ionisation energy of the reactant metal ion was higher than the ionisation energy of the neutral metallocene. The ionisation energy of ferrocene (6.71 ± 0.08 eV [63]) is higher than the ionisation energies of any of the lanthanide and actinide metals studied (which vary from 5.42585 ± 0.00002 eV for Lu up to 6.308 ± 0.003 eV for Th [63]) and, accordingly, charge exchange reactions were not observed in our case.

The primary product ion abundances reported for the two systems in Tables 1 and 2 indicate that significant differences in relative reactivity of the metallic ions exist along the lanthanide series and for the actinides studied.

Important differences in reactivity along the lanthanide and actinide series were verified before in studies of the reactions of Ln^+ [8,11,13,14,16–18,21,25,27–29,35] and An^+ [9,12,22,26,30–34] cations with hydrocarbons and other organic molecules. These differences were related with the electronic configurations of the reactant metal cations and the magnitude of the excitation energies to configurations with two non-f electrons that could participate in bond-insertion reactions with organic molecules.

With iron complexes as reactants, it is arguable that bond insertion mechanisms are occurring. In the case of $Fe(CO)_5$, the formation of $MFe(CO)_x^+$ ions could involve initial coordination of the metal ions to the carbonyl oxygens (akin to the isocarbonyl linkages found in bimetallic complexes in condensed phase [36], see Section 1), that may be followed by coordination of the electron-rich iron centre and consequent elimination of neutral CO ligands. In the case of $Fe(C_5H_5)_2$, formation of the metallocenes $M(C_5H_5)_2^+$ and of neutral Fe could result from initial sideways coordination of the metal cations to the two cyclopentadienyl ligands, followed by slippage of the rings to the lanthanide or actinide cations, with simultaneous electron transfer to the iron centre.

In the lanthanide and actinide metallocene cations $M(C_5H_5)_2^+$, the cyclopentadienyl ligand can be formally considered as $C_5H_5^-$, which leaves the metals formally in the 3+ oxidation state. If we use this same type of ionic description for the case of $MFe(CO)_x^+$ species, we can consider that the loss of one, two and three CO groups from $Fe(CO)_5$ formally corresponds to the formation of $Fe(CO)_4^-$, $Fe(CO)_3^{2-}$ and $Fe(CO)_2^{3-}$ ligands, respectively, and the $MFe(CO)_x^+$ ions can be regarded as species in which the lanthanide and actinide metals formally are in the oxidation states 2+ for $x = 4$, 3+ for $x = 3$ and 4+ for $x = 2$. (Theoretical studies on the model condensed-phase complex $(C_5H_5)_2(I)Th–Ru(C_5H_5)(CO)_2$ have described the metal–metal bonding as being of the donor–acceptor type, with $Ru(C_5H_5)(CO)_2$ behaving as an halide ligand [64].)

In Fig. 1, we show a plot of the third ionisation energy (3rd IE) of the lanthanide metals. Th and U have 3rd IEs in between the values for La and Ce [65]. If we take this quantity as a measure of the relative stability of the 2+ and 3+ oxidation states in the gas phase, we can satisfactorily interpret the differences in reactivity observed in the present work, for both $Fe(CO)_5$ and $Fe(C_5H_5)_2$ systems, and manifested in the different product ions formed in the primary reactions and in the corresponding reaction efficiencies.

In terms of product distributions, we can see in Table 1 that the lanthanide metals with the more stable 2+ oxidation states produced $MFe(CO)_4^+$ ions, while both

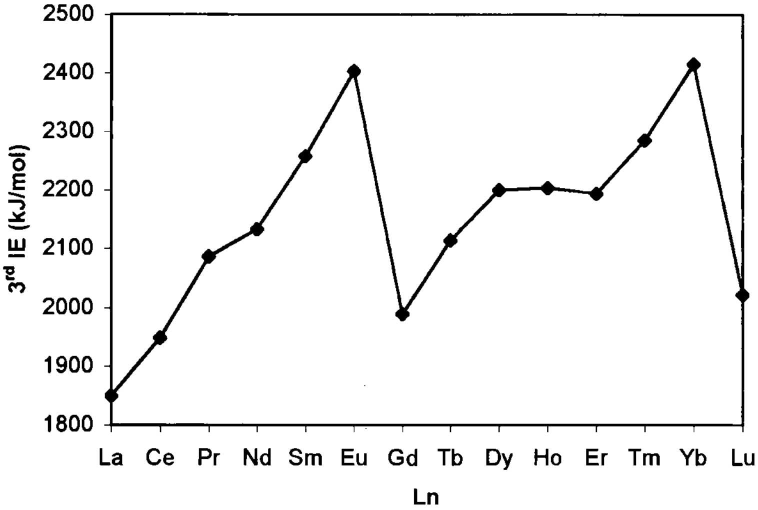

Fig. 1. Third ionisation energies (3rd IE) of the lanthanide metals (Ln) [64].

$MFe(CO)_3^+$ and $MFe(CO)_4^+$ ions were formed by the lanthanide metals coming next in the 2+ oxidation state stability and $MFe(CO)_3^+$ ions were the only products formed by the remaining of the lanthanides, with more stable 3+ oxidation states. For Th and U, with accessible 4+ oxidation states (also 5+ and 6+ in the case of U), $MFe(CO)_2^+$ ions were obtained in combination with $MFe(CO)_3^+$ ions. It is interesting to refer at this point the results obtained by Freiser and co-workers in reactions of Group 2 Mg^+ cations with $Fe(CO)_5$, exclusively observing formation of $MgFe(CO)_4^+$ ions [52], of Group 3 Sc^+ cations forming $ScFe(CO)_3^+$ ions [51] and of Group 5 Nb^+ cations that yielded both $NbFe(CO)_2^+$ and $NbFe(CO)_3^+$ ions [50].

In Table 2, we can see that the formation of the 'adduct' ions $MFe(C_5H_5)_2^+$ occurred only for the metals that present a more stable 2+ oxidation state. (Sm, Eu and Yb are the lanthanide metals for which there are numerous examples of stable bis(cyclopentadienyl) complexes in the condensed phase [36].)

The results obtained in the reactions of actinide oxide and hydroxide cations with $Fe(CO)_5$ and $Fe(C_5H_5)_2$ and of lanthanide oxide and hydroxide cations with $Fe(C_5H_5)_2$, described in the previous section, also appear to fit in the interpretative model that we have been using. The lanthanide cations LnO^+ and $LnOH^+$, formally 3+ and 2+ species, yielded only the respective 'adducts' $LnOFe(C_5H_5)_2^+$ and $Ln(OH)Fe(C_5H_5)_2^+$. ThO^+, $ThOH^+$ and $ThO(OH)^+$ ions yielded product ions corresponding to formal oxidation states not exceeding 4+: $ThOFe(CO)_4^+$, $ThOFe(C_5H_5)_2^+$, $Th(OH)(C_5H_5)_2^+$ and $ThO(OH)Fe(C_5H_5)_2^+$, with one exception, $ThOFe(CO)_3^+$ (the formally 5+ thorium dioxide ion ThO_2^+ can be easily formed by the reaction of ThO^+ with N_2O [26]). UO^+ formed the $UOFe(CO)_3^+$ and the $UO(C_5H_5)_2^+$ ions, formally corresponding to 5+ oxidation states of U, while UOH^+ gave rise to $U(OH)(C_5H_5)_2^+$ ions, formally 4+. UO_2^+, a very stable cation with U already formally in the 5+ oxidation state [12,23,24,26], produced only the $UO_2Fe(CO)_5^+$ and the $UO_2Fe(C_5H_5)_2^+$ 'adduct' ions.

We should mention here that the gas-phase reactivity of different metal cations, including several lanthanides, with fluorocarbons and the formation of MF_x^+ species has been interpreted in terms of the relative stability of the oxidation states of the metals [28].

Concerning the reaction efficiencies obtained in the kinetic studies (see Tables 1 and 2), they also appear to be in agreement with the relative reactivity of the lanthanide and actinide metal cations as related to the relative stability of the 2+ and 3+ oxidation states in the gas phase. In Fig. 2, a plot of these reaction efficiencies along the lanthanide series more easily shows the approximate inversely parallel trend relating the k/k_L values with the 3rd IEs of the metals (see Fig. 1). A short comment can be made at this point concerning the fact that some of the k/k_L values for the more reactive Ln and An cations are larger than one. Al-

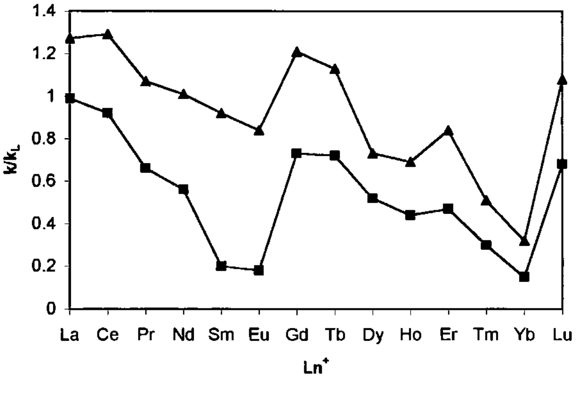

Fig. 2. Efficiencies (k/k_L) of the reactions of lanthanide metal cations (Ln^+) with $Fe(CO)_5$ (triangles) and $Fe(C_5H_5)_2$ (squares).

though these values are still within the estimated absolute error of 50% indicated in Section 2, we consider that the approximate method used for estimating the polarisabilities of the neutral organometallic reagents, described in Section 2, could be largely responsible for that fact.

A few thermochemical estimates can be attempted for both the $Fe(CO)_5$ and the $Fe(C_5H_5)_2$ systems, considering that only exothermic reactions are observed in the present FT-ICR/MS experiments. The formation of the $MFe(CO)_x^+$ ions implies that $D(M^+ - Fe(CO)_x)$ should be larger than the bond dissociation enthalpies of the first CO ligand in $Fe(CO)_5$ for $x = 4$, of the first and second CO ligands for $x = 3$ and of the first, second and third CO ligands for $x = 2$. Using available thermochemical data [63], that is, $D((CO)_4Fe–CO)$ and the average $D(Fe–CO)$ in $Fe(CO)_5$, we can calculate the following lower limits for $D(M^+ - Fe(CO)_x)$: 174 ± 16 kJ mol^{-1} for $x = 4$, 278 ± 18 kJ mol^{-1} for $x = 3$ and 382 ± 18 kJ mol^{-1} for $x = 2$. As the second and third iron–carbonyl bond dissociation enthalpies were calculated from the difference between the average D and the first bond enthalpy, we can try to obtain what we consider a more reliable estimate of these lower limits for $D(M^+ - Fe(CO)_x)$ by using the existing thermochemical data for the $Co(CO)_5^+$ ion [5], isoelectronic with neutral $Fe(CO)_5$ (the first Fe–CO bond dissociation enthalpy in $Fe(CO)_5$, 174 ± 16 kJ mol^{-1} [63], is equal to the first Co^+–CO bond dissociation enthalpy in $Co(CO)_5^+$, 174 ± 7 kJ mol^{-1} [5]). With this approach, we obtain the values 327 ± 18 kJ mol^{-1} for $x = 3$ and 409 ± 18 kJ mol^{-1} for $x = 2$. We can compare these $D(M^+ - Fe(CO)_x)$ lower limits with the value reported by Huang and Freiser [49] for $D(La^+–Fe)$ in $LaFe^+$ ions, 201 ± 21 kJ mol^{-1}, as determined by photodissociation experiments in the gas phase, and with the metal–metal bond dissociation enthalpies in solution determined by Marks and co-workers [67] by solution calorimetry for the complexes $(C_5H_5)_3U–M(C_5H_5)(CO)_2$, 129 ± 13 kJ mol^{-1} for M = Fe and 169 ± 17 kJ mol^{-1} for M = Ru.

The formation of the bis(cyclopentadienyl) ions $M(C_5H_5)_2^+$ indicates that the average $M^+–C_5H_5$ bond dissociation enthalpy in these species should be larger than the average $Fe–C_5H_5$ bond dissociation enthalpy in ferrocene. Depending on the source for the value of the enthalpy of formation of cyclopentadienyl used in the calculation, we obtain 328 ± 7 [66], 339 ± 15 [63] or 347 ± 10 kJ mol^{-1} [2] as lower limits for the average $D(M^+ - C_5H_5)$ in $M(C_5H_5)_2^+$ ions. In the case of La, Pr, Yb and U, with available values for the enthalpies of formation of $Ln(C_5H_5)_3$ and $U(C_5H_5)_4$ species and for the appearance energies of $Ln(C_5H_5)_2^+$ and $U(C_5H_5)_2^+$ ions [63] and with values for the enthalpies of formation of the metal ions [66], we can calculate values for the average $D(M^+ - C_5H_5)$ in $M(C_5H_5)_2^+$ ions, which can be compared with the above lower-limit estimations. Again depending on the source for the value of the enthalpy of formation of cyclopentadienyl, we obtain for average $D(La^+–C_5H_5)$ 279 ± 34 [66], 295 ± 34 [63] or 307 ± 34 kJ mol^{-1} [2], for average $D(Pr^+–C_5H_5)$ 272 ± 27 [66], 288 ± 27 [63] or 300 ± 27 kJ mol^{-1} [2], for average $D(Yb^+–C_5H_5)$ 239 ± 26 [66], 255 ± 26 [63] or 267 ± 26 kJ mol^{-1} [2], and for average $D(U^+–C_5H_5)$ 127 ± 53 [66], 149 ± 53 [63] or 165 ± 53 kJ mol^{-1} [2], values that are all significantly lower than the above estimations, especially in the case of uranium. Although in the case of Yb^+, which does not form $Yb(C_5H_5)_2^+$ in the reaction with ferrocene, the values of average $D(Yb^+–C_5H_5)$ could be consistent, in the remaining cases, and particularly in the case of U^+, doubts can be raised on some of the literature data, namely appearance energies, which are known to be reliable for thermochemical computations only when there are no potential barriers in the fragmentation reactions and no kinetic shifts in the experimental determinations [63,66].

As final comments, we can say that, in what concerns the formation of bimetallic species, the CID experiments described in Section 3.1 and Section 3.2 indicated that, for the $MFe(CO)_x^+$ ions, M^+–Fe bonds were formed (successive elimination of CO groups and formation of MFe^+ ions) and were absent in the case of the $LnFe(C_5H_5)_2^+$ species (elimination of an intact ferrocene molecule and formation of Ln^+). The emergence of polymetallic species in the secondary and subsequent reactions with $Fe(CO)_5$ (up to $MFe_5(CO)_{20}^+$ ions) apparently corresponds to the formation of cluster species involving iron–iron bonds, as described in gas-phase ion chemistry studies of iron and other transition metal carbonyls [41–45].

The formation of lanthanide and actinide biscyclopentadienyl species $M(C_5H_5)_2^+$ in the reactions of the corresponding metal cations M^+ with $Fe(C_5H_5)_2$ is a new way of gas-phase synthesis of lanthanide and actinide metallocenes. In previous works [10,11], we have shown that, in the case of the lanthanides, biscyclopentadienyl species could be obtained in reactions of the metal or the metal oxide cations with pentamethylcyclopentadiene.

5. Conclusions

We were able to show that gas-phase reactions of lanthanide and actinide cations with $Fe(CO)_5$ yielded bimetallic species with direct Ln–Fe and An–Fe bonds, while reactions with $Fe(C_5H_5)_2$ led to the formation of lanthanide and actinide metallocenes $M(C_5H_5)_2^+$. The product ion distributions and the reaction efficiencies obtained with the two organometallic reagents could be accounted for by the relative stability of the accessible formal oxidation states of the metals, unravelling new patterns of gas-phase reactivity for lanthanide and actinide cations.

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