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PAPER

Gas-phase reactions of doubly charged actinide cations with alkanes and alkenes—probing the chemical activity of 5f electrons from Th to Cm

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Small alkanes (methane, ethane, propane, *n*-butane) and alkenes (ethene, propene, 1-butene) were used to probe the gas-phase reactivity of doubly charged actinide cations, An^{2+} (An = Th, Pa, U, Np, Pu, Am, Cm), by means of Fourier transform ion cyclotron resonance mass spectrometry. Different combinations of doubly and singly charged ions were observed as reaction products, comprising species formed *via* metal-ion induced eliminations of small molecules, simple adducts and ions resulting from electron, hydride or methide transfer channels. Th^{2+}, Pa^{2+}, U^{2+} and Np^{2+} preferentially yielded doubly charged products of hydrocarbon activation, while Pu^{2+}, Am^{2+} and Cm^{2+} reacted mainly through transfer channels. Cm^{2+} was also capable of forming doubly charged products with some of the hydrocarbons whereas Pu^{2+} and Am^{2+} were not, these latter two ions conversely being the only for which adduct formation was observed. The product distributions and the reaction efficiencies are discussed in relation to the electronic configurations of the metal ions, the energetics of the reactions and similar studies previously performed with doubly charged lanthanide and transition metal cations. The conditions for hydrocarbon activation to occur as related to the accessibility of electronic configurations with one or two 5f and/or 6d unpaired electrons are examined and the possible chemical activity of the 5f electrons in these early actinide ions, particularly Pa^{2+}, is considered.

1. Introduction

One of the recurring themes in actinide chemistry is the participation of the 5f electrons of the early actinides (An) in the observed processes. Gas-phase reactivity studies are an exceptional way to probe the chemical role of the valence electrons of the actinides as direct relationships between reaction products and kinetics, and the electronic structures and energetics of the reactant ions can be attained. Small hydrocarbons are ideal substrates to establish those types of correlations, as extensively demonstrated in the last decades for mainly singly charged d-block and also f-block metal cations.[1–15]

We have recently reported a combined experimental (Fourier transform ion cyclotron resonance mass spectrometry-FTICR/MS) and computational (density functional theory-DFT) study of the gas-phase reactions of Th^{2+} and U^{2+} with methane, ethane and propane.[16] Th^{2+} reacted with all three substrates, notably with CH_4 to produce $ThCH_2^{2+}$, whereas U^{2+} reacted with C_2H_6 and C_3H_8 with different product distributions than for Th^{2+}. The comparative reactivities of Th^{2+} and U^{2+} were well explained by the computational studies, which indicated that all the reactions proceeded by bond insertion. Additionally, it was found[16] that the computed energetics for insertion were consistent with an empirical model[13–15] which relates insertion efficiency to the energy needed to promote the An ion from its ground state to a divalent state with two non-5f valence electrons ($6d^2$) suitable for the formation of two bonds in the activated intermediates.

We have previously performed several FTICR/MS studies of the reactivity of An^{2+} ions, with An from Th to Cm,[17–20] comprising mostly reactions with a variety of oxidants and also an early investigation of the reactivity of Th^{2+} and U^{2+} with arenes.[21] Jackson *et al.* have studied the reactivity of U^{2+} with oxygen and water using a quadrupole ion trap.[22] A few recent theoretical studies have also used DFT to examine the reactivity of Th^{2+} or U^{2+} ions with water,[23,24] nitrous oxide[25] and methane.[26]

We have also recently studied the reactivity of doubly charged lanthanide cations, Ln^{2+} (Ln = all lanthanides except Pm), with small alkanes and alkenes.[27] The different accessibilities of d^1 electronic configurations and the range of electron affinities of the Ln^{2+} ions allowed for a detailed analysis of the reactivity trends and the conditions for occurrence of different reaction channels.

Tonkyn and Weisshaar were the first to show that doubly charged d-transition metal cations were not limited to electron

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transfer in their reactions with hydrocarbons, with doubly charged bond activation products and H^- or CH_3^- transfer channels being also observed.[28] Freiser and co-workers, using FTICR/MS, expanded this initial study and reported on the gas-phase reactivity with alkanes of several transition-metal dipositive ions with d^1 (Sc^{2+},[29] Y^{2+},[29] La^{2+} [30]), d^2 (Zr^{2+} [31]) and d^3 (Nb^{2+},[32,33] Ta^{2+} [31]) ground states and a wide range of second ionization energies (11.1–16.2 eV). Freiser and co-workers showed that the d^1 and the d^2 and d^3 metal ions led to the formation of different doubly charged products and related these observations to the occurrence of distinct reaction mechanisms.[29,34] Recently, Armentrout and co-workers re-examined in detail the reaction of Ta^{2+} with CH_4, both experimentally and by DFT.[35]

A simple one-dimensional potential energy curve-crossing model, as first described by Spears *et al.*,[36] has been used and expanded by several authors to explain the observed behavior for different systems involving doubly or, in general, multiply charged ions.[6–7,28,29,34,37–43] Armentrout and co-workers have recently commented that this model is an oversimplification as some curve crossings may not actually occur because they are in distinct reaction coordinates.[35]

The An^{2+} ions have electronic configurations that may provide evidence for the chemical activity of 5f electrons.[44] Protactinium in particular is a key actinide in terms of its electronic structure as the 5f and 6d shells are almost degenerate in energy, as very recently emphasized by Mrozik and Pitzer in high-level theoretical calculations of the energies of low-lying electronic states of Pa and Pa^{2+}.[45] Remarkably, our previous FTICR/MS examination of the reactivity of An^+ and AnO^+ ions (An = Th to Cm) with small alkanes and alkenes presented evidence for the chemical activity of the 5f electrons of Pa, in Pa^+ and more so in PaO^+, as shown by high-level theoretical calculations of the electronic structure of this monoxide cation.[46]

With this background and the goal of probing 5f electron participation in actinide chemistry, in the work reported here we performed a FTICR/MS study of the gas-phase reactions of doubly charged early actinide cations, An^{2+} (An = Th, Pa, U, Np, Pu, Am, Cm), with small alkanes (CH_4, C_2H_6, C_3H_8, n-C_4H_{10}) and alkenes (C_2H_4, C_3H_6, 1-C_4H_8). For completeness, we will include here our previously reported results of the reactions of Th^{2+} and U^{2+} with methane, ethane and propane.[16] A spin-off of the present work was recently reported as we have used the electron-transfer efficiencies of the An^{2+} reactions with hydrocarbons described herein to propose estimates for the second ionization energies of the An, IE[An^+].[12,47]

2. Experimental section

The experimental procedure has been described in detail before[16,18,27] and only a summary is presented here. We used an Extrel/Finnigan FT/MS 2001-DT 3-Tesla FTICR mass spectrometer, controlled by a Finnigan Venus Odyssey data system. The actinide samples were binary alloys of the actinide metal in a Pt matrix, with compositions (wt. percent) ranging from ~5% Pa, Np, Pu, Am and Cm, to ~20% Th and U. The hydrocarbons (>99.9% purity) were introduced into the spectrometer through a leak valve to pressures in the range of 3×10^{-8} to 2×10^{-7} Torr. The pressures were measured with a Bayard-Alpert type ionization gauge calibrated using standard reactions and were corrected for the relative sensitivities to the reagents. The doubly charged actinide cations were produced by laser desorption/ionization using a Spectra-Physics Quanta-Ray GCR-11 Nd:YAG laser operated at the fundamental wavelength (1064 nm). The reactant ions were thermalized by collisions with argon introduced into the spectrometer through pulsed valves to pressures of $\sim 10^{-5}$ Torr or through a leak valve to pressures in the range of (1–5) $\times 10^{-6}$ Torr. The reproducibility of the product distributions and reaction kinetics, as well as the linearity of the kinetics plots indicated thermalization of the reactant ions. Rate constants, k, were determined from the pseudo-first-order decay of the relative signals of the reactant ions as a function of time at constant neutral pressures. Reaction efficiencies, k/k_{COL}, were obtained using the collisional rate constants from the modified variational transition-state/classical trajectory theory of Su and Chesnavich,[48] calculated using experimental molecular polarizabilities and dipole moments of the hydrocarbons.[49] We estimate absolute errors of ±50% and relative errors of ±20% in the rate constants.

3. Results

The results obtained in this FTICR/MS study of the gas-phase reactions of An^{2+} ions (An = Th, Pa, U, Np, Pu, Am, Cm) with small alkanes (methane, ethane, propane, *n*-butane) and alkenes (ethene, propene, 1-butene) are presented in Tables 1 and 2, respectively, as product distributions, reaction rate constants (k) and reaction efficiencies (k/k_{COL}). In Table 3 we show the low-lying electronic configurations and the corresponding energies for the An^{2+} ions, as well as their electron affinities (EA[An^{2+}], that is IE[An^+]), which will be essential for the discussion below. In Table 4 we present the ionization energies of the studied hydrocarbons.

The primary products of the reactions of An^{2+} ions with alkanes (Table 1) and alkenes (Table 2) consisted of doubly charged ions resulting from bond-activation or adduct formation, and singly charged ions resulting from electron, hydride (H^-) and/or methide (CH_3^-) transfer channels, as summarized by eqn (1)–(10). For the transfer reactions identified in this work, eqn (8)–(10), it was not possible to establish whether they were nondissociative or dissociative and with this caveat we will refer simply to electron, hydride and/or methide transfer channels.

$$An^{2+} + C_mH_n \rightarrow AnC_mH_n^{2+} \quad (1)$$

$$An^{2+} + C_mH_n \rightarrow AnC_mH_{n-2}^{2+} + H_2 \quad (2)$$

$$An^{2+} + C_mH_n \rightarrow AnC_mH_{n-4}^{2+} + 2H_2 \quad (3)$$

$$An^{2+} + C_mH_n \rightarrow AnC_mH_{n-6}^{2+} + 3H_2 \quad (4)$$

$$An^{2+} + C_mH_n \rightarrow AnC_{m-1}H_{n-4}^{2+} + CH_4 \quad (5)$$

$$An^{2+} + C_mH_n \rightarrow AnC_{m-1}H_{n-6}^{2+} + H_2 + CH_4 \quad (6)$$

$$An^{2+} + C_mH_n \rightarrow AnC_{m-2}H_{n-6}^{2+} + C_2H_6 \quad (7)$$

$$An^{2+} + C_mH_n \rightarrow An^+ + C_mH_n^+ \quad (8)$$

Table 1 Product distributions, rate constants (k), and efficiencies (k/k_{COL}) of the reactions of An^{2+} ions with alkanes[a]

	C_2H_6			C_3H_8			C_4H_{10}		
An^{2+}	Products	k	k/k_{COL}	Products	k	k/k_{COL}	Products	k	k/k_{COL}
Th^{2+}	$ThC_2H_2^{2+}$ (100)	0.28	0.15	$ThC_2H_2^{2+}$ (35) $ThC_3H_4^{2+}$ (55) $ThCH_3^+$ (10)	0.26	0.13	$ThC_3H_4^{2+}$ (20) $ThC_4H_4^{2+}$ (25) $ThC_4H_6^{2+}$ (45) $ThCH_3^+$ (10)	0.32	0.16
Pa^{2+}	$PaC_2H_2^{2+}$ (20) $PaC_2H_4^{2+}$ (80)	0.34	0.18	$PaC_2H_2^{2+}$ (15) $PaC_3H_4^{2+}$ (80) $PaCH_3^+$ (5)	0.31	0.16	$PaC_3H_4^{2+}$ (45) $PaC_4H_4^{2+}$ (25) $PaC_4H_6^{2+}$ (35) $PaCH_3^+$ (10)	0.32	0.16
U^{2+}	$UC_2H_4^{2+}$ (100)	0.34	0.18	$UC_2H_4^{2+}$ (15) $UC_3H_6^{2+}$ (40) UH^+ (10) UCH_3^+ (35)	0.42	0.22	$UC_2H_4^{2+}$ (20) $UC_4H_6^{2+}$ (60) UCH_3^+ (20)	0.40	0.20
Np^{2+}	—	—	—	$NpC_2H_4^{2+}$ (55) $NpC_3H_6^{2+}$ (30) NpH^+ (5) $NpCH_3^+$ (10)	0.32	0.17	$NpC_2H_4^{2+}$ (50) $NpC_3H_6^{2+}$ (20) $NpC_4H_6^{2+}$ (10) $NpC_4H_8^{2+}$ (10) $NpCH_3^+$ (10)	0.39	0.20
Pu^{2+}	—	—	—	$PuC_3H_8^{2+}$ (25) PuH^+ (70) $PuCH_3^+$ (5)	0.049	0.033	$PuC_4H_{10}^{2+}$ (20) PuH^+ (60) $PuCH_3^+$ (20)	0.43	0.22
Am^{2+}	—	—	—	$AmC_3H_8^{2+}$ (5) AmH^+ (90) $AmCH_3^+$ (5)	0.17	0.089	$AmC_4H_{10}^{2+}$ (5) AmH^+ (80) $AmCH_3^+$ (15)	0.41	0.21
Cm^{2+}	—	—	—	$CmC_2H_4^{2+}$ (5) CmH^+ (10) $CmCH_3^+$ (85)	0.32	0.16	$CmC_2H_4^{2+}$ (20) Cm^+ (10) CmH^+ (10) $CmCH_3^+$ (60)	0.35	0.18

[a] Product distributions in %; k in units of 10^{-9} cm^3 $molecule^{-1}$ s^{-1}. A dash means that no reaction was observed ($k < 5 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}; $k/k_{COL} < 0.0005$). Only Th^{2+} reacted with CH_4: products-$ThCH_2^{2+}$ (100%); $k = 0.22 \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1}; $k/k_{COL} = 0.11$. Results for the reactions of Th^{2+} and U^{2+} with CH_4, C_2H_6 and C_3H_8 were previously reported in ref. 16.

Table 2 Product distributions, rate constants (k), and efficiencies (k/k_{COL}) of the reactions of An^{2+} ions with alkenes[a]

	C_2H_4			C_3H_6			C_4H_8		
An^{2+}	Products	k	k/k_{COL}	Products	k	k/k_{COL}	Products	k	k/k_{COL}
Th^{2+}	$ThC_2H_2^{2+}$ (100)	0.43	0.22	$ThC_2H_2^{2+}$ (15) $ThC_3H_2^{2+}$ (45) $ThC_3H_4^{2+}$ (5) Th^+ (35)	0.43	0.21	$ThC_2H_2^{2+}$ (20) $ThC_4H_4^{2+}$ (30) Th^+ (50)	0.42	0.20
Pa^{2+}	$PaC_2H_2^{2+}$ (100)	0.43	0.22	$PaC_2H_2^{2+}$ (15) $PaC_3H_2^{2+}$ (15) $PaC_3H_4^{2+}$ (40) Pa^+ (30)	0.42	0.20	$PaC_3H_4^{2+}$ (10) $PaC_4H_4^{2+}$ (30) Pa^+ (60)	0.37	0.18
U^{2+}	$UC_2H_2^{2+}$ (100)	0.26	0.13	$UC_2H_2^{2+}$ (45) $UC_3H_4^{2+}$ (25) U^+ (30)	0.56	0.27	$UC_3H_4^{2+}$ (10) $UC_4H_4^{2+}$ (10) $UC_4H_6^{2+}$ (15) U^+ (50) UCH_3^+ (15)	0.53	0.26
Np^{2+}	—	—	—	$NpC_2H_2^{2+}$ (65) Np^+ (35)	0.35	0.17	$NpC_4H_6^{2+}$ (35) Np^+ (40) NpH^+ (5) $NpCH_3^+$ (20)	0.31	0.15
Pu^{2+}	—	—	—	Pu^+ (100)	0.35	0.17	Pu^+ (70) PuH^+ (25) $PuCH_3^+$ (5)	0.41	0.20
Am^{2+}	—	—	—	Am^+ (100)	0.48	0.23	Am^+ (90) AmH^+ (5) $AmCH_3^+$ (5)	0.58	0.28
Cm^{2+}	Cm^+ (100)	0.044	0.023	Cm^+ (100)	0.60	0.28	Cm^+ (100)	0.86	0.42

[a] Product distributions in %; k in units of 10^{-9} cm^3 $molecule^{-1}$ s^{-1}. A dash means that no reaction was observed ($k < 5 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}; $k/k_{COL} < 0.0005$).

Table 3 Low-lying electronic configurations, corresponding energies and electron affinities of the An^{2+} ions

An^{2+}	Electronic configuration[a]	Energy (eV)[b]	EA[An^{2+}] (eV)[c]
Th^{2+}	$5f^16d^1$	0	11.65 ± 0.3
	$6d^2$	0.008	
	$5f^17s^1$	0.313	
	$6d^17s^1$	0.684	
	$5f^2$	1.878	
Pa^{2+}	$5f^26d^1$	0	11.6 ± 0.3
	$5f^27s^1$	0.5 ± 0.1	
	$5f^3$	0.6 ± 0.1	
	$5f^16d^2$	1.2 ± 0.7	
	$5f^16d^17s^1$	2.1 ± 0.5	
U^{2+}	$5f^4$	0	11.7 ± 0.3
	$5f^36d^1$	0.026	
	$5f^37s^1$	0.464	
	$5f^26d^2$	2.407	
	$5f^26d^17s^1$	3.353	
Np^{2+}	$5f^5$	0	11.55 ± 0.3
	$5f^46d^1$	0.7 ± 0.4	
	$5f^47s^1$	1.2 ± 0.5	
	$5f^36d^2$	4.2 ± 0.7	
	$5f^36d^17s^1$	5.1 ± 0.6	
Pu^{2+}	$5f^6$	0	11.8 ± 0.3
	$5f^56d^1$	1.6 ± 0.4	
	$5f^57s^1$	2.1 ± 0.5	
	$5f^46d^2$	6.2 ± 0.7	
	$5f^46d^17s^1$	7.1 ± 0.6	
Am^{2+}	$5f^7$	0	12.2 ± 0.3
	$5f^66d^1$	3.0 ± 0.4	
	$5f^67s^1$	3.3 ± 0.5	
	$5f^56d^2$	8.7 ± 0.6	
	$5f^56d^17s^1$	9.6 ± 0.6	
Cm^{2+}	$5f^8$	0	12.4 ± 0.3
	$5f^76d^1$	0.6 ± 0.4	
	$5f^77s^1$	0.6 ± 0.6	
	$5f^66d^2$	7.8 ± 0.9	
	$5f^66d^17s^1$	8.3 ± 0.9	

[a] Ref. 44. [b] Ref. 44; the energies correspond to the lowest levels of each configuration [c] Ref. 47; EA[An^{2+}] = IE[An$^+$]

$$An^{2+} + C_mH_n \rightarrow AnH^+ + C_mH_{n-1}^+ \qquad (9)$$

$$An^{2+} + C_mH_n \rightarrow AnCH_3^+ + C_{m-1}H_{n-3}^+ \qquad (10)$$

In the reactions of An^{2+} ions with alkanes (Table 1), we verified that only Th^{2+} was reactive with methane, inducing dehydrogenation, as indicated by eqn (2), to form ThCH$_2^{2+}$ as single product. With ethane, Th^{2+}, Pa^{2+}, and U^{2+} were reactive *via* single and/or double dehydrogenations, corresponding to eqn (2) and (3), respectively, and the remaining An^{2+} ions were unreactive. With propane and *n*-butane, all the An^{2+} ions were reactive by one or more of the channels represented by eqn (1)–(10).

With regard to the reactions of An^{2+} ions with alkenes (Table 2), Th^{2+}, Pa^{2+} and U^{2+} reacted with ethene by dehydrogenation, as in eqn (2), Cm^{2+} reacted by electron transfer, as in eqn (8), and the three remaining An^{2+} ions were unreactive. With propene and 1-butene, all the An^{2+} ions were reactive by one or more of the channels denoted by eqn (2), (3), (5), (7), (8), (9) and (10); notably, Cm^{2+} reacted only by electron transfer (eqn (8)).

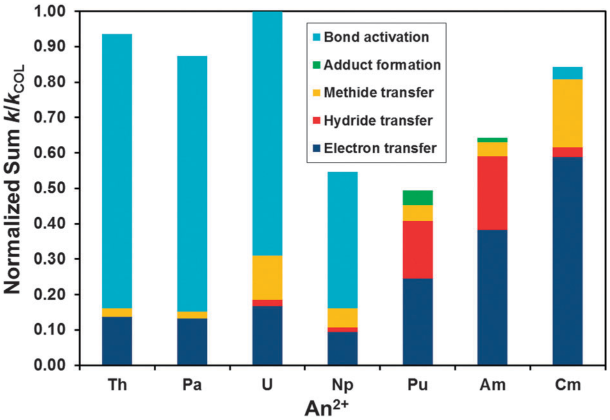

Fig. 1 Chart showing the normalized sum of the fractions of the k/k_{COL} values corresponding to the five different types of reaction channels, for all the hydrocarbons; the normalization was relative to U^{2+} which had the greatest sum of reaction efficiencies.

The reactions proceeded with moderate efficiencies k/k_{COL} averaging 0.19 ± 0.07, with the few exceptions of Pu^{2+} and Am^{2+} with propane and of Cm^{2+} with ethene which were below 0.01, and of Cm^{2+} with 1-butene which was clearly higher at 0.42.

In Fig. 1 we present a chart of the normalized sum of the fractions of the k/k_{COL} values corresponding to the five different types of reaction channels, electron, hydride and methide transfers, adduct formation and bond activation, for all the hydrocarbons.

Fig. 1 shows the prevalence of each reaction channel as well as the overall relative reactivity for the different An^{2+} ions. It is immediately apparent that there is a dominance of the bond activation channels (eqn (2)–(7)) for the early An^{2+} ions from Th^{2+} to Np^{2+}, while for the An^{2+} ions from Pu^{2+} to Cm^{2+} the transfer channels (eqn (8)–(10)), particularly electron transfer, prevail. Also apparent is the absence of bond activation for Pu^{2+} and Am^{2+} and the minor significance of this reaction channel for Cm^{2+}. It is also evident from Fig. 1 that adduct formation (eqn (1)) is a minor channel which only occurs in the cases of Pu^{2+} and Am^{2+}. Intriguingly, it can also be seen that hydride transfer (eqn (9)) is absent for Th^{2+} and Pa^{2+} but rather important for Pu^{2+} and Am^{2+}, while methide transfer (eqn (10)) is insignificant for Th^{2+} and Pa^{2+} but is significant in the cases of U^{2+} and Cm^{2+}.

4. Discussion

In our recent study of the reactions of Ln^{2+} with small alkanes and alkenes,[27] we have used the different accessibilities of

Table 4 Ionization energies of the studied hydrocarbons[a]

RH	CH$_4$	C$_2$H$_6$	C$_3$H$_8$	n-C$_4$H$_{10}$	C$_2$H$_4$	C$_3$H$_6$	1-C$_4$H$_8$
IE (eV)	12.51 ± 0.01	11.52 ± 0.01	10.95 ± 0.05	10.53 ± 0.10	10.507 ± 0.004	9.73 ± 0.02	9.58 ± 0.02

[a] From ref. 50.

d^1 electronic configurations and the range of electron affinities of the Ln^{2+} cations to analyse in detail the conditions for the occurrence of electron, hydride, and methide transfers, adduct formation and bond activation, including estimates of the respective thermodynamic thresholds. In the present study, due to the more restricted set of metal ions and the uncertainties in the existing values of IE[An^+], as previously discussed,[47] an analysis of the transfer channels similar to that made in the case of the Ln^{2+} would be ineffective. We have conversely opted to use the present set of observations for the electron transfers along the An series to produce new estimates for the IE[An^+] (see Table 3),[47] based on the aforementioned observations with the Ln and also a few studies with other metals.

Therefore, we will only make a few general comments here related to the transfer channels. In spite of the significant uncertainties in the IE[An^+] (see Table 3), it seems evident that IE[Cm^+] > IE[Am^+] > IE[Pu^+] > IE[Np^+] ~ IE[U^+] ~ IE[Pa^+] ~ IE[Th^+]. The prevalence of electron transfer, as shown by Fig. 1, in the order Cm^{2+} > Am^{2+} > Pu^{2+} > other An^{2+} is in clear agreement with the IE[An^+] ordering indicated above. Also, from the detailed results in Tables 1 and 2 it is evident that the importance of the electron transfer channel also follows the ionization energies of the hydrocarbons (see Table 4), with the lower ionization energies of the alkenes as compared to those of the alkanes leading to a larger overall relevance of electron transfer for the alkenes.

For the other transfer channels, a proper analysis should also take into account the thermodynamics involved but there is a dearth of data for the dissociation energies of both An^+-H and An^+-CH_3 bonds, with the single available value being that for U^+-H from an early ion beam study by Armentrout *et al.*[51] Nonetheless, we have previously observed for the case of the Ln that the IE[M^+] is a strong determinant of hydride and methide transfers,[47] and Fig. 1 is clear in showing that the aggregate weight of these reaction channels is larger for the An^{2+} from Pu^{2+} to Cm^{2+}.

We will now focus on the adduct formation and bond activation channels which, as more directly related with the electronic structures of the An^{2+} ions, will have a more direct relevance to the stated main purpose of the present study, the probing of the participation of 5f electrons in the observed reactivity of An^{2+} ions with hydrocarbons.

The first definite experimental evidence in this respect is that the two An^{2+} that do not induce bond activation are precisely the only ones for which adduct formation is observed, Pu^{2+} and Am^{2+}. According to the energetics presented in Table 3, these two actinide ions have $5f^n$ ground states and the highest promotion energies to states with one or two non-f electrons.

Hydrocarbon activation by singly charged actinide cations seems to proceed by bond insertion and the reaction efficiencies inversely correlate with the promotion energies from the ground states to states with two non-f electrons suitable for the formation of two bonds in activated intermediates.[12–15] Our previous systematic FTICR/MS study of the reactivity of the An^+ with An from Th to Cm and the same hydrocarbons of the present study showed that Pu^{2+} and Am^{2+} were the least reactive of the An^+, with Am^+ entirely unreactive and Pu^+ only reactive with 1-C_4H_8.[46] In the case of the An^{2+}, our recent combined experimental and computational study of the reactions of Th^{2+} and U^{2+} with methane, ethane and propane indicated that all the reactions proceeded by bond insertion and that the reaction efficiency relates to the promotion energy from the ground state to a divalent state with two non-5f valence electrons ($6d^2$).[16]

Freiser and co-workers proposed that, in the reactions of doubly charged transition metal ions with alkanes, the different doubly charged products of d^2 and d^3, on one hand, and d^1 metal ions, on the other hand, were related to the occurrence of bond insertion or a concerted electrostatic mechanism, respectively.[29,34] In the case of d^1 metal ions, these authors specify that the more likely mechanism would involve the formation of a multicentered $M^{2+}\bullet C_mH_n$ intermediate which directly eliminates dihydrogen or an alkane; alternatively, it could involve an initial hydrogen abstraction to form a H-$M^{2+}\bullet C_mH_{n-1}$ intermediate, which then eliminates dihydrogen or an alkane *via* a multicentered transition state.[29,34]

Our recent examination of the reactivity of Ln^{2+} with alkanes and alkenes[27] showed that only ions with accessible $5d^1$ configurations, La^{2+}, Ce^{2+}, Gd^{2+} and Tb^{2+},[52] were capable of activating the hydrocarbons to form doubly charged organometallic ions (Lu^{2+} also with an accessible $5d^1$ state but a rather high electron affinity reacted mainly by electron transfer). Our Ln^{2+} study also indicated that there was a close match of the doubly charged products obtained with those observed by Freiser and co-workers for the d^1 metal ion Y^{2+}.[29]

Comparing the doubly charged bond-activation products of the An^{2+} reactions with alkanes (Table 1) with those reported by Freiser and co-workers[29] for d-transition metal dications with d^n ground states,[53] specifically Y^{2+} (d^1), Zr^{2+} (d^2) and Nb^{2+} (d^3), we observe, in the first place, that like the d^2 and d^3 metal dications Th^{2+} is capable of activating methane to form the same type of product, MCH_2^{2+}. With ethane, U^{2+} produced only $MC_2H_4^{2+}$, Pa^{2+} yielded both $MC_2H_4^{2+}$ and $MC_2H_2^{2+}$, and Th^{2+} led to $MC_2H_2^{2+}$; for assessment, Y^{2+} yielded $MC_2H_4^{2+}$, Zr^{2+} a combination of MCH_2^{2+}, $MC_2H_2^{2+}$ and $MC_2H_4^{2+}$, and Nb^{2+} only $MC_2H_2^{2+}$. With propane, Th^{2+} and Pa^{2+} produced, like Zr^{2+}, $MC_2H_2^{2+}$ and $MC_3H_4^{2+}$ ions, while U^{2+} and Np^{2+} yielded $MC_2H_4^{2+}$ and $MC_3H_6^{2+}$ ions like Y^{2+}, and Cm^{2+} formed only $MC_2H_4^{2+}$. Finally, with *n*-butane, Th^{2+} and Pa^{2+} formed once more the same type of products as Zr^{2+}, $MC_3H_4^{2+}$, $MC_4H_4^{2+}$ and $MC_4H_6^{2+}$, Np^{2+} reacted similarly to Y^{2+}, yielding $MC_2H_4^{2+}$, $MC_3H_6^{2+}$, $MC_4H_6^{2+}$ and $MC_4H_8^{2+}$, Cm^{2+} produced only $MC_2H_4^{2+}$, and U^{2+} formed $MC_2H_4^{2+}$ and $MC_4H_6^{2+}$.

With the alkenes, the bond-activation reactivity of the An^{2+} cations (Table 2) can only be compared with that of the Ln^{2+} ions[27] which merely bear ground or accessible d^1 states[52] (and prohibitively large promotion energies to configurations with two non-4f valence electrons[54]). On the whole, the An^{2+} ions were clearly more reactive than the Ln^{2+}, with Th^{2+}, Pa^{2+} and U^{2+} dehydrogenating ethylene to produce $AnC_2H_2^{2+}$, a reaction not observed for any of the Ln^{2+}. With propene, the An^{2+} induced CH_4 loss for An from Th to Np, H_2 loss from Th to U and double H_2 loss for Th^{2+} and Pa^{2+}; the only Ln^{2+} capable of bond activation were La^{2+} and Gd^{2+}, precisely the only ones having d^1 ground states, which formed products deriving from CH_4 and H_2 losses, and interestingly also a product of H loss in the case of La^{2+}. With 1-butene, the reactive ions were again Th^{2+}, Pa^{2+}, U^{2+} and Np^{2+}, inducing dehydrogenation (Np^{2+} and U^{2+}), double dehydrogenation (Th^{2+}, Pa^{2+} and U^{2+}), demethanation (Pa^{2+} and U^{2+}) or ethane loss (Th^{2+}); the reactive Ln^{2+} were La^{2+}, Ce^{2+} and Tb^{2+}, that formed products of dehydrogenation, as well as products of CH_3 loss for La^{2+} and Ce^{2+}, and H loss for La^{2+}.

The above comparisons of the doubly charged products of hydrocarbon activation, particularly in the case of the alkanes, generally indicate that Th^{2+} and Pa^{2+} reacted similarly to transition metal ions with d^2 or d^3 ground states, while Np^{2+} and Cm^{2+} reacted similarly to Ln^{2+} ions with only one accessible non-4f valence electron and Y^{2+} ions with a d^1 ground state and no low-lying excited states with more than one valence electron; U^{2+}, especially if the reactions with the alkenes are considered, was intermediate between d^1 and d^2 or d^3 in comparison with the other metal dications. These comparisons could be an indication that Th^{2+} and Pa^{2+} react by bond insertion, Np^{2+} and Cm^{2+} follow the electrostatic mechanism proposed by Freiser and co-workers[29,34] and U^{2+} is ambiguous. However, it is questionable that product distributions alone can indicate what type of mechanism might be occurring, especially as the types of products, corresponding mostly to small molecule eliminations, are essentially similar, with the key differences being the occurrence of multiple eliminations for the more reactive metal ions. As stated previously, in our recent experimental and computational examination of the reactions of Th^{2+} and U^{2+} with methane, ethane and propane,[16] the comparative reactivities were well explained by the computational studies, which indicated that the reactions proceeded by bond insertion and that the promotion energies from the ground states to $6d^2$ states were a determinant of the observed reactivity.

We turn now, therefore, to an analysis of the accessible electronic configurations of the An^{2+} ions as presented in Table 3.[44] It should be noted, however, that only in the cases of Th^{2+} and U^{2+} do the configurations and corresponding energies bear low uncertainties, and the following analysis will consequently present inherent limitations.

The An^{2+} from U^{2+} to Cm^{2+} all have $5f^n$ ground states, with $5f^{n-1}6d^1$ states at energies which increase from 0.026 eV for U^{2+} up to ~3 eV for Am^{2+}, then decreasing again to ~0.6 eV for Cm^{2+}. The $5f^{n-2}6d^2$ states for the An^{2+} from U^{2+} to Cm^{2+} start at 2.4 eV for U^{2+} and appear only at rather high energies, ~4–9 eV, for Np^{2+} to Cm^{2+}. In contrast, Th^{2+} has a $5f^16d^1$ ground state and a $6d^2$ state at a very low energy (0.01 eV). According to the estimates in Table 3,[44] Pa^{2+} has a $5f^26d^1$ ground state, $5f^27s^1$ and $5f^3$ states at moderate energies (~0.5 eV) and a $5f^16d^2$ state at higher energy (~1.2 eV). Mrozik and Pitzer have recently performed high-level theoretical calculations of the relative energies of the $5f^26d^1$ and $5f^16d^2$ states of Pa^{2+},[45] which confirmed the $5f^26d^1$ ground state and indicated an excitation energy of 1.65 eV to the lowest level of the $5f^16d^2$ configuration.

In the case of Th^{2+}, the low-energy $6d^2$ state presumably accounts for the observed reactivity as has been detailed in our previous experimental/computational study.[16] Nonetheless, a reasonable doubt can be raised concerning the relevance of the $5f^16d^1$ ground state, the participation of which would imply chemical activity of the 5f electron in a bond insertion mechanism.

In the case of Pa^{2+}, it is conceivable that the ground state $5f^26d^1$ and/or the $5f^27s^1$ and $5f^3$ states at lower energies could be determining the observed reactivity, but the uncertainties in the energies of the excited configurations of Pa^{2+} preclude an interpretation that 5f electrons are participating in bond activation. Moreover, the $5f^16d^2$ state, at ~1.2 eV as indicated by Table 3 or at 1.65 eV as computed by Mrozik and Pitzer,[45] may be at an accessible energy for a doubly charged metal cation, and can account for the observed reactivity and the similarities with Th^{2+} and d^2 or d^3 transition metal dications.

In the case of U^{2+}, and as previously demonstrated,[16] the $5f^26d^2$ state at 2.41 eV (see Table 3) may still be accessible for a doubly charged metal cation to react by bond insertion and it is doubtful that the $5f^4$ ground state of U^{2+} can be responsible for the observed reactivity. This significant promotion energy to the $5f^26d^2$ configuration could explain the lower overall reactivity of U^{2+} when compared with Th^{2+} and Pa^{2+}. On the other hand, due to the rather low-energy $5f^36d^1$ configuration at 0.026 eV and the similarities in the product distributions of U^{2+} and the d^1 metal dications described above, it is impossible to exclude a non-insertion mechanism.

In the case of Np^{2+}, the occurrence of the $5f^46d^1$ state at a fairly low energy (~0.7 eV) and of the $5f^36d^2$ state at a rather high energy (~4.2 eV) seems to be in agreement with an overall reactivity of this An^{2+} ion bearing strong similarities with the d^1 metal dications in terms of product distributions. The lower overall bond-activation reactivity of Np^{2+} when compared to Th^{2+}, Pa^{2+} and U^{2+}, as shown in Fig. 1, is additional evidence for the ocurrence of a non-insertion reaction mechanism for the case of Np^{2+}. On the other hand, as both Np^{2+} and U^{2+} ions have accessible $6d^1$ configurations, the lower reactivity of Np^{2+} relative to U^{2+} may be an indication that U^{2+} reacts by a bond-insertion mechanism.

In the cases of Pu^{2+} and Am^{2+}, which did not yield any doubly charged bond-activation products, the promotion energies from their $5f^n$ ground states to $5f^{n-2}6d^2$ states are excessively high (~6.2–8.7 eV) while those to the $5f^{n-1}6d^1$ states are much lower (~1.6 eV for Pu^{2+} and ~3.0 eV for Am^{2+}) such that these d^1 configuration may be significant in the examined reactions. It should be remarked that in a previous study of the Ln^{2+},[27] we observed that for bond activation to occur the Ln^{2+} ions needed to have an accessible d^1 configuration with an energy threshold lying between ~1.1 eV for reactive Tb^{2+} and ~1.6 eV for unreactive Pr^{2+}.

In the case of Cm^{2+}, the promotion energy from the $5f^8$ ground state to the $5f^66d^2$ state is, like for Pu^{2+} and Am^{2+}, prohibitively high (~7.8 eV), but that to the $5f^76d^1$ is much lower (~0.6 eV), similar to that of Np^{2+}, in agreement with the observation of bond activation by Cm^{2+} for some hydrocarbons. The lower reactivity of Cm^{2+} as compared to Np^{2+} is well accounted for by the higher electron affinity of Cm^{2+} (see Table 3) which favours the occurrence of transfer channels, particularly electron transfer.

From the above considerations, it may be concluded that the $5f^n$ ground states of the An^{2+} from Np^{2+} to Cm^{2+} do not play a role in the observed reactivity. The role of the 5f states in the reactivities of the earlier An^{2+} is less certain.

We will now briefly address adduct formation. Only for the Pu^{2+} and Am^{2+} ions was adduct formation observed, specifically in their reactions with propane and *n*-butane (see Table 1). In our previous study of the Ln^{2+} ions,[27] adduct formation was also observed, apparently only when the alternative transfer and bond-activation channels were both not favourable. This also seems to be the case for the An^{2+} as it were precisely the ions with the lower ability for bond activation which exhibited adduct formation. The non-observation of adducts for the cases of propene and 1-butene, which have high polarizabilities like propane and *n*-butane,[49] is easily explained by their lower ionization energies (see Table 4) which resulted in a prevalence of transfer channels.

Freiser and co-workers in their studies of the reactivity of M^{2+} ions with alkanes did not report any adducts as primary products.[29–34] However, several displacement reactions of alkenes by alkanes in $MC_nH_{2n}{}^{2+}$ species were described, which were explained by an electrostatic type of bonding between the M^{2+} ions and the neutral hydrocarbons.[29,55] Interestingly, in our experiments with propane and *n*-butane, presumed $An(alkene)^{2+}$ primary products in the cases of Th^{2+}, Pa^{2+} and U^{2+} did not further react with the alkanes, while for Np^{2+} and Cm^{2+} displacement reactions did occur, as for example, $NpC_2H_4{}^{2+} + C_3H_8 \rightarrow NpC_3H_8{}^{2+} + C_2H_4$ ($k = 0.42 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, $k/k_{COL} = 0.22$). These observations may be a manifestation of stronger bonding (softer or more covalent) in the cases of Th^{2+}, Pa^{2+} and U^{2+} as compared to the more lanthanide-like (harder or more ionic) transuranium An^{2+}.

5. Conclusions

In an effort to enhance fundamental understanding of actinide chemistry and particularly to probe the chemical activity of 5f electrons in the early actinides, we examined the reactions of doubly charged actinide ions, An^{2+} (An = Th, Pa, U, Np, Pu, Am, Cm), with small alkanes and alkenes. The reaction products consisted of doubly charged organometallic ions which originated from metal-ion induced eliminations of small molecules from the hydrocarbons or from adduct formation, and singly charged ions that resulted from electron, hydride, and/or methide transfers from the hydrocarbons to the metal ions.

By comparing the doubly charged bond-activation products of the An^{2+} reactions with those previously described for the reactions of Ln^{2+} cations and d-transition metal dications, and by a detailed analysis of the available values, several only estimates, for the electronic structures and energetics of the An^{2+} ions, evidence was obtained for the high reactivity of Th^{2+}, Pa^{2+} and U^{2+} being associated with a bond-insertion mechanism. For the transuranium An^{2+} ions, the lower reactivities of Np^{2+} and Cm^{2+}, as well as the non-observation of doubly charged bond-activation products for Pu^{2+} and Am^{2+}, were attributed to the occurrence of a previously proposed radical-like electrostatic mechanism associated with metal dications having only one chemically active valence electron. The reactivities of the transuranium An^{2+} ions indicated that their 5f electrons are inactive in bond activation. For Th^{2+}, Pa^{2+} and U^{2+}, $6d^2$ states presumably account for the observed reactivities, but 5f-electron involvement in bond activation remains conceivable for Th^{2+} and more so for Pa^{2+}, within the limitations of the available electronic structure data.

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