Reactions of actinide ions with pentamethylcyclopentadiene: atypical hydrocarbon activation

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Abstract

Gas-phase reactions of 1,2,3,4,5-pentamethylcyclopentadiene (HCp*) with three actinide ions, Np^+, Pu^+, and Am^+, were studied by laser ablation mass spectrometry. The primary goal was to determine if an unusual, non-insertion mode of C–H activation reported for lanthanide ions, Ln^+, with this substrate obtains for the homologous actinide ions; the Cp* ligand is central in organoactinide chemistry and the interaction of the quasivalence $5f$ electrons with HCp* is of special interest. It was found that Np^+ and Pu^+ behave similarly to the "reactive" Ln^+, and that Am^+ is similar to the "inert" group of Ln^+. For both Ln^+ and An^+, reactivity appears to reflect the energy necessary to excite the ground state metal ion to a configuration with two non-f valence electrons. Evidently Am^+, which exhibits a large excitation energy, comparable to those of the inert Ln^+, induces C–H activation and single-H_2-elimination from HCp* by a non-insertion process not seen with other alkenes; this lanthanide-like behavior suggests no distinctive role of the $5f$ electrons in the Am^+–HCp* interaction. Activation by Np^+ and Pu^+ of the methyl groups of a tetramethylfulvene intermediate results in double- and triple-dehydrogenation which evidently proceeds by a conventional insertion process involving a C–An^+–H complex, in accord with the relatively small Np^+ and Pu^+ excitation energies. Results for reactions of AnO^+ with HCp* revealed an enhanced dehydrogenation activity of NpO^+ compared with LnO^+, which may be a result of the greater accessibility of high oxidation states at the Np metal center. (Int J Mass Spectrom 202 (2000) 19–29) © 2000 Elsevier Science B.V.

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1. Introduction

Reports of reactions of 1,2,3,4,5-pentamethylcyclopentadiene, "HCp*" where Cp* represents the pentamethylcyclopentadienyl radical ligand, with naked lanthanide cations, Ln^+, have suggested reaction mechanisms different from those seen with reactions of Ln^+ with other alkenes [1,2]. In particular, dehydrogenation as a significant reaction channel for Eu^+ and Yb^+, as for alkaline earth monopositive ions, was indicative of a mechanism which does not require insertion of the metal ion into a C–H bond (i.e. C–Ln^+–H) to achieve C–H activation and subsequent dehydrogenation. Because the gas-phase organometallic chemistry of actinide ions, An^+, is generally reminiscent of that of Ln^+ with regard to the apparent mechanistic and resulting dependence of C–H and C–C activation efficiencies (i.e. dehydrogenation and cracking) on metal ion electronic structures and energetics [3–16], it was of interest to determine if enhanced reactivity of typically inert An^+ is also

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achieved with HCp* as a reagent. Most reactions of naked Ln^+ and An^+ with alkenes involve C–H or C–C bond activation by a mechanism which requires two non-f valence electrons capable of forming two σ-type bonds in a C–M^+–H or C–M^+–C intermediate. Accordingly, the reactivities of these f-element ions correlate closely with the promotion energies, PE[M^+], needed to excite from the ground state to a prepared "divalent" state. For example, PE[Pu^+] = 104 kJ mol^{-1} is the energy required for the electronic excitation: ground $Pu^+/\{[Rn]5f^67s^1\}$ → $Pu^{+*}/\{[Rn]5f^56d^17s^1\}$ [17]. The PE[Ln^+] range from 0 for Gd^+ ([Xe]$4f^75d^16s^1$ ground state) to 362 kJ mol^{-1} for Eu^+ ($4f^76s^1$ → $4f^65d^16s^1$) [18]. The PE[An^+] for the three actinides studied here cover a broad range: 0 for Np^+ ([Rn]$5f^46d^17s^1$ ground state); 104 kJ mol^{-1} for Pu^+ ($4f^66s^1$ → $4f^56d^17s^1$); and 245 kJ mol^{-1} for Am^+ ($4f^77s^1$ → $4f^66d^17s^1$) [17]. The large promotion energies for Eu^+ and Am^+ are generally attributed to the high stability of the high-spin half-filled $4f^7$ and $5f^7$ subshells.

A technique, LAPRD, based on laser ablation of ions, followed by their prompt reaction with a gas and detection of product ions by time of flight mass spectrometry has been employed to investigate the gas-phase chemistry of transuranium actinide ions. A primary rationale for applying LAPRD to these particular elements is that only beyond U in the actinide series are substantial PE[An^+] exhibited. Accordingly, studies of Th^+ and U^+ (as well as Np^+) generally cannot effectively address the role of electronic excitation in determining actinide ion reaction pathways, mechanisms and efficiencies, and gas-phase studies of heavier and more radioactive actinide ions are needed to accomplish these goals. Fourier transform ion cyclotron resonance mass (FTICR) spectrometry, had been employed in previous studies of {Ln^+ + HCp*} reactions [1,2], and representative Ln^+ were studied in the present LAPRD investigation to establish concurrence between results obtained by the two techniques specifically for HCp* as the reactant molecule. Subsequently, An^+ with widely varying degrees of reactivities towards other alkenes (An = Np, Pu, Am [14,15]) were investigated with HCp* for comparison. Ancillary results for reactions

of actinide monoxide ions, AnO^+, with HCp* are also presented.

2. Experimental

The LAPRD experimental technique and its application to actinides have been described in detail elsewhere [7,13–16] and the same procedures were employed in the present study. Essentially, monopositive metal ions, M^+ (and some MO^+), were ablated from a solid target by a pulsed excimer laser (λ = 308 nm), and propagated through a ~3 cm long reaction zone during a period of ~35 μs. The reactant pressure was indeterminate but roughly invariant between experiments. The reactant pressure measured ~1 m from the ablation target and adjacent to the turbomolecular pump was ~5 × 10^{-6} Torr. Because the gas inlet was in immediate proximity to the reaction zone, it is certain that the pressure encountered by ablated ions was minimally an order of magnitude greater than 5 × 10^{-6} Torr, and probably at least 10^{-4} Torr. The experimental configuration did not permit an accurate estimate of the pressure. Compared with FTICR experiments [1,2], the LAPRD reaction time was orders of magnitude shorter (~1 s for FTICR versus ~10^{-5} s for LAPRD) whereas the reactant pressure was orders of magnitude greater (~10^{-7} Torr for FTICR versus ≳ 10^{-4} Torr for LAPRD). Following metal ion–molecule reactions, positively charged product ions were injected into the flight tube of a reflectron time-of-flight mass spectrometer (RTOF-MS). Because nascent laser-ablated ions were employed, the possibility for an appreciable contribution to the observed reaction patterns from excited state ions, M^{+*}, should be considered. It was somewhat surprising that previous studies with Ln^+ [7] and An^+ [13–16] clearly demonstrated that gas-phase f-element ion chemistry studied under LAPRD conditions reflects ground state ion electronic structures and energetics; evidently, few excited state ions survive the expansion of the ablation plume under the conditions employed here.

The HCp* was a commercial product with a specified purity of 95%. Following removal of vola-

tile impurities by at least two freeze–evacuate–thaw cycles, HCp* vapor was admitted into the reaction zone through a constant leak valve. A 100 eV electron impact mass spectrum was obtained for the commercial HCp* ($C_{10}H_{16}$) reagent, employing an electron gun incorporated into the RTOF-MS ion source. The primary peaks—at 121, 136, and 105 u—coincide with the main peaks reported for HCp* in the literature [19]. An additional peak at 123 u (~20% intensity relative to the dominant peak at 121 u), not reported for HCp*, is presumably indicative of an impurity. This 123 u peak, 2 u above the dominant HCp* peak, may be reasonably assigned to CH_3 loss from singly hydrogenated HCp*, pentamethylcyclopentene, $C_{10}H_{18}$; fortunately, this particular impurity should not appreciably affect the interpretations of the reactivity results obtained in the present study.

The ablation targets were those used in previous studies of other aspects of lanthanide and actinide gas-phase organometallic chemistry. The lanthanide targets were $CeSi_2$, Yb metal, a 3.3 at. % $EuO_{1.5}$ + 2.7 at. % $TbO_{1.5}$ − copper pellet, and the arc-melted alloys specified in [7]. The actinide targets were all copper pellets containing a few (1–5) atomic percent of one or more actinide oxide, as described previously: ***U/Pu***(^{238}U + ^{242}Pu) [14]; ***Pu***(^{242}Pu) [20]; ***Np/Am*** (^{237}Np + ^{243}Am) [15]; and ***Am*** (^{243}Am) [15].

3. Results and Discussion

3.1. Lanthanides

Previously, Marcalo et al. [1] found that all Ln^+ (Pm^+ was not studied) were reactive toward HCp*, this in contrast to other alkene reagents toward which Sm^+, Eu^+, Tm^+, and Yb^+ were found to be essentially inert [5,6]. The efficacy of C–H and C–C activation of most alkenes by Ln^+ has been found to correlate with the energy necessary to achieve an electronic configuration at the metal center with two non-*f* valence electrons [3–7], implying activation by way of an insertion mechanism to produce a C–Ln^+–H or C–Ln^+–C intermediate. With HCp*, Sm^+, Eu^+, Tm^+, and Yb^+ distinctively induced H

loss to produce $Ln(Cp*)^+$, presumably lanthanide pentamethylcyclopendienyl complexes; CH_3 loss to produce $Ln[C_5(CH_3)_4H]^+$, presumably lanthanide tetramethylcyclopentadienyl complexes; and H_2 loss to produce $Ln[C_5(CH_3)_4CH_2]^+$, presumably lanthanide tetramethylfulvene complexes [1,2]. In contrast, the more reactive Ln^+ did not induce H loss or CH_3 loss to produce the cyclopentadienyl complexes but instead formed the fulvene complex, and additionally substantial amounts of multiple H_2-loss products not evident with Eu^+ and other typically unreactive Ln^+ [1]. In view of the distinct differentiation between the Ln^+ with large promotion energies required to achieve a configuration with two non-*f* valence electrons suitable for participation in covalent bonding and the Ln^+ with two non-*f* valence electrons in ground or low-lying electronic states, it was postulated [1] that two distinct mechanisms were operative. The normally unreactive ions such as Eu^+ were proposed to activate HCp* by means of strong coordination and concomitant weakening of C–H and C–C bonds at the saturated C^5 ring site. Processes involving direct insertion of Ln^+ into C–H and/or C–C bonds were considered dominant for the normally reactive lanthanide ions.

To establish that the LAPRD experimental technique revealed the unique variations in the character of *f*-element interactions with HCp*, several representative lanthanides were studied by LAPRD prior to proceeding to the actinides—qualitative concurrence with the FTICR experiments was confirmed. The studied lanthanide ions were Ce^+, Pr^+, Eu^+, Gd^+, Tb^+, Dy^+, Ho^+, Tm^+, and Yb^+. The intent of these lanthanide experiments was not to quantitatively compare reactivities or the significance of different reaction channels but rather to confirm the ability to positively identify the substantially different behaviors between the two general types of Ln^+. It was previously reported [1] that Sm^+, Eu^+, Tm^+, and Yb^+ behaved distinctively from those Ln^+ with relatively small PE[Ln^+]. The largest PE[Ln^+] among the more reactive group of lanthanide ions is PE[Lu^+] = 142 kJ mol^{-1} [18,21] whereas the smallest PE[Ln^+] among the four distinctive lanthanide ions is PE[Tm^+] = 199 kJ mol^{-1}. Evidently, the

ability for a Ln^+ to readily insert into a C–H (or C–C) bond diminishes substantially between $PE[Ln^+]$ values of 150 and 200 kJ mol^{-1}.

Among the Ln^+ studied in the present work, only Eu^+ eliminated H and CH_3, in accord with the FTICR results; no reaction products were detected with Yb^+. In addition to the dominant radical-loss products, Eu^+ also appeared to induce a lesser degree of H_2 elimination; most significantly, multiple H_2 elimination was not evident whatsoever in the case of Eu^+. In distinct contrast, each of the other Ln^+ (except unreactive Yb^+) eliminated at least one, and as many as three, dihydrogen molecules. Additionally, Pr^+ eliminated CH_4, and Ce^+ eliminated {CH_4,H_2} (i.e. methane + hydrogen), both of which were channels also seen by FTICR [1]. Only for Eu^+ was the complex corresponding to intact HCp* detected and this is considered to be the adduct, $Eu^+ \cdot$ {HCp*}; the observation of this adduct suggests a strong interaction between the metal ion and the π bonds of the ring, in accord with the strong complexation proposed to account for the non-insertion reactivity of otherwise inert ions such as Eu^+. The distinctive retention of the $Eu(HCp^*)^+$ condensation product further suggests a relatively low reactivity between Eu^+ and HCp*. It is consistent that no reaction was detected between Yb^+ and HCp*, although relative reaction cross sections could not be derived from these results.

For the particularly oxophilic lanthanides, Ce, Pr, and Tb, appreciable quantities of LnO^+ were ablated. The compositions of the resulting three oxygen-containing species were the condensation products, $Ce(OHCp^*)^+$ and $Pr(OHCp^*)^+$; and the H_2-elimination product, $Tb(OHCp^*–H_2)^+$. Again, these results are consistent with the FTICR results (additional products were detected by FTICR for the {TbO^+ + HCp*} reaction) [1]. The structures of these products are indeterminate but the Ce^+–O and Pr^+–O bonds are particularly strong, with respective dissociation energies (D^0) of 849 and 792 kJ mol^{-1} [22]. Accordingly it is probable that the Ln–O bond remains intact and candidate products are the coordination complexes, $O=Ln^+ \cdot$ {HCp*}, and the ionically bonded hydroxy-cyclopentadienylides, $HO–Ln^+–Cp^*$, in which the formal oxidation state at the metal center is

+3 in both. The Tb^+–O bond is somewhat weaker— $D^0[Tb^+–O] = 718$ kJ mol^{-1} [22]—and perhaps the interaction between a metal center with a lower effective positive charge and the HCp* molecule is sufficiently strong that C–H bond weakening and H_2 elimination at the saturated cyclic carbon (C^5) site occurs to produce a $O=Tb^+ \cdot$ {tetramethylfulvene} complex. A role for the oxygen ligand of LnO^+ in inducing H_2 loss has also been suggested [1], and the changing degree of oxygen radical character correlated with the bond strength: highly reactive and weakly bonded $Ln^+–O^{\cdot}$ at one extreme, and inert $Ln^+=O$ at the opposite extreme of very strong bonding.

Whereas the product distributions were qualitatively similar between the FTICR and LAPRD experiments on lanthanides, not all products which had been previously reported [1] were positively identified in the present work. The diminished sensitivity of the LAPRD method, designed specifically to accommodate transuranic actinides, is an intrinsic disadvantage, and reflects the relatively short reaction timescale (<100 μs) and fewer number of ion–molecule interactions. In addition, the relative abundances of those products which were identified differed somewhat between FTICR and LAPRD. With Eu^+, H_2 loss (to fulvene) was dominant under FTICR conditions whereas H loss and CH_3 loss (to cyclopentadienyl radicals) were dominant with LAPRD. With both Tb^+ and Ho^+, the LAPRD results indicated relatively minor differences in product abundances, in the order: H_2 loss (fulvene) $\cong$ $3H_2$ loss $\gtrsim$ $2H_2$ loss; in contrast, the FTICR orderings were: $2H_2$ loss $>$ H_2 loss $\cong$ $3H_2$ loss for Tb^+, and H_2 loss $>$ $2H_2$ loss $>$ $3H_2$ loss for Ho^+. The qualitative differences between the FTICR and LAPRD results may reflect, among other factors, the hyperthermicity of the LAPRD reaction conditions, which effect may have been particularly significant in enhancing the elimination of the radicals, H and CH_3, by Eu^+, and up to $3H_2$ by Tb^+ and Ho^+.

The essential result of the lanthanide LAPRD experiments was the confirmation of qualitative agreement with results for FTICR experiments with HCp*. It was considered desirable to reestablish the validity of the LAPRD methods vis-a-vis intrinsic

Table 1
Abundances of product ions, $An(L)^+$, from reactions with HCp* (L = [HCp*–F])[a]

	F = H_2	$2H_2$	$3H_2$	CH_4
U/Pu[b]				
$Pu(L)^+$ $I[Pu^+]$ = 330	0.48	0.24	0.33	0.30
Pu[c]				
$Pu(L)^+$ $I[Pu^+]$ = 560	0.98	0.52	0.73	0.57
Np/Am[d]				
$Np(L)^+$ $I[Np^+]$ = 240	0.08	0.04	0.13	(<0.04)
$Am(L)^+$ $I[Am^+]$ = 400	0.13	(<0.03)	(<0.03)	(<0.02)
Am				
$Am(L)^+$ $I[Am^+]$ = 110	0.20	(<0.02)	(<0.02)	0.04

[a] Product abundances correspond to the percent of product ion relative to that of unreacted An^+ (or AnO^+): $A[An(L)^+]$ = {$I[An(L)^+]$/$I[An^+]$} × 100 ($I[An(L)^+]$ = ion peak height). Oxygen-containing ion abundances are relative to unreacted AnO^+, $I[AnO^+]$. Product ions are identified by net composition, $An^+ \cdot L$ where L = [HCp*–F] [i.e. HCp* from which fragment(s) of net composition F has been eliminated].
[b] $I[U^+]$ = 6 mV (no U^+–L detected); $I[UO^+]$ = 80; $I[UO_2^+]$ = 29; $I[PuO^+]$ = 130; $A[U(OHCp*–H_2)^+]$ = 0.33; $A[Pu(OHCp*)^+]$ = 0.12.
[c] $A[Pu(HCp*–CH_4,H_2)^+]$ = 0.32; $A[Pu(HCp*–CH_4,2H_2)^+]$ = 0.38; $I[PuO^+]$ = 147; $A[Pu(OHCp*)^+]$ = 1.2; $A[Pu(OHCp*–H_2)^+]$ = 0.4.
[d] $I[NpO^+]$ = 250; $I[NpO_2^+]$ = 1.5; $I[AmO^+]$ = 1.1; $A[Np(OHCp*)^+]$ = 0.04; and $A[Np(OHCp*–H_2)^+]$ = 0.04 [no $Am(OL)^+$ detected].

f-element ion reactivities with this particular reagent prior to proceeding to actinide studies in view of the evidently novel mechanistic and reaction channels revealed for {Ln^+ + HCp*} reactions [1]. Significant amounts of LnO^+ and AnO^+ were co-ablated with the naked metal ions for the more oxophilic *f* elements, even for nominally oxygen-free targets such as alloys. The evident unimportance of LnO^+ in altering the abundance distributions of O-free products is consistent with the difficulty in cleaving the Ln^+–O bonds, and the presence of ablated AnO^+ in the reaction zone should similarly not affect the results inferred for the naked An^+ component of the LAPRD ablation plume. The FTICR study [1] revealed that some LnO^+ reacted with HCp* to produce water and $Ln(HCp*–H_2)^+$ (presumably a fulvene complex); no other oxygen-free products were identified for these reactions. Because both types of naked Ln^+, "reactive" and "unreactive," also produced the $Ln(HCp*–H_2)^+$ product via H_2 elimination (rather than LnO^+-induced H_2O elimination), the possible role of the dehydration pathway does not obscure conclusions regarding comparative intrinsic metal ion reactivities.

3.2. Actinides

Results for the four actinide targets are given in Table 1, and product ion mass spectra are shown for the **Pu** target in Fig. 1 and for the **Np/Am** target in Fig. 2. As the results in Table 1 indicate, the absolute extent of reaction was rather low for the three actinide ions—Np^+, Pu^+, and Am^+—for which products were detected. Typical aggregate product yields were of the order of ~1% relative to the unreacted An^+, which is roughly comparable to yields obtained under similar reaction conditions for reactive An^+ with reagents such as cyclohexene [14]. The amount of U^+ ablated from the **U/Pu** target was minor and no reaction products for the naked uranium ion were detected. The representative mass spectra in Figs. 1 and 2 illustrate the limited resolution of the technique, and it is expected that minor products may not have been identified. The emphasis was on identifying the most significant products and ascertaining the comparative nature of the interactions between these three adjacent but electronically and energetically diverse actinide ions, Np^+, Pu^+, and Am^+.
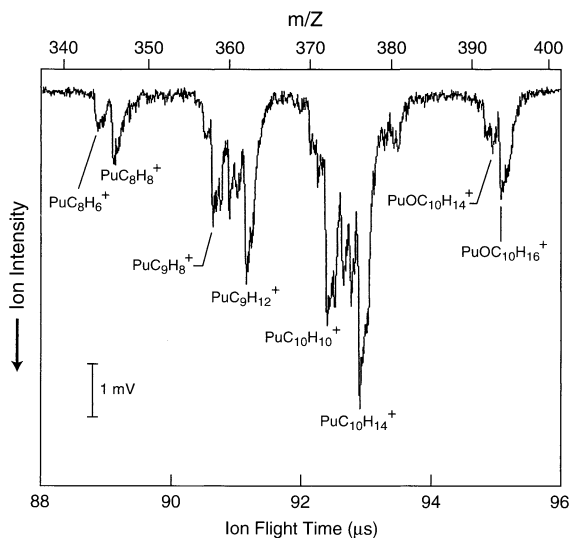
Fig. 1. Mass spectrum of primary product positive ions resulting from ablation of the ***Pu*** target into HCp*. This particular spectrum was obtained using $t_d = 40$ μs. The peak between $PuC_9H_8^+$ and PuC_9H_{12} corresponds to PuC_9H_{10}, and that between $PuC_{10}H_{10}$ and $PuC_{10}H_{14}$ to $PuC_{10}H_{12}$. The peak intensity for the unreacted Pu^+ was 560 mV, that for PuO^+ was 150 mV and that for PuO_2^+ was 1.5 mV.

Fig. 2. Mass spectrum of primary product positive ions resulting from ablation of the ***Np–Am*** target into HCp*. The peak intensities (mV) for unreacted ions were: Np^+/240; NpO^+/250; NpO_2^+/1.5; Am^+/390; AmO^+/1.1; and AmO_2^+/<0.1 (not detected). The asterisked peak at 353 Da corresponds to $AmC_8H_{14}^+$. In addition to the major $AmC_{10}H_{14}^+$ peak, a spectrum for the ***Am*** target additionally exhibited a minor peak corresponding to $AmC_9H_{12}^+$.

For Np^+ and Pu^+, the dominant reactions were loss of H_2, $2H_2$, $3H_2$, and CH_4 from HCp* (the last channel was below the detection limit for Np^+—see Table 1). When the Pu^+ intensity was sufficient, specifically from the ***Pu*** target, both {CH_4, H_2} loss and {CH_4, $2H_2$} loss were also evident. Relatively minor peaks corresponding to $PuC_8H_8^+$ and $PuC_8H_6^+$, identified in Fig. 1, may have resulted from Pu^+-induced elimination of {C_2H_6, H_2} and {C_2H_6, $2H_2$}, respectively. Essentially, the primary reaction products for Np^+ and Pu^+ correspond to those found for the reactive Ln^+, which includes all except Sm^+, Eu^+, Tm^+, and Yb^+ [1]. The primary reaction pathways for the reactive Ln^+ are loss of one or multiple stable molecules: H_2, $2H_2$, $3H_2$, CH_4, {CH_4, H_2}, etc. [1]; this was precisely the behavior apparent with Np^+ and Pu^+. In analogy to the LAPRD results with Ln^+, it was found that triple dehydrogenation was a somewhat more consequential reaction pathway than was double dehydrogenation; as with the lanthanides, this particular product distribution may reflect the hyperthermal nature of the LAPRD reaction conditions.
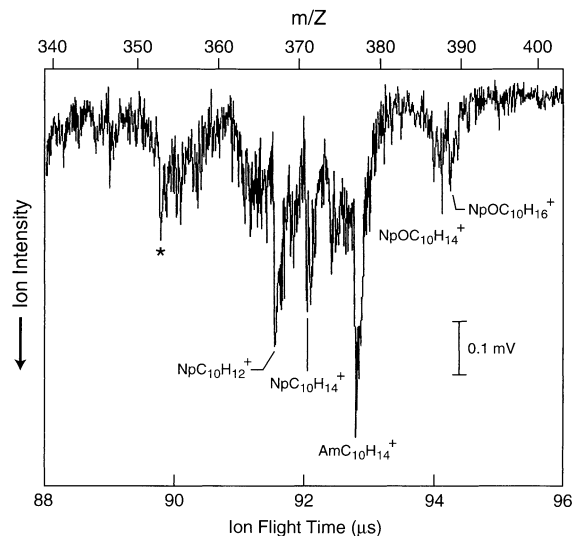
The initial An^+-induced H_2 loss is presumed to result in a fulvene complex, in analogy with the interpretation of corresponding FTICR studies of Sm^+ [2]. That single H_2 loss occurs for all Ln^+, including those which are normally unreactive, suggests that direct C–H bond activation by insertion may not be the dominant mechanism, but rather that bond weakening at the saturated C^5 cyclic carbon of HCp* by strong coordination to the metal ion may result in H_2 elimination and ultimately additional coordination of the metal ion to the methylene π bond of the fulvene product. Although the absolute reaction efficiencies (product ion abundances) varied significantly between experiments, comparison of the results for Pu^+ from the ***U/Pu*** and ***Pu*** targets (Table 1) shows that the product distribution was quite reproducible. For Pu^+, single H_2 loss was the dominant channel whereas for Np^+, triple H_2 loss was dominant. This is in accord with the Ln^+ results where the reaction efficiencies (k/k_{ADO}) correlated with the promotion energies; because $PE[Np^+] = 0$ and $PE[Pu^+] = 104$
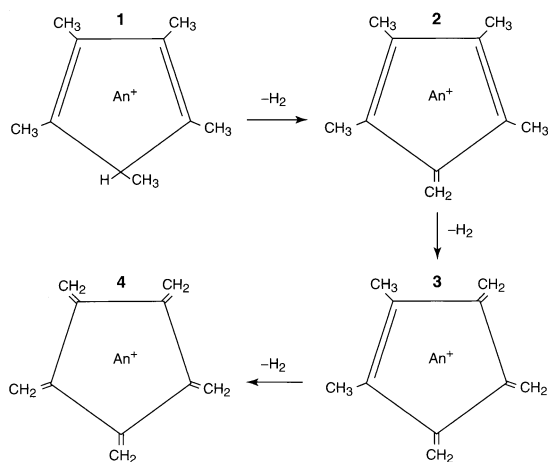
Fig. 3. Postulated structures of products of sequential triple dehydrogenation of HCp*: (**1**) 1,2,3,4,5-pentamethylcyclopentadiene (HCp*); (**2**) 1,2,3,4-tetramethylfulvene; (**3**) 1,2-dimethyl-3,4,5-trimethylenecyclopentene; and (**4**) pentamethylenecyclopentane.

kJ mol^{-1}, a greater efficiency for insertion reactions—which are presumed necessary to achieve multiple dehydrogenation—is to be expected for Np$^+$.

The LAPRD approach does not directly illuminate the bonding/structures of the product ions and it is only possible to speculate in this regard. The supposition of formation of tetramethylfulvenide upon the initial H$_2$ loss is based upon FTICR studies of Sm$^+$ [2]. That the unreactive Ln$^+$ induce only elimination of one H$_2$ is consistent with activation at the distinctive saturated ring carbon; formation of fulvene by way of dehydrogenation of cyclopentadiene requires only 128 kJ mol^{-1} [1]. The two sequential H$_2$ losses from the primary tetramethylfulvene product presumably occur by a mechanism involving activation by insertion of a M$^+$ into a C–H bond of a methyl substituent and α,β-H$_2$ elimination; shown in Fig. 3 are the possible products, **3**: 1,2-dimethyl-3,4,5-trimethylenecyclopentene, and **4**: pentamethylenecyclopentane. Although no thermochemical values are available for these particular reactions, an enthalpy estimate can be obtained by considering the dehydrogenation of 2-butene to produce 1,3-butadiene, which requires 120 kJ mol^{-1}. Accordingly, the triple dehydrogenation sequence shown in Fig. 3 might require ~350 kJ mol^{-1}; conjugation of all five double bonds

in structure **4** (Fig. 3) should provide additional stabilization. Although products **3** and **4** are represented as methylenes, the suggestion of conjugation stabilization is equivalent to postulating a (minor) role of the resonance structure in which some double-bond character is retained within the ring and σ-type bonding occurs directly between the dehydrogenated carbons—this would imply cyclobutene character external to the C$_5$ ring, but the formation of cyclobutene from 1,3-butadiene requires ~50 kJ mol^{-1} [19] and the polymethylene configuration should be thermodynamically favored. The thermodynamic driving force for triple dehydrogenation, which was also observed with Ln$^+$ under essentially thermoneutral conditions [1], is presumably the coordination of the metal ion to the entire π-bonding system. A probable origin of the CH$_4$ loss product is loss of methane from the saturated ring carbon site. The structure of this product presumably involves direct bonding of the metal ion to the resulting unsaturated ring carbon, C^5, perhaps a M=C carbene bond instead of the C=C bond in fulvene. Speculation regarding probable structures of other products such as Pu(HCp*–CH$_4$, nH$_2$)$^+$ becomes increasingly uncertain and it is indeed rather remarkable that such extensive fragmentation of the HCp* molecule is evidently thermodynamically favorable; in this regard it is emphasized that the same degree of HCp* fragmentation was found to occur under relatively gentle (i.e. nearly thermoneutral) FTICR conditions [1].

The interaction of Am$^+$ with HCp* was clearly distinguishable from that of Np$^+$ and Pu$^+$. For Am$^+$, the dominant product corresponded to single H$_2$ loss, with no indication of multiple H$_2$ loss and only a minor ($\leqq$20%) contribution from CH$_4$ loss. Additionally, the overall reactivity (net product yield) for Am$^+$ was evidently below that for Np$^+$ (see the *Np/Am* data in Table 1), consistent with the reduced facility of insertion into C–H and C–C bonds by Am$^+$ (PE = 245 kJ mol^{-1}) when compared with Np$^+$ (PE = 0). The dominance of the single-H$_2$-loss channel distinctly for Am$^+$ is comparable to the behavior of the unreactive lanthanide ions, particularly Tm$^+$ and Yb$^+$, for all three of which the M(HCp*–H$_2$)$^+$ comprised 80%–90% of all product ions [1]. The results

were somewhat different for those obtained by LA-PRD for Eu^+; unlike Eu^+, the H-loss and CH_3-loss products were not detected for Am^+. Considering the FTICR product distribution for the four unreactive Ln^+ [1], the (relatively small) contribution from the CH_4-loss channel suggests that Am^+ behaves most similarly to Tm^+ among the Ln^+ in its gas-phase chemistry with HCp*. Although the Ln^+ can reasonably be divided into two groups, it is not clear that the product abundance distributions distinctly reflect the comparative PE[Ln^+] within these groupings. Specifically considering the four unreactive Ln^+, the ordering of PE[Ln^+] is $Eu^+ > Yb^+ > Sm^+ > Tm^+$ [18] whereas the relative abundance of the H_2-loss product, Ln(HCp*–H_2)$^+$, was $Yb^+ \cong Tm^+ > Sm^+ \cong Eu^+$ [1]. The key point is that no multiple H_2-loss products were evident for any of the unreactive Ln^+, a characteristic also clearly evident for Am^+. At 245 kJ mol^{-1} [17], PE[Am^+] lies in the range of those of the unreactive Ln^+, PE[Tm^+] = 199 kJ mol^{-1} to PE[Eu^+] = 362 kJ mol^{-1}, and its chemistry with HCp* indicates lanthanide-like behavior. Particularly notable is that the valence $5f$ electrons are evidently chemically inert in the Am^+–HCp* interaction. This is in agreement with results for the reactions of Am^+ with other alkenes [15] but is particularly noteworthy because of the central role of the cyclopentadienyl ligand, Cp, and its substituted derivatives, including Cp*, in f-element organometallic chemistry, particularly organoactinide chemistry [23]. Specifically, americium tris-cyclopentadienyl, AmCp$_3$, is among the very few americium compounds involving direct metal–carbon bonding which have been isolated [24]. The gas-phase chemistry results suggest a Am^+–Cp^- interaction which primarily involves the partially filled $6d/7s$ valence orbitals at the metal center and not the quasivalence $5f$ orbitals, which are evidently effectively localized in these types of organometallic systems.

As proposed by Marcalo et al. [1], the distinctive behavior of the four lanthanide ions, Sm^+, Eu^+, Tm^+, and Yb^+, toward HCp* can presumably be attributed to a strong interaction between the metal ion and the intraring π bonds which results in a weakening of the C–H and/or C–C bond(s) at the saturated ring carbon,

without direct bond cleavage by insertion of the metal ion; a similar interaction evidently occurs in the case of Am^+. That this type of mechanism, which is unusual for alkene activation by f-element ions, should appear distinctively in the case of cyclopentadiene, Cp, and its substituted derivatives, such as Cp*, can be rationalized based on thermochemical considerations [19]. The C–H bond energy at the saturated carbon, C^5, in Cp is only ~330 kJ mol^{-1} and a similarly small (or even smaller) value is anticipated for D[H–Cp*] [1]. A reaction pathway to the Am^+–fulvenide complex might proceed by initial complexation of Am^+ to HCp* followed by H–Cp* bond cleavage, a {$Am^+ \cdot Cp^* + H$}^{T} transition state, and rapid abstraction of a second H atom from a methyl group to eliminate H_2 and produce the electrostatically bonded fulvenide product. Deuterium labeling of one of the two types of methyl groups in HCp* could address whether abstraction of the second H atom occurs exclusively at the C^5–CH_3 site or can occur at neighboring methyl groups (e.g. at C^4–CH_3). The observed elimination of CH_4 could proceed by abstraction of a methyl group from a {$Am^+ \cdot Cp^* + H$}^{T} transient, or by initial cleavage at the c-C^5–CH_3 to yield a {$Am^+ \cdot C_5(CH_3)_4H + CH_3$}^{T} intermediate followed by H abstraction; ^{13}C tagging (e.g. c-C^5–$^{13}CH_3$) could elucidate the CH_4-elimination mechanism. The product distribution for the Am^+/HCp* reaction is evidently more similar to that for Tm^+/HCp*—i.e. primarily H_2 loss and minor CH_4 loss—than to that for Eu^+/HCp* where substantial H loss and CH_3 loss was seen by both FTICR [1] and LAPRD. For Eu^+, Tm^+, and Am^+, non-insertion {$M^+ \cdot Cp^* + H$}^{T} and/or {$M^+ \cdot C_5(CH_3)_4H + CH_3$}^{T} transients are postulated but evidently the reaction dynamics are quite discrepant between the three; perhaps Eu^+ induces a greater degree of C–C cleavage, resulting in the second intermediate. As noted above, the differences between the four unreactive Ln^+, the three studied alkaline earth M^+, and now Am^+ do not obviously correlate with the conspicuous ion energetics and the origin of these evidently significant differences in product distributions warrant closer examination.

3.3. Actinide oxides

For An = U, Np, and Pu, the metal–oxygen bond energies are sufficient that substantial amounts of AnO^+ were co-ablated from the oxide target along with the naked An^+. Amounts of ablated AnO^+ and oxygen-containing products are given in the annotations to Table 1. The Am–O bond is relatively weak [25] so that only minuscule amounts of AmO^+ were ablated, and no oxygen-containing reaction product ions were detected. The dissociation energies of the three abundant actinide monoxide ions $D^0[An^+–O]$ are as follows, in kJ mol^{-1} with approximate uncertainties indicated in parentheses [25,26]: $UO^+/$820(20); $NpO^+/790(10)$; $PuO^+/730(50)$. As for the strongly bonded LnO^+ [1], the An–O bonds can be presumed to remain intact in the oxygen-containing product ions. For Np and Pu, condensation products with compositions corresponding to $An(OHCp^*)^+$ were detected, presumably corresponding to the oxide–cyclopentadiene adduct, $O=An^+ \cdot \{HCp^*\}$, and/or the hydroxide–cyclopentadienylide complex, $HO–An^+–Cp^*$. For U, Np, and Pu, the dehydrogenation product, $An(OHCp^*–H_2)^+$, was also detected. Whereas insufficient NpO_2^+ or PuO_2^+ were ablated to reasonably account for their $An(OHCp^*–H_2)^+$, the significant amount of ablated UO_2^+ introduces the possibility of the dehydration reaction: $UO_2^+ + HCp^*$ $\rightarrow U(OHCp^*–H_2)^+ + H_2O$. The $OU^+–O$ bond energy of ~ 510 kJ mol^{-1} is only slightly greater than the $H_2–O$ bond energy of 491 kJ mol^{-1} [19], and the UO_2^+/HCp^* dehydration reaction would be more exothermic than the indistinguishable UO^+/HCp^* dehydrogenation reaction if the indeterminate $UO^+ \cdot \{HCp^*–H_2\}$ interaction is only moderately greater than the $UO_2^+ \cdot \{HCp^*–H_2\}$ interaction. Specifically, if the cited $D^0[OU^+–O]$ is accurate, an enhancement in the ion-molecule interaction energy of only $510–491 \cong 20$ kJ mol^{-1} would be required to make the UO_2^+-induced dehydration reaction thermodynamically competitive with UO^+-induced dehydrogenation. Although the $UO(HCp^*–H_2)^+$ may have derived primarily from UO_2^+, for Np and Pu the dearth of ablated AnO_2^+ reactant ion indicates AnO^+ as the source of the $An(OHCp^*–H_2)^+$. That both the condensation and dehydrogenation products were obtained for NpO^+ was unanticipated based on the results for LnO^+ in view of the correlation of $\{LnO^+ + HCp^*\}$ product distributions with oxide bond strengths, $D^0[Ln^+–O]$ [1]. Because $D^0[Np^+–O] = 790$ kJ mol^{-1} [25,26] is similar to $D^0[Pr^+–O] = 792$ kJ mol^{-1} [22], and only the condensation product, $Pr(OHCp^*)^+$, was found under both FTICR [1] and LAPRD conditions, only condensation was anticipated for NpO^+. Greater activation of HCp^* by the metal center in NpO^+ may be due to the accessibility of high oxidation states, Np(IV) and Np(V), or the greater chemical activity of the $5f$ versus $4f$ valence electrons. Because $D^0[Pu^+–O]$ is comparable to $D^0[Tb^+–O]$ (see previous discussion), it was expected, and found, that some dehydrogenation of HCp^* would be induced by PuO^+, in analogy with the results obtained for TbO^+. To further address the evidently distinctive character of the AnO^+ vis-a-vis the LnO^+, it would be desirable to isolate UO^+ ($D^0 = 820$ kJ mol^{-1}) from UO_2^+ to determine if UO^+ is also capable of dehydrogenating HCp^*. The proposed UO_2^+-induced dehydration reaction should also be studied under conditions where the oxide ions can be mass-selected and isolated from one another—an ion trap experiment would enable such studies.

4. Conclusions

Reactions of Ln^+ and LnO^+ with HCp^* confirmed concurrence of the LAPRD results for these reactions with those previously obtained by FTICR [1,2]. In particular, most Ln^+ induced multiple-dehydrogenation of HCp^* whereas Eu^+, which is representative of a group of four relatively unreactive lanthanide ions, Sm^+, Eu^+, Tm^+, and Yb^+, induced primarily CH_3 loss and H loss, and no multiple H_2 loss. These results were in accord with the FTICR results and clearly demonstrated that LAPRD reveals the intrinsic interaction of Ln^+, and presumably An^+, ions with HCp^*. Results for LnO^+ were also in accord with those from FTICR.

Among the three studied naked actinide ions, Np^+ and Pu^+ behaved in a similar manner to the members of the reactive group of Ln^+. In particular, double and particularly triple dehydrogenation were primary reactions. In distinct contrast, Am^+ induced almost exclusively single H_2 loss, exhibiting similar character to the group of four relatively unreactive Ln^+. These contrasting results between Np^+/Pu^+ and Am^+ suggest that an insertion mechanism requiring a divalent metal center is involved in multiple dehydrogenation and that the energy necessary to promote a quasivalence $5f$ electron of Am^+ to a valence $6d$ orbital is too great to enable facile C–H activation by means of direct cleavage. A direct inference of this finding is that the valence $5f$ electrons of Am^+ are chemically inert regarding the insertion process and cannot form effective direct σ-type bonds with carbon or hydrogen. This finding is particularly significant for the HCp* system because cyclopentadienyl ligands are ubiquitous in f-element organometallic chemistry and are particularly important among the few transuranic organoactinide compounds which have been isolated.

Reactions of $UO_{1,2}^+$, NpO^+, and PuO^+ with HCp* were also assessed. The possibility of concurrent and indistinguishable dehydration by UO_2^+ and dehydrogenation by UO^+ resulted in uncertain interpretation of the results there. In the case of PuO^+, the observation of both condensation and dehydration was in accord with results for lanthanide oxides in the context of a model which correlates reactivities with M^+–O bond strengths. Based on this model, it was expected that NpO^+ would be essentially inert and result only in the condensation product. However, it was found that NpO^+, like PuO^+, induced appreciable dehydrogenation of HCp*. This result suggests distinctive behavior from the LnO^+ and may relate to the accessibility of oxidation states above +3 for the actinides in this region of the series and/or chemical activity of the $5f$ electrons at the metal center of NpO^+. It is entirely feasible that the ability of the quasivalence $5f$ electrons to participate in chemical bonding diminishes drastically between Np and Am (as is found with actinide metals).

Acknowledgements

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