Actinide Gas-Phase Chemistry: Reactions of An^+ and AnO^+ [An = Th, U, Np, Pu, Am] with Nitriles and Butylamine

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Laser ablation with prompt reaction and detection was applied to study gas-phase reactions of actinide ions, An^+ and AnO^+ [An = Th, U, Pu, Np, Am], with nitriles and butylamine; Tb and Tm were included for comparison. Particular emphasis was on Np and Am as this is the region of the An series where a transition to Ln-like character is manifested. A goal was to assess the role of the coordinating N: site on actinide ion−molecule interactions. The results for the nitriles were generally reminiscent of those for reactions with alkenes and the inert character of Pu^+ and Am^+ with regard to dehydrogenation, despite adduct formation, indicated that C−H activation requires two non-5f electrons to produce a $C-An^+-H$ complex. With the butyronitriles and valeronitrile, Am^+ produced $AmC_2H_4^+$, possibly via an "ion/dipole" interaction. Most MO^+ exhibited only adduct formation with the nitriles although ThO^+ was distinctively reactive, consistent with a description of Th as a quasi-d-block element. Both Np^+ and Tb^+ were substantially effective at dehydrogenating butylamine and Am^+ exhibited a lesser degree of reactivity. Reactions of the MO^+, TbO^+, NpO^+, and AmO^+ with butylamine revealed a dramatic effect of oxo-ligation: AmO^+ was at least as reactive as TbO^+ and NpO^+. It is postulated that the MO^+ reactions proceeded via a multicentered intermediate without insertion into a C−H bond. Bis-complexes were produced with nitriles and butylamine, attesting to strong complexation with the :N functionality. An ancillary discovery was Am_2^+−An dimers/clusters should elucidate the nature of actinide intermetallic bonding, including the role of 5f electrons.

Introduction

The study of gas-phase chemistry of transition metal ions has developed into an important tool to examine fundamental chemical processes in an elementary environment free of secondary effects such as solvation, coordination or competing reactions.[1−3] Early studies focused on the activation of the C−H and C−C bonds of hydrocarbons by the ubiquitous and technologically important first-row transition metal ions, Cr^+, Mn^+, Fe^+, Co^+, Ni^+, etc.; other organic substrates and transition metals have since received increased attention.[1−7]

The f-block inner transition metal series, the lanthanides (Ln) and actinides (An), are characterized by sequential filling of the 4f or 5f orbitals. There have been reports on gas-phase reactions of naked lanthanide (Ln^+)[8−14] and lanthanide oxide (LnO^+)[15−17] ions with hydrocarbons. A close correlation was established between Ln^+ reactivity and the energy needed to excite an electron from a 4f orbital to a 5d orbital,[13,14] indicating that the 4f electrons are chemically inert. Cornehl et al.[15] studied the interactions of LnO^+ with hydrocarbons and discovered entirely different behavior and mechanistics. Reports have appeared on gas-phase reactions of Ln^+ with alcohols,[16] S_8,[17] and methanol clusters.[18]

The condensed phase chemistry of the elements of the first half of the actinide series exhibits a diversity not evident for the lanthanides.[19] The light actinides manifest a variety of oxidation states, up to Np(VII), which is attributable to the relatively small energy required to excite an electron from a 5f orbital to a 6d orbital. The actinide 5f orbitals are spatially extended relative to the outer s/p/d orbitals compared with the core-like lanthanide 4f electrons, and may participate in bonding.[20] Early gas-phase studies of U^+ chemistry were performed by Armentrout et al.[21,22] and recent studies have examined the

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activation of hydrocarbons by Th$^+$, U$^+$, ThO$^+$, and UO$^+$.[23−26] Both Th$^+$ and U$^+$ comprise two non-5f valence electrons in their ground states[27] and their high reactivities do not illuminate the role of the 5f electrons. Cornehl et al.[25] suggested that the greater dehydrogenation activity of UO$^+$ vs NdO$^+$ points to participation of 5f electrons of UO$^+$ in C−H activation.

To address the necessity for non-5f valence electrons at an An$^+$ metal center for hydrocarbon activation it is desirable to employ transuranium (TRU) An$^+$ which have $5f^{n-2}7s^1$ ground-state configurations. The $5f^{n-2}7s^1 \rightarrow 5f^{n-3}6d^17s^1$ promotion energies (kJ mol^{-1}) for Np$^+$, Pu$^+$, and Am$^+$ are 0, 104, and 245, respectively,[27] and this series of An$^+$ is well-suited to assess the role of 5f electrons. The available TRU nuclides are synthetic with most undergoing decay by α-emission, and a laser ablation mass spectrometer has been installed into an α-containment glovebox to enable investigation of their gas-phase chemistry by laser ablation with prompt reaction and detection (LAPRD) using sub-milligram samples. The efficacy of LAPRD was established by concurrence of results for lanthanides[14] and U and Th[26] with those from FTICR-MS experiments.[13,23−25]

Initial TRU LAPRD experiments examined reactions of Np$^+$, Pu$^+$, NpO$^+$, PuO$^+$, and Am$^+$ with alkenes.[28,29] The order of dehydrogenation activity was Np$^+$ > Pu$^+$ > Am$^+$, consistent with a mechanism involving 5f → 6d promotion prior to insertion into a C−H bond and β-H elimination; the 5f electrons of TRU An$^+$ are insufficiently delocalized to facilitate C−H activation. Comparison of reactivity results for NpO$^+$ and PuO$^+$ with those for UO$^+$ suggested chemically active 5f electrons only for the latter; decreasing bonding of the 5f electrons across the actinide series is well-established.[20] Among the alkenes studied, only 1,5-cyclooctadiene (COD) was dehydrogenated by Am$^+$,[29] perhaps indicating 5f-electron interaction with symmetrically compatible substrates.[30]

Alkyl nitriles offer an effective coordinating functionality, N:,[31] the influence of which can illuminate reaction mechanistics. Gas-phase reactions of d-block M$^+$ with alkyl nitriles have been extensively investigated.[32,33] Attachment of M$^+$ to the nitrile in an end-on orientation (i.e. C≡N:−M$^+$) results in activation of the tail portion of the alkyl chain, an effect termed “remote functionalization” by Schwarz and co-workers.[34−39] Side-on complexation to the C≡N: moiety is also possible[40] and can enable activation of shorter alkyl chains or the proximate segment of a long alkyl group.[40−43] Analogous coordination modes obtain in hetergeneous catalysis involving adsorption of a nitrile onto metal surfaces.[44] In the gas-phase, increasing the length of the alkyl chain decreases steric restrictions and stabilizes nascent $M^+{-}{:}N{\equiv}C{-}(CH_2)_nCH_3$ complexes against dissociation by accommodation of complexation energy.[45,46]

Primary amines also provide the N: complexation site [47] and {M$^+$ + amine} reactions have been reported.[32,33] In the present context, primary amines differ from nitriles in two fundamental aspects: (1) the availability of N−H bonds for cleavage and (2) the proximity of the α-CH$_2$ group to an M$^+$ coordinated to the trigonal amine. Both effects might enable distinctive reaction mechanisms and products.[48,49] The comparative behaviors of An$^+$ and AnO$^+$ are of interest because ligation of the metal ion can have a profound effect on reactivities [50] and metal oxides are relevant to heterogeneous catalysis where the behavior of nitriles, for example, is entirely distinctive on metal vs metal oxide surfaces.[51]

Having initially examined reactions of the first three TRU An$^+$ with alkenes, it is reasonable to progress to reactions with alkyl substrates comprising a N: functionality. It was anticipated that discrepant behaviors might illuminate the role of initial coordination (adduct formation) on reactivities. A particularly intriguing issue is the role of the 5f electrons in enabling coordination with suitable substrates such as COD and COT—the N: site should effectively anchor M$^+$ with little specificity for 5f ions, and the comparative efficacy for Am$^+$ to dehydrogenate nitriles (vs COD) was of particular interest. Effects of oxo-ligation were also probed and are relevant to adsorption of nitriles on clean and oxygenated metal surfaces. In addition to the fundamental interest in elementary processes, the interactions of An ions with :N-comprising substrates are germane to the behavior of actinide ions in biological and environmental media where the N: functionality is ubiquitous. In the work reported here, Th$^+$, U$^+$, Np$^+$, Pu$^+$, Am$^+$, and the corresponding AnO$^+$ were reacted with several nitriles and butylamine. The most comprehensive results were obtained for Np$^+$ and Am$^+$ because their widely disparate 5f → 6d promotion energies and proximity in the actinide series effectively illuminate the role of An$^+$ electronic structures and energetics. The lanthanide ions, Tb$^+$ and Tm$^+$ (and TbO$^+$), were included as Ln$^+$ with suitable 4f

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→ 5d promotion energies for comparative purposes (39 kJ mol^{-1} Tb^+ and 199 kJ mol^{-1} Tm^+ [52]).

Experimental Section

The instrument and experimental procedures have been described previously[14,26,28,29] and are only briefly summarized here. Ions were ablated from a target consisting of small amounts of one or more metal oxide contained in a matrix of compressed copper powder. The attenuated output (~3 mJ; ~15 ns pulse width) of a XeCl excimer laser ($\lambda = 308$ nm) was focused normal to the target surface to a ~0.5 mm^2 spot, providing a nominal irradiance in the range of 10^7-10^8 W cm^{-2}. Ablated ions propagated ~3 cm through the reactant gas maintained at a constant but indeterminate ($>10^{-5}$ mbar) pressure, and both unreacted and product positive ions were orthogonally injected into the reflectron time-of-flight mass spectrometer (RTOF-MS) after some time delay, t_d, following the laser pulse. The intensities of the ablated reactant ions, M^+ and MO^+, were maximized around $t_d = 15$ μs ($\upsilon \approx \{3 \text{ cm}/15\ \mu\text{s}\} = 2$ km s^{-1}) but the best sensitivities to product ions were generally achieved for $t_d \approx 35$ μs, the condition under which all of the reported results were obtained (relative reactivities and product distributions were essentially invariant with t_d). That most reacted ions were apparently in their ground electronic states was previously established in LAPRD studies with lanthanides[14] and actinides[26,28,29] and may be partly attributed to the selective monitoring of relatively slow (<1 km s^{-1}), low-energy ablated ions. All of the observed reactions employed hyperthermal ions and the center-of-mass collisional energies (KE_{CM}) are estimated to be in the approximate range of 15 kJ mol^{-1} ($^{159}Tb^+$ + acetonitrile) to 30 kJ mol^{-1} ($^{243}Am^+$ + valeronitrile); the masses of the five studied An were sufficiently similar ($^{232}Th - {}^{243}Am$) that their KE_{CM} were essentially identical. It should be noted that different product distributions might be obtained under lower-energy and/or longer reaction time conditions such as typically obtain in FTICR-MS experiments.

The ablation target pellets, comprising 0.5−5 atom percent of the An or Ln, as AnO_2 or Ln_2O_3, dispersed in a compressed copper matrix, were those employed in the alkene studies.[28,29] The following reactant ions were ablated in substantial amounts from the seven targets employed in the present study: $^{232}Th^+$ and $^{232}ThO^+$ from target "Ti−Ce−Th" (Ti^+ and Ce^+ were minor and are not considered here); $^{238}U^+$, $^{238}UO^+$, $^{238}UO_2^+$, $^{242}Pu^+$, and $^{242}PuO^+$ from "U−Pu"; $^{237}Np^+$, $^{237}NpO^+$, $^{237}NpO_2^+$, $^{242}Pu^+$, and $^{242}PuO^+$ from "Np−Pu"; $^{242}Pu^+$ and $^{242}PuO^+$ from "Pu"; $^{243}Am^+$ from "Am"; $^{237}Np^+$, $^{237}NpO^+$, $^{237}NpO_2^+$, and $^{243}Am^+$ from "Np−Am"; and $^{243}Am^+$, $^{159}Tb^+$, $^{159}TbO^+$, and $^{169}Tm^+$ from "Am−Tb−Tm." Despite that AmO^+ was only a minor ablated ion, several products resulting from it were detected. Small amounts of $^{237}NpO_2$ were present in the Am and Am−Tb−Tm targets, as a result of cross-contamination during sample preparation, and $^{237}NpO_2^+$ precluded reliable identification of isobaric $^{243}AmC_2H_2^+$. All of the actinides were of at least 99% isotopic purity, and ^{159}Tb and ^{169}Tm are the only naturally occurring isotopes of those elements. The two primary impurity isotopes detected in the Am material were ~0.5% ^{239}Pu and ~0.2% ^{241}Am. The latter was presumably present from the genesis of the material and the former is consistent with the decay of ^{243}Am during the ~30 years since its original purification: ^{243}Am ($t_{1/2} = 7500$ years) → $^4He + {}^{239}Np$ ($t_{1/2} = 2.4$ days) → $\beta^- + {}^{239}Pu$ ($t_{1/2} = 24\,000$ years). The presence of ~0.5% ^{239}Pu can be significant given the substantially greater reactivity of Pu compared with Am. The organic reactants were commercial products of at least 99% purity.

Table 1. Abundances of MO^+−Nitrile Adducts[a]

	$-C_2H_3N$	$-C_3H_5N$	$-C_3H_3N$	$-n-C_4H_7N$	$-i-C_4H_7N$	$-C_5H_9N$
ThO^+	1.2	0.7	*b*	*b*	*b*	*b*
PuO^+	11	4.0	*b*	*b*	*b*	*b*
AmO^+	*c*	90	77	170	200	410
NpO^+	*c*	52	8.1	51[d]	200	120
AmO^+	*c*	90	48	420	470	200
TbO^+	*c*	21	4.2	*e*	*e*	3.0

[a] **A[**MO^+−nitrile] ≡ {$I[MO^+$−nitrile]/$I[MO^+]$} × 10^3. It is presumed that the species correspond to the intact nitrile coordinated to MO^+. [b] Experiment not performed. [c] Assessment precluded by residual butylamine. [d] Also detected $NpO_2C_4H_7N^+$. [e] $TbO^+-C_4H_7N$ at 244 Da was obscured by $^{243}Am^+$.

Table 2. Products from Acetonitrile, Propionitrile, and Acrylonitrile[a]

M	$I[M^+]$	$A[MC_2HN^+]$	$A[MC_2H_3N^+]$	$R[\mathbf{D}/\mathbf{A}]$
		For Acetonitrile (C_2H_3N)		
Th	235	3.8	0.9	4
U	380	11	<0.3	>40
Pu	550	<0.18	<0.2	−
Np	88	11	<0.5	>20
Pu	260	<0.023	0.3	<0.08
Pu	940	<0.03	0.5	<0.06
Am	3200	<0.03	1.0	<0.03

M	$I[M^+]$	$A[MC_2H_2^+]$[c]	$A[MC_3H_3N^+]$	$A[M\{C_3H_5N\}^+]$	$R[\mathbf{D}/\mathbf{A}]$
		For Propionitrile (C_3H_5N)[b]			
Th	280	21	2.7	<0.4	>7
U	85	5.5	5.2	<0.6	>9
Pu	260	0.9	<0.2	0.6	<0.3
Np	210	4.8	8.1	<0.4	>20
Pu	590	0.3	<0.2	0.2	<1
Pu	1040	1.4	<0.08	0.8	<0.1
Am	2200	0.3	<0.4	0.7	<0.6
Np	39	1200	75	39	1.9
Am	832	*d*	0.5	6.7	0.07
Am	600	(<0.7)[d]	<0.10	1.2	<0.08
Tb	290	12	12	2.0	6
Tm	590	<1.0	<0.3	2.5	<0.1

M	$I[M^+]$	$A[MC_2H_2^+]$[c]	$A[MC_3HN^+]$	$A[MC_3H_3N^+]$	$R[\mathbf{D}/\mathbf{A}]$
		For Acrylonitrile (C_3H_3N)			
Np	250	200	19	27	0.7
Am	2440	*d,e*	<0.3	1.2	<0.3
Am	420	*d,e*	<0.6	<0.6	−
Tb	500	220	11	8.2	1.3
Tm	500	<3	<0.6	<1.5	−

[a] $I[M^+]$ = ion intensity (peak height) in mV corresponds to the figure scales. $A[ML^+] = \{I[ML^+]/I[M^+]\} \times 10^3$; uncertainties are the greater of 10% or one digit in the last reported significant figure. Upper limits are given for undetected ions. $R[\mathbf{D}/\mathbf{A}] = \{A[MC_mH_{n-2}N]/A[C_mH_nN]\}$ ($m = 2$, $n = 3$ for acetonitrile); $R[\mathbf{D}/\mathbf{A}]$ provides a measure of the single-dehydrogenation efficiency relative to adduct formation. [b] $A[ThO(OH)^+] = 4.4$; $A[ThO(C_2H_2)^+] = 2.8$; $A[ThO\{C_2H_2\}\{C_3H_5N\}^+] = 0.5$; $A[NpO_2\{C_3H_5N\}^+] = 75$; $A[Np\{C_2H_2\}\{C_3H_5N\}^+]$ detected. Small amounts of $M\{HCN\}^+$ and $M\{C_2H_4\}^+$ were evident for M = Th, U, and Np. [c] Some ligand assignments are presumptive; specifically, C_2H_2 is isobaric with CN. [d] Isobaric with NpO_2^+ (NpO_2 was a minor contaminant in the "*Am*" and "*Am−Tb−Tm*" targets). [e] Reaction of Am^+ from the "*Am*" target with $t_d = 45$ μs yielded $Am\{C_2H_2\}^+$ (and/or $Am\{CN\}^+$).

Results and Discussion

The LAPRD method provides an assessment of ion reactivities and product distributions but does not directly illuminate reaction kinetics, mechanistics, product structures or thermodynamics. Semiquantitative measures of comparative ion reactivities are best obtained by comparing results for ions co-ablated from a multicomponent target. Probable ion structures and/or reaction mechanisms might be reasonably postulated and approximate thermodynamic limits on ion−ligand bond energies can be estimated. The use of ^2H- and/or ^{13}C-labeled reagents

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Table 3. Products from Butyronitrile, Isobutyronitrile and Valeronitrile[a]

M	$I[M^+]$	$A[MC_2H_2^+]^b$	$A[MC_2H_4^+]$	$A[MC_4H_3N^+]$	$A[MC_4H_5N^+]$	$A[MC_4H_7N^+]$	$R[\mathbf{D}/\mathbf{A}]$
			For Butyronitrile (n-C_4H_7N)				
Am	3100	c	1.0	<0.09	<0.09	43	<0.002
Np[d]	480	21	69	13	26	9	3
Am	1790	*c*	2.1	<0.2	<0.2	63	<0.003
Am	103	*c*	2.8	<1	<1	4.9	<0.2
Tb[e]	590	10	<5	8.5	24	6.7	4
Tm	1030	1.4	0.9	<1	2.4	13	0.2
			For Isobutyronitrile (i-C_4H_7N)[f]				
Am	3000	*c*	6.9	<0.14	<0.14	6.9	<0.2
Np[e]	68	240	3500	52	140	87	1.6
Am	1170	*c*	36	(5.0)[g]	<2	23	<0.09
Am	210	*c*	5	(2.2)[g]	<0.9	11	<0.08
Tb[e,h]	470	3	3	10.1	14	5	3
Tm	1330	1.9	1.4	1.9	3.0	26	0.1

M	$I[M^+]$	$A[C_5H_5N^+]$	$A[C_5H_7N^+]$	$A[C_5H_9N^+]$	$R[\mathbf{D}/\mathbf{A}]$
		For Valeronitrile (C_5H_9N)			
Am[i]	3100	<0.2	<0.2	8.5	<0.02
Np	66	62	45	<20	>2
Am	1210	<1.5	<1.5	16	<0.09

[a] I, A, $R[\mathbf{D}/\mathbf{A}]$, and uncertainties are defined in Table 2. [b] Some ligand assignments are presumptive; specifically, C_2H_2 is isobaric with CN. [c] Isobaric with NpO_2^+ (NpO_2 was a minor contaminant in the "*Am*" and "*Am*−*Tb*−*Tm*" targets). [d] Also, Np^+−L (A in the range of 10−50) at $L =$ 39 Da (CH_3CN?); 40 Da (C_3H_4?); 52 Da (C_4H_4?). [e] $A[TbC_8H_{10}N_2^+] = 2.0$ from butyronitrile; $A[TbC_8H_{10}N_2^+] = 6.9$ and $A[NpC_8H_{10}N_2^+] = 32$ from isobutryonitrile. [f] The isobutyronitrile pressure was roughly five times greater than for the other reactants. [g] Isobaric with $^{239}PuC_4H_7N$ (^{239}Pu present as a decay product of ^{243}Am). [h] $A[TbC_4HN^+] = 8.5$. [i] $A[Am_2^+] = 0.02$ (Am_2O^+ and Am_2O_2+ were produced in greater abundances).

Table 4. Products from Butylamine ($C_4H_{11}N$)[a]

			$A[ML^+]^b$			
M	$I[M^+]$	CH_3N	C_4H_7N	C_4H_9N	$C_4H_{11}N$	$R[\mathbf{D}/\mathbf{A}]$
Am	1080	0.8	<0.3	0.8	8	0.1
Am[c]	2350	<0.3	<0.2	<0.2	2.3	<0.09
Np[c]	2.4	2100	340	490	<90	>5
Tb[d]	94	62	80	40	3	13

					$A[MOL^+]^b$				
MO	$I[MO^+]$	NH_3	CHN	CH_3N	CH_5N	C_4H_7N	C_4H_9N	$C_4H_{11}N$	$R[\mathbf{D}/\mathbf{A}]$
AmO[e]	6.2	330	76	110	380	380	700	890	0.8
AmO	4.1	<110	<100	<100	430	150(50)	150(50)	150(50)	~1
NpO[c]	200	30	10	18	35	31	35	35	1
TbO[d]	140	44	40	44	44	*f*	21	21	1

[a] I, A, $R[\mathbf{D}/\mathbf{A}]$ and uncertainties are defined in Table 2. Larger uncertainties are in parentheses. [b] The presumed **L** compositions are specified but alternative assignments are feasible (e.g., NH_3 is isobaric with OH); structures are not implied (e.g., "CHN" is probably H−C≡N). [c] $A[NpC_8H_{16}N_2^+] = 150$; $A[NpC_8H_{18}N_2^+] = 180$; $A[NpC_8H_{20}N_2^+] = 180$ (corresponding AmL^+ were undetected to $A < 0.05$); $A[NpOC_8H_{22}N_2^+] = 1.5$; $A[NpO_2C_4H_{11}N^+] = 150$. [d] The reactivity of Am^+ was as for the other targets; insufficient $AmO^+$was generated to assess its reactivity. The only peak definitively attributable to reaction of Tm^+ was the adduct, $A[Tm^+{-}C_4H_{11}N] = 3$ (concurrently, $A[Am^+{-}C_4H_{11}N] = 4.1$); TmO^+ and its reaction products were undetected. Also: $A[TbC_8H_{14}N_2^+] =13$; $A[TbC_8H_{16}N_2^+] = 11$; $A[TbC_8H_{18}N_2^+] = 5$; $A[TbC_8H_{20}N_2^+] = 3$. Additional unassigned peaks presumably resulted from reactions of Tb^+ or TbO^+. [e] $A[AmOC_8H_{16}N_2^+] = 60$; $A[AmOC_8H_{18}N_2^+] = 130$; $A[AmOC_8H_{20}N_2^+] = 60$; $A[AmOC_8H_{22}N_2^+] = 40$. [f] $TbOC_4H_7N^+$ at 244 Da was obscured by the intense $^{243}Am^+$ peak.

could potentially elucidate mechanistics and structures but previous studies suggested appreciable H-scrambling.[53]

The primary results are given in Tables 1−4 and representative LAPRD mass spectra are shown in Figures 1−3. The product ion abundances, A, are defined as follows: $A[ML^+] = \{I[ML^+]/I[M^+]\} \times 10^3$, and $A[MOL^+] = \{I[MOL^+]/I[MO^+]\} \times 10^3$; $I[M^+]$ and $I[MO^+]$ represent the intensities of the unreacted M^+ and MO^+ peaks, and $I[ML^+]$ and $I[MOL^+]$ those of the product ions. The abundance uncertainties are generally the greater of 10% or one digit in the terminal significant figure. As a indicator of the facility of C−H activation/dehydrogenation (**D**) following complexation of the M^+ to a nitrile or amine (adduct formation, **A**), abundance ratios, $R[\mathbf{D}/\mathbf{A}]$, are also tabulated: $R[\mathbf{D}/\mathbf{A}] = \{A[MC_mH_{n-2}N^+]/A[MC_mH_nN^+]\}$, where C_mH_nN is the reactant molecule. Discrepancies between detection limits reflect variations in the intensities of the reactant ion peaks. Ions co-ablated from a target are grouped together in the tabulated results. All significant products are specified only for the acetonitrile and propionitrile reactions. Particularly for reactions of Np^+ and Tb^+ with the other nitriles, the mass spectra indicated additional cracking channels and only the primary products are specified; an example of additional products is seen in the Np^+ + butyronitrile mass spectrum in Figure 2. The extent of cracking generally paralleled that of dehydrogenation, which served as a reliable indicator of net reactivities; it has been shown that early transition metal ions, including La^+, induce primarily dehydrogenation in alkyl nitriles.[35,36,38] Establishing mechanistics and reaction pathways

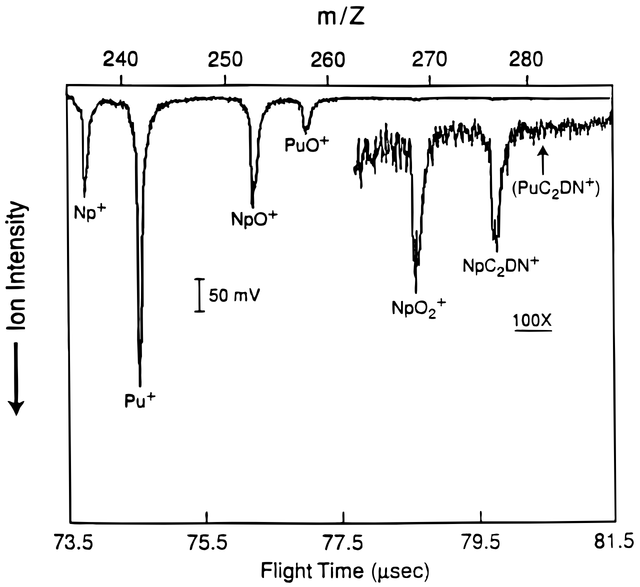

Figure 1. Mass spectrum for ablation of the Np−Pu target into deuterated acetonitrile.

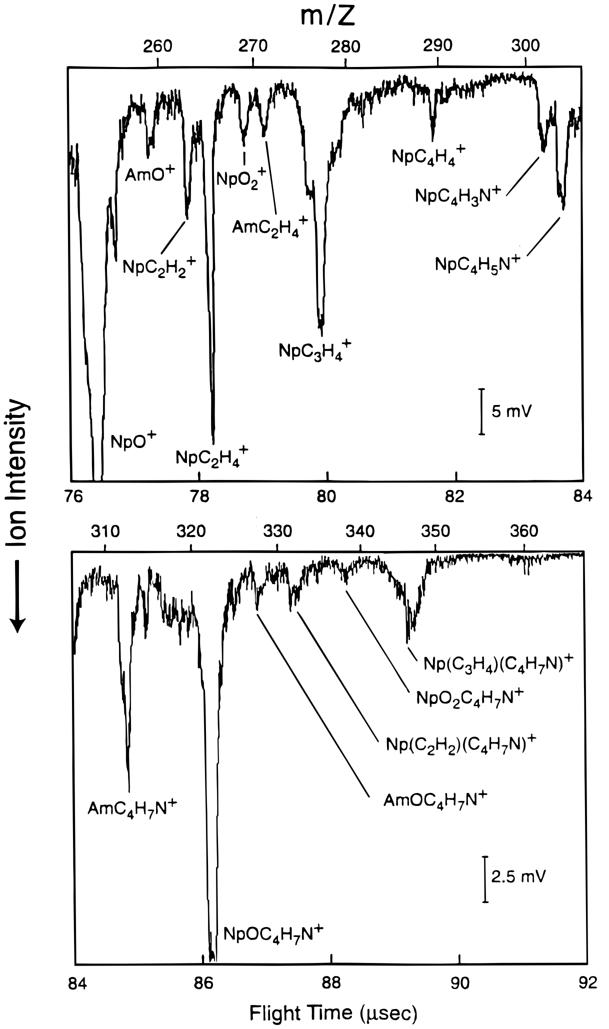

Figure 2. Mass spectrum for ablation of the Np−Am target into butyronitrile.

was not the goal of reaction survey and it was found that Am$^+$ and Tm$^+$ (the least reactive M$^+$ studied) typically did not induce C−C activation; an exception for Am$^+$ is noted.

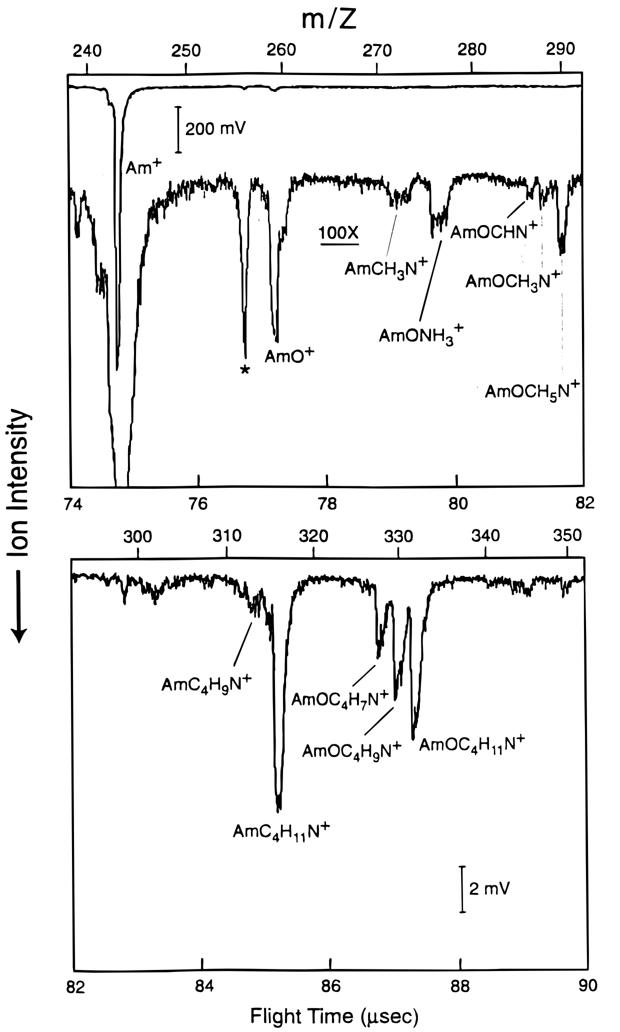

Figure 3. Mass spectrum for ablation of the Am target into butylamine. The asterisked peak could be assigned to AmCH$^+$ but is considered likely to have resulted from metastable decay in the RTOF-MS.

These experiments did not probe the structures of the detected product ions and the specified ligand compositions, ”L,” might correspond to the intact reactant (i.e., adduct formation), an intact fragment of the reactant (e.g., dehydrogenation), and/or multiple moieties coordinated to the metal ion (e.g., “C_2H_3CN” $\Rightarrow$ $\{H_2C{=}CH{-}C{\equiv}N\}$, $\{HC{\equiv}CH + HC{\equiv}N\}$, etc.). Speculations are offered as to probable structures with implicit acknowledgment of uncertainties. The nomenclature M$^+$-{X} designates a product ion composed of the metal, M, and a ligand(s) of net mass X (Da). In some cases the mass of a ligand could result in assignment of two or more reasonable compositions, such as L = C_2H_2 or CN (26 Da).

Reactions with Nitriles. The MO$^+$ did not evidence reaction with any nitrile, with the sole exception of ThO$^+$ + propionitrile, as discussed below—the detected MO$^+$−nitrile adducts are specified in Table 1. It is presumed that these adducts correspond to $M^{\delta+}{=}O^{\gamma-}$ coordinated to the intact nitrile, probably in an approximately end-on fashion: $CH_3{-}(CH_2)_n{-}C{\equiv}N{:}{-}M^{\delta+}{=}O^{\gamma-}$. The efficiency of such association reactions should increase with the size of the nitrile, as the number of vibrational modes to accommodate the internal energy of the complex increases.[45,46] Metastable decay on a time scale longer than that of LAPRD is possible, but the results in Table 1 provide an indication of the propensity of the MO$^+$-nitrile adducts to form and survive for at least ~100 μs. For AmO$^+$ and NpO$^+$ the data are sufficient to conclude that there appears to be a significant increase in AnO^+−nitrile adduct formation between propionitrile and butyronitrile. Propionitrile also appeared to form adducts more effectively than its dehydrogenated derivative, acrylonitrile. These observations are consistent with a role for the carbon chain in accommodating the initial complexation energy. As noted in Table 1, the amount of ablated NpO_2^+ was sufficient that a small amount of the NpO_2^+−butyronitrile adduct was detected. The exclusion of UO^+ and TmO^+ from Table 1 does not imply that these ions do not form nitrile adducts because both were ablated in only relatively small amounts (in the case of TmO^+ due to its small dissociation energy[54]).

Appreciable ablated MO^+ provided the advantage of assessing its reactions but introduced the possibility for O-transfer reactions which might interfere with interpretation of the naked M^+ reactivity results. Reactions such as shown in eqs 1 and 2 could not be differentiated.

$$M^+ + CH_nN \rightarrow M^+{-}\{CH_{n-2}N\} + H_2 \qquad (1)$$

$$MO^+ + CH_nN \rightarrow M^+{-}\{CH_{n-2}N\} + H_2O \qquad (2)$$

Reactions such as eq 2 can generally be dismissed as unimportant for the studied M based upon thermodynamic grounds.[29] Specifically, $H_2 + O \rightarrow H_2O + 491\ \text{kJ mol}^{-1}$ [55] requires that the M^+−O bond energy be less than ~500 kJ mol^{-1} for eq 2 to be thermochemically favored over eq 1, a condition fulfilled for few LnO^+ (Ln = Eu, Tm, Yb).[54] Based upon the known D[An−O][56] and the similarity between D[LnO] and $D[LnO^+]$,[54] it can be concluded that eq 2 should proceed only for AmO^+ among the AnO^+ studied here. Propitiously, those MO^+ (e.g., TmO^+ and AmO^+) which exhibit relatively small dissociation energies are ablated in insufficient quantities to account for the inferred M^+ chemistries.

With acetonitrile, Th^+, U^+, and Np^+ induced dehydrogentation to produce MC_2HN^+, presumed to be $M^+{=}(CH){-}C{\equiv}N$ in accord with the formation of the corresponding compounds for Sc^+ and Y^+.[57] The apparent formation of actinide carbenes is significant in view of the dominance of single σ-bonded An-C compounds in condensed phase organoactinide chemistry.[58,59] In addition, $MC_2H_3N^+$ adducts were detected for M = Th, Pu, and Am (Table 2). A LAPRD spectrum for the Np−Pu target and deuterated acetonitrile is shown in Figure 1, exhibiting the absence of reactivity of Pu^+ compared with Np^+. The complete absence of reactivity of both Pu^+ and Am^+, despite the formation of An^+−acetonitrile adducts, indicates that 5f → 6d promotion is necessary and that acetonitrile dehyrogenation proceeds by insertion to produce a $C{-}An^+{-}H$ intermediate.

For acetonitrile reacting with Th^+, U^+, Np^+, and possibly Pu^+, small amounts of a $M^+{-}\{14\}$ species were detected, presumed to be MCH_2^+, rather than MN^+ based upon thermodynamic considerations. Because thermodynamic data are sparse for the actinides and lanthanides, those for Ti^+ are considered to support this conjecture:[3,55]

$$Ti^+ + C_2H_3N + 190\ \text{kJ mol}^{-1} \rightarrow TiN^+ + C_2H_3 \qquad (3)$$

$$Ti^+ + C_2H_3N + 70\ \text{kJ mol}^{-1} \rightarrow TiCH_2^+ + HCN \qquad (4)$$

Also, the absence of $M^+{-}\{14\}$ upon reaction with CD_3CN supports this presumption (e.g., see Figure 1; note that MCD_2^+ is isobaric with MO^+).

The results for propionitrile and acrylonitrile are included in Table 2. In addition to the tabulated $MC_2H_2^+$ (and/or MCN^+) products, minor peaks attributable to $MC_2H_4^+$ were evident for M = Th and Np upon reaction with propionitrile. Although the focus of the comparative reactivity results is on the dehydrogenation products, the substantial products corresponding to $M^+{-}\{26\}$ should be addressed. The 26 Da ligand can reasonably be assigned to C_2H_2 and/or CN (an ambiguity which could be resolved employing deuterated nitriles). In co-ablation of solid AnO in a polyimide matrix under high-energy conditions, radicals such as CN can combine with An^+, and $An^+{-}\{26\}$ peaks were assigned as $AnCN^+$.[60] Under the moderately hyperthermal LAPRD conditions, thermodynamic considerations can be applied. From propionitrile, abstraction of CN (+ C_2H_5) requires ~500 kJ mol^{-1} whereas the formation of C_2H_2 (+ CH_3N) requires ~300 kJ mol^{-1}.[55] The An^+−CN bond energy is likely greater than that for $An^+{-}\{C_2H_2\}$: values are not available for the actinides but estimates can be inferred from $D[Sc^+{-}\{C_2H_2\}]$ (220 kJ mol^{-1})[3] vs $D[Pr^+{-}\{CN\}]$ (590 kJ mol^{-1}).[54,55,61] The thermochemisty is not definitive but that the $An^+{-}\{26\}$ species did not appear upon reaction with acetonitrile suggests C_2H_2 as the primary 26 Da ligand because abstraction of CN from acetonitrile, like propionitrile, requires ~500 kJ mol^{-1}.[55] The 26 Da ligand is tentatively assigned as C_2H_2, with the caveat that CN may be significant—the reactivity assessments are independent of this assignment.

The primary results for the propionitrile and acrylonitrile reactions are summarized by the R[D/A] values in Table 2. As with acetonitrile, it is apparent that Pu^+ and Am^+ complex with these larger nitriles but fail to induce C−H activation and dehydrogenation. Nor does Tm^+ dehydrogenate these substrates, and it is evident that f → d promotion to provide two non-f valence electrons is requisite for both the lanthanides and transneptunium actinides. The chemical activity of the 5f electrons for the An^+ preceding Pu^+ cannot be directly assessed and it is feasible that they play a role in C−H activation. The data for acrylonitrile suggest that it is less readily dehydrogenated than propionitrile, in contrast to the more facile dehydrogenation of unfunctionalized alkenes vs alkanes.[13] For hydrocarbons and nitriles, dehydrogenation of a saturated C_mH_n or alkyl C_mH_nCN is generally less endothermic than dehydrogenation of the corresponding C_mH_{n-2} or $C_mH_{n-2}N$.[55] The discrepant dehydrogenation reactivites of alkyl nitriles vs alkanes presumably reflects the essential role of complexation to provide a sufficiently stable and long-lived adduct which may undergo C−H activation. For propionitrile and acrylonitrile, the carbon backbone is doubtless too short to allow an "end-on" coordinated M^+ (i.e., $\{M^+{-}{:}N{\equiv}C^{\alpha}{-}C^{\beta}H_n\ ...\}$) to approach and insert into a remote C−H bond. Rather, the primary mechanism is presumed to involve "side-on" coordinated $M^+{-}\{{:}N{\equiv}C^{\alpha}\text{-}\}$[43]

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with the M^+ inserting into a nearby C−H bond, probably at the C^β site. The additional π-bond of acrylonitrile, $H_2C{=}CH{-}C{\equiv}N$, might be expected to enhance "side-on" coordination compared with propionitrile, $H_3C{-}CH_2{-}C{\equiv}N$, but an appreciable enhancement in adduct formation was not discerned for acrylonitrile, perhaps reflecting the reduction in C−H vibrational modes available to stabilize the M^+−acrylonitrile complex.

A few additional products of reactions with propionitrile are noted in Table 2; the products comprising multiple ligands presumably resulted from a product complex coordinating to a second propionitrile molecule. The "$ThO\{C_2H_2\}\{C_3H_5N\}^+$" complex is noteworthy in that the availability of only one free valence electron at the metal center of ThO^+ implies a noninsertion, multi-centered activation process. This is a case where "C_2H_2" may actually correspond to CN and the product may actually be a coordinated cyanate, $\{C_3H_5N\}\{Th^+{-}OCN\}$, or oxycyanide, $\{C_3H_5N\}\{O{=}Th^+{-}CN\}$, the latter of which would satisfy the distinct preference for Th to exist in a tetravalent state.[19] The $\{NpO_2{}^+\}\{C_3H_5N\}$ adduct is distinctive with regards to congestion about the metal center.

The results for butyronitrile, isobutyronitrile, and valeronitrile are compiled in Table 3. Most of the important products are included in the table but additional cracking products appeared for the more reactive M^+, as is seen for Np^+ in the Np−Am + butyronitrile product mass spectrum shown in Figure 2. The dehydrogenation activities for each of these three nitriles are in correspondence with the results for the shorter chain nitriles: Np^+ and Tb^+ induced dehydrogenation while Am^+ was apparently inert. Whereas Tm^+ did not detectably dehydrogenate the smaller nitriles, some dehydrogenation was evident with the butyronitriles. The greater dehydrogenation activity of Tm^+ vs Am^+ may be attributed to the greater f → d promotion energy for the latter: 245 kJ mol^{-1} Am^+ [27] vs 199 kJ mol^{-1} Tm^+.[52] Also noted in Table 3 are $NpC_8H_{10}N_2{}^+$ and $TbC_8H_{10}N_2$ produced from reactions with two butyronitrile molecules. These bis-complexes which result from a net double-dehydrogenation of two butyronitrile molecules could correspond to $\{C_4H_5N{:}\}$-$M^+\{{:}NC_4H_5\}$ and/or $\{C_4H_3N{:}\}M^+\{{:}NC_4H_7\}$.

A remarkable result was that whereas Am^+ did not dehydrogenate the butyronitriles, significant amounts of $AmC_2H_4{}^+$ were produced ($AmC_2H_4{}^+$ was also produced from valeronitrile); the abundance of $MC_2H_4{}^+$ was greater for Am than for Tm. This suggests a mechanism which does not require C−C activation by direct insertion of a M^+ with two non-f valence electrons. Based upon the data in Table 3, it appears that the Am^+-mediated formation of C_2H_4 from isobutyronitrile is somewhat more facile than from butyronitrile. Assuming "side-on" coordination, a reasonable mechanistic scenario can be proposed in analogy with the "ion/dipole" mechanism discerned by Eller et al.[32,33,38] The proposed intermediate resulting from "side-on" coordination to butryonitrile would be $\{H_3C{-}HC^{\cdot+}$-$CH_3\}{-}\{AmCN\}$, and it is apparent why isobutyronitrile should relatively readily produce this 2° carbonium ion via cleavage of its C−CN bond. Exchange of Am and a CH_3 group from the carbonium ion would result in the products, $AmC_2H_4{}^+ + H_3C{-}C{\equiv}N$. The formation of C_2H_4 and acetonitrile from either butyronitrile or isobutyronitrile is endothermic by only ∼100 kJ mol^{-1}, an energy undoubtedly smaller than the $Am^+{-}C_2H_4$ bond energy.[3]

To further assess the role of the N: functionality, experiments were carried out in which ions ablated from the Am-containing targets were exposed to pentane. No adduct or dehydrogenation products were detected to abundance ($A[ML^+]$) limits of 0.1 for Tb^+, 0.9 for Tm^+, and 0.2 for Am^+. Minor amounts of products were identified for Np^+/NpO^+: $A[NpC_5H_{10}{}^+] = 0.5$; $A[NpC_5H_8{}^+] = 0.5$; and $A[NpOC_5H_{10}] = 0.4$. The minor adduct and dehydrogenation product yields accord with the difficulty in activating alkanes and confirm the central role of the coordinating N: site in facilitating adduct formation and C−H activation.

Reactions with Butylamine. The primary results for the reactions with butylamine are summarized in Table 4 and a mass spectrum for ablation of Am^+/AmO^+ into butylamine is shown in Figure 3. The mass of the peak marked with an asterisk in Figure 3 corresponds to that of $AmCH^+$; based on results for other metal ions and thermodynamic considerations, it is judged that this peak is more likely attributable to metastable decay of a heavier complex ion in the RTOF-MS,[62] although this could not be verified.

The results for dehydrogenation of butylamine by Am^+, Np^+, and Tb^+ qualitatively coincide with those for the nitriles in that Am^+ was the least reactive and induced only single-dehydrogenation whereas both Np^+ and Tb^+ effected both single and double H_2 elimination. It is significant that whereas Am^+ was essentially inert with the alkyl nitriles it exhibited some reactivity with butylamine. The enhanced reactivity of Am^+ with butylamine might reflect insertion into a proximate N−H bond. Alternatively,[49] amine dehydrogenation might proceed by C−H activation; the proposal of N−H activation is based on the distinctive reactivity of Am^+ with the amine. Assuming N−H activation, the $MC_4H_9N^+$ probably correspond to the imine rather than the less stable enamine complexes.[32,63] Presuming that the M^+ is coordinated to the N: functionality in the imine, the second dehydrogenation by Np^+ and Tb^+ could occur by remote functionalization to produce $H_2C{=}CH{-}CH_2{-}CH{=}NH$ or by insertion into the remaining N−H bond to produce butyronitrile, $CH_3{-}(CH_2)_2{-}C{\equiv}N$. In addition to the dehydrogenation product, MCH_3N^+ (+ C_3H_8) was detected for Np^+, Tb^+, and even Am^+−insertion of M^+ into the $C_\alpha{-}C_\beta$ bond of butylamine would presumably result in the carbene, $M^+{=}CH{-}NH_2$. Referring to Figure 3, it is evident that the "$AmCH_3N^+$" peak was quite small and broad; since this butylamine fragment requires C−C activation (presumably by M^+ insertion), its formation in even minuscule quantities via Am^+-attack is remarkable and may reflect the energy released in formation of the M^+−:N bond, which could enable Am^+ insertion into a C−C bond by a "curve-crossing" mechanism.[13,29] Based upon the relatively minor reactivity of Am^+, it can be concluded that the observed dehydrogenation reactions of M^+ with butylamine require insertion of a M^+ with two non-f electrons into a C−H or N−H bond.

The reactivity of Np^+ with butylamine was extreme, and only a minuscule amount of unreacted Np^+ remained; the nearly complete depletion of Np^+ indicates that the local reactant pressure was sufficient that most M^+ experienced multiple encounters with reactant molecules. Reaction with two butylamine molecules was indicated by the appearance of the bis-coordinated species footnoted in Table 4, $NpC_8H_nN_2{}^+$ ($n = 16$, 18, 20) and $TbC_8H_nN_2{}^+$ ($n = 14$, 16, 18, 20). For the mono-coordinated M^+ products, only single- and double-dehydrogenation of the amines was evident, and the appearance of $C_8H_{16}N_2$ (net triple-dehydrogenation) and $C_8H_{14}N_2$ (net quadruple-dehydrogenation) implies that a M^+ coordinated to a dehydro-

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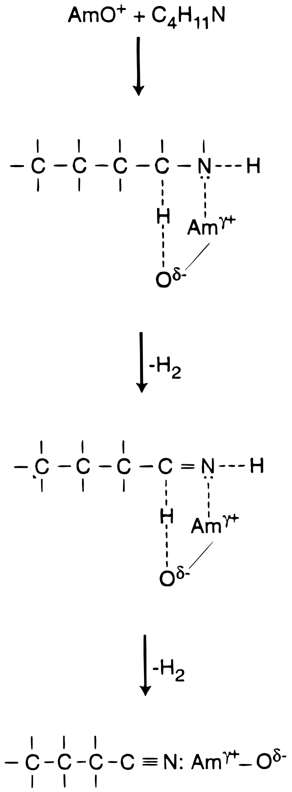

Figure 4. Schematic representation of a postulated mechanism for dehydrogenation of butylamine by AmO^+.

genated C_4H_7N was able to coordinate/dehydrogenate a second $C_4H_{11}N$. Assuming the dehydrogenation of the second amine to proceed via M^+ insertion into a N−H or C−H bond, this process indicates that the two non-f valence electrons remain available for bonding in the $M^+-\{:NC_4H_7\}$ complex and that the $M^+-:N$ bonding is primarily of electrostatic, rather than covalent, character.

In addition to the products from reactions of the three naked M^+, the oxo-ligated species, MO^+, also reacted with butylamine, in distinct contrast to the nitriles, where MO^+−nitrile adducts were generally the only significant products. Results for reactions of NpO^+, AmO^+, and TbO^+ with butylamine are given in Table 4 and Figure 3 shows a mass spectrum of the {AmO^+ + butylamine} products. Despite the small ablation yield of the reactant ion, AmO^+, it is apparent that this oxide exhibited a degree of reactivity comparable to that of NpO^+ and TbO^+. It is certain that TbO^+ does not comprise two non-4f electrons at the metal center which would enable bond cleavage via an insertion process. Similarly, the valence f-electrons of the two AnO^+ are presumably in relatively localized 5f orbitals;[27] the similar reactivities of the lanthanide oxide ion, TbO^+, and the AnO^+ argues against participation of the 5f electrons of the latter in the reaction mechanisms. In Figure 4 is presented a schematic representation of a potential mechanism which might achieve H_2 elimination via a multicentered AmO^+-butylamine intermediate without the necessity for insertion into a N−H or C−H bond. That such reactions were not evident for the nitrile substrates implicates the $:NH_2$ functionality as requisite. The formation of MO^+-NH_3, for example, presumably results from transfer of an H atom from the alkyl chain, possibly via a C- - -H- - -O hydroxyl intermediate such as shown in Figure 4. Both naked Np^+ and Tb^+ were more reactive than their oxo-ligated ions, MO^+, suggesting that the insertion processes are more efficient. In the case of Am^+, the addition of the oxo-ligand introduces an alternate pathway which does not require f → d promotion and the reactivity of AmO^+ is greater than that of Am^+. The effect of oxo-ligation on activation of butylamine is reminiscent of the recent discovery by Cornehl et al. [15] of oxo-ligation as a "reactivity switch" in gas-phase reactions of lanthanide ions with butadiene. The present results demonstrate a similar effect with the actinides and a non-π-bonded substrate. Such dramatic effects of ligation on the activation of organic molecules is of fundamental interest and is relevant to understanding interactions of reactant molecules with catalysts.

Americium Dimer. A small amount of the americium dimer ion, Am_2^+, was detected in some ablation mass spectra (e.g., see footnote *i* of Table 3). Characteristic metal oxide clusters, such as Am_2O^+ and $Am_2O_2^+$, were concurrently produced in greater abundances. It is presumed that the oxide clusters can be represented as $Am-\{\mu\text{-}O\}-Am^+$ and $Am-\{\mu\text{-}O\}_2-Am^+$, in which the electropositive Am assume formal valence states of Am^+, Am^{2+}, or Am^{3+}. Actinide dimer ions, An_2^+, were not detected for any of the other studied actinides and the distinctive appearance of Am_2^+ can be attributed to coalescence of the dominant naked ion, Am^+, and neutral Am. Transition metal−An and An−An bonded species have been elusive in organoactinide chemistry[58] yet are of particular interest for defining the role of the 5f orbitals in intermetallic bonding. The issue of actinide 5f bonding remains indeterminate even for extensively studied solids comprising actinides through Pu,[64] and investigations of small actinide clusters could illuminate this theme. The synthesis of the Am_2^+ dimer presents the possibility for probing the nature of An-An bonding in that region of the series where the 5f orbitals become fully localized relative to the outer valence 6d/7s electrons and accordingly increasingly nonbonding. The optical spectroscopy of matrix isolated species such as Am_2 could serve to elucidate the extent of 5f bonding and the effect of the Am−Am interaction on the 5f energy levels; spectroscopic studies of matrix-isolated laser-ablated Ln_2 have been reported.[65]

Conclusions

Gas-phase reactions were carried out with representative Ln^+ and several An^+ and AnO^+ from the first half of the actinide series. The reactant substrates employed, nitriles and butylamine, comprise the coordinating N: functionality and provide a basis to assess the role of complexation on the reactivities of f-element ions. Of particular interest was the role of the 5f electrons and manifestations of the transition, in the vicinity of Am, from multivalent d-block transition-like behavior (e.g., U) to primarily trivalent lanthanide-like behavior (e.g., Am). With the exception of ThO^+, which is distinctive among the AnO^+, all other MO^+ were inert toward the nitriles, forming only the adduct complexes, presumably $\{O{=}M^+\}-\{:N{\equiv}C-C\cdots\}$. This inert character reflects the dearth of non-f valence electrons at the metal centers in the MO^+ to enable C−H activation via insertion. The formation of substantial amounts of oxide−nitrile adducts attests to the efficacy of the :N functionality in complexing cations. The behavior of the naked M^+ toward the nitrile substrates was generally remiscent of results with alkenes except that the chemically inert metal ions more efficiently complexed to the $:N{\equiv}C-C-C\cdots$ species. Both Np^+ and Tb^+ were substantially more effective at dehydrogenating the nitriles than were Pu^+, Am^+ and Tm^+, consistent with a mechanism involving M^+ insertion into a C−H bond and requiring two non-f valence electrons at the metal center to form the two σ-type covalent

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(64) Manes, L., (Ed.) *Actinides: Chemistry and Physical Properties*; Springer-Verlag: Berlin, 1985.

(65) Suzer, S.; Andrews, L. *J. Chem. Phys.* **1988**, *89*, 5514.

bonds in the C−M^+−H activated intermediate. This result indicates that the 5f electrons of the transneptunium An^+ are chemically inert (localized) with respect to this activation process. The chemically inert M^+ formed significant amounts of M^+−nitrile adduct, establishing that complexation is necessary but not sufficient for activation of alkyl C−H bonds by f-element M^+. A somewhat surprising finding was the formation of substantial $MC_2H_4^+$ for all of the studied M^+: it is proposed that some of these products could result from an "ion/dipole" mechanism.

The naked metal ions, Np^+, Tb^+, and Am^+, exhibited reactivity with butylamine, with Am^+ the least reactive. Dehydrogenation may have proceeded via N−H or C−H activation. In contrast to the naked M^+, NpO^+, TbO^+, and AmO^+ were approximately comparable in their reactivities with butylamine (dehydrogenation and cracking) and it is proposed that these reactions proceeded via a common mechanism which involves a multicentered activated complex and is less efficient than activation by direct insertion. Finally, the preparation of Am_2^+ was noted with regard to its novelty and potential significance for elucidating An−An bonding.

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