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Articles

High-Energy Organometallic Chemistry of Curium: Laser Ablation of Cm_7O_{12} Dispersed in Polyimide

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Gas-phase curium organometallic ions were synthesized by metal/polymer co-ablation. Vacuum laser ablation of a dilute dispersion of curium oxide in polyimide resulted in several organocurium ions, evidently formed by nucleation of Cm^+ and various neutral polymer fragment radicals in the ablation plume. The compositions and abundances of simple species, such as CmC_2^+, CmC_2H^+, and $CmCN^+$, can be rationalized on the basis of the electronic structure and energetics of the curium ion, Cm^+. The results for curium are in accord with a general thermochemical model previously employed to understand the organometallic speciation of preceding actinides. The identification of the above-specified species, along with several larger organocurium ions, extends the realm of organoactinide chemistry; specifically, it represents identification of a series of unique curium complexes which presumably incorporate substantially covalent (σ) Cm−C bonding. Also identified in the ablation plume were small clusters incorporating two or three curium atoms. Simple clusters, such as $Cm_3O_4^+$, reveal a trivalent, lanthanide-like character for curium and reflect the tendency toward bulk, solid-state chemical behavior upon coalescence of only a few atoms. Finally, a notable ancillary observation was the formation of several clusters in which C_2 evidently substituted sequentially for an O atom, revealing the pseudo-oxygen character of the dicarbide moiety.

Introduction

Developing the field of organoactinide chemistry beyond uranium is a prominent goal in view of the substantial variations in chemical behavior that occur across the actinide series and the central issue regarding the role of the quasi-valence 5f electrons in organometallic bonding. We have developed techniques to examine conventional gas-phase metal ion−organic molecule reactions for transuranic actinides and have carried out such studies for Np, Pu, Am, and Cm.[1−3] These archetypical reactions were generally dominated by elimination of a stable moiety from the reactant molecule, such as H_2 from alkenes, resulting in an actinide ion, An^+, electrostatically (π) bonded to a nonradical, intrinsically stable, organic moiety. An illustrative example is dehydrogenation of cyclohexadiene to produce an actinide−benzene complex ion: $An^+ + cyclo\text{-}C_6H_8 \rightarrow An^+{-}C_6H_6 + H_2$. Several corresponding π-bonded organoactinide complexes have been isolated in the condensed phase, particularly those incorporating allyl, cyclopentadienyl (Cp), and cycooctatetraene (COT) ligands, including the celebrated actinocene sandwich complexes, COT−An−COT.[4] Solid-state π-bonded organometallics have been prepared on the microscale for actinides as heavy as californium: $Cf(Cp)_3$.[5]

The generally more challenging synthesis of organometallics incorporating An-C σ-bonds has been dominated by the least radioactive actinides, Th and U, as summarized by Marks.[6] Representative compounds include $Cp_3An(CH_3)$ and $Cp^*_2An(CH_2C_6H_5)_2$ (An = Th, U; Cp* = pentamethylcyclopentadienyl). Among the few isolated transuranic σ-bonded organoactinides is $Cp_3Np(n\text{-}C_4H_9)$. In contrast to the case for the d-block transition metals,[7] actinide carbene (alkylidene) and carbyne (alkylidyne) chemistry represents virgin territory. In the Transuranium Research Laboratory at Oak Ridge National Laboratory (ORNL), we have employed a technique to prepare a variety of gas-phase organometallic species which incorporate unique types of actinide−carbon bonding. The method, referred to as metal−polymer co-ablation (MPCA), entails pulsed UV

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laser ablation in a vacuum of a solid target comprised of an actinide oxide in a polymer matrix, such as polyimide. Ablation of such a target results in a dense ablation plume, which incorporates actinide ions, An^+ and AnO^+, and highly reactive organic fragments from the polymer, such as C_2, C_2H, CN, etc.[8] Several neutral radicals, including C_2H, CN, C_2H_3, and C_4H, were specifically identified as being emitted from polyimide under MPCA conditions.[9]

Metal ion–organic radical aggregation in MPCA has been found to produce substantial yields of organoactinide ions, including AnC_2^+, AnC_2H^+, $AnCN^+$, and several larger complexes, for An = U,[10] Np, Pu,[11] and Am.[9] The substantial variations in organoactinide abundance distributions across the series are comprehensible in the context of direct actinide–carbon bonding and the differing electronic structures and energetics of the actinide ions. On the basis of the results of more conventional gas-phase metal ion–molecule reactions, we have determined that the 5f electrons of the transneptunium actinides do not directly participate in such An–C or An–H bonding/activation; the role of 5f bonding in organouranium and organoneptunium complexes remains less certain.

We have now extended the MPCA method to the next member of the actinide series, Cm. Examination of organoactinide chemistry by conventional condensed-phase synthetic approaches becomes increasingly intractable upon proceeding across the actinide series. Studies as described here are valuable for providing fundamental insights into the nature of the actinide series of elements, particularly the systematics of organoactinide chemistry. Curium, the 5f homologue of Gd, is a singular member of the actinide series because both the free neutral atom and the +1 ion exhibit a ground-state electronic configuration comprising a stable, half-filled $5f^7$ sub-shell. The Cm^+ ground state, $[Rn]5f^7 7s^2$, furthermore comprises a filled $7s^2$ valence orbital and ostensibly should be chemically inert.

We report here on the preparation of organocurium species by the MPCA method, employing polyimide as the reactive matrix. The species' compositions and abundance distributions are compared with those for the lighter actinides and are interpreted in the context of the electronic structure and energetics of the curium ion, Cm^+. Also discussed is the ion–radical coalescence mechanism by which these unique, "high-temperature" organometallic species may form. Small curium cluster ions (i.e., species with ≥2 Cm atoms) were also produced, and their compositions reveal important aspects of curium chemistry as well as illuminate the bonding character of elementary organic ligands, such as C_2, with actinides.

Experimental Section

The MPCA experimental procedures have been described elsewhere,[9–11] and only a brief description of the technique and specific details pertinent to the present study are included here. The ablation target was prepared using a dispersion of 1.5 mg of $^{248}Cm_7O_{12}$ (~97% ^{248}Cm; ~3% ^{246}Cm) in 10 mg of polyimide (PI), $[-C_{23}H_{10}O_5N_2-]_n$; this corresponds to 0.54 μmol of ^{248}Cm and 58 μmol of C (as PI) or 0.9 atom % curium relative to carbon. A smaller amount of ^{248}Cm was employed compared with the amounts of lighter actinides used in previous MPCA studies due to the scarcity of the ^{248}Cm isotope, produced in the DOE heavy-element program at ORNL. The ^{248}Cm has an α-decay half-life of 340 ky (with an ~8% spontaneous fission channel). The more abundant ^{244}Cm isotope has a half-life of only 18 y and a more intense γ-radiation field. Previous MPCA targets incorporating lower-*Z* actinides were prepared with a 3 mm diameter pellet press, but a smaller 1.6 mm diameter pellet was prepared in the present study by compressing the ^{248}Cm–PI mixture in a custom die.[3]

The 308 nm output of a XeCl excimer laser was focused to a spot of area ~0.5 mm^2 to produce an estimated irradiance on the target of ~10^8 W cm^{-2}. The positive ions from an ~6 mm^2 cylindrical portion of the expanding ablation plume were orthogonally injected into the −2 kV flight tube of a reflectron time-of-flight mass spectrometer (RTOF-MS) after a time delay, t_d, following the laser pulse. The distance between the target and the ion injection region was ~3 cm, and typical values of t_d were in the range of 30–70 μs; this corresponds to ablated ion velocities in the approximate range of 1–0.4 km s^{-1}. A ^{248}Cm ion propagating at 1 km s^{-1} possesses a translational energy (temperature) of ~1.3 eV (~15 kK).

Results and Discussion

Organocurium Species. A typical mass spectrum for the small ions comprised of a single Cm atom is shown in Figure 1. Only singly charged positive ions were considered in the present study; the plethora of polymer fragment ion peaks in the relatively low mass regions of the spectra (e.g., Figure 2) precluded effective identification of Cm-containing doubly charged ions. The mass spectrometer was not configured to ionize ablated neutrals or detect negative ions. The value of t_d used to obtain this spectrum was 50 μs, which provided high product ion intensities and good mass resolution. The relative intensities of different product ions were essentially invariant with t_d. The intensity of the peak assigned as $^{246}Cm^+$ in Figure 1 is in reasonable accord with the anticipated level (~3%) of this isotope; the exact concentration of ^{246}Cm was uncertain, and the fact that the $^{246}Cm^+$ peak intensity suggests a concentration of somewhat greater than ~3% may be partly due to detector saturation and peak broadening for the very intense $^{248}Cm^+$ peak. Significant amounts of other Cm isotopes were not expected or detected.

The peak at *m/z* 274 Da has been assigned as $CmCN^+$, rather than isobaric $CmC_2H_2^+$, on the basis of comparative lanthanide MPCA results employing polyimide and the nitrogen-free polymer polystyrene.[11] Other assignments similarly assume a CN rather than a C_2H_2 moiety, consistent with the substantially stronger bonding interaction expected between a Cm^+ metal center and an unsaturated radical species, such as CN, rather than a stable species, such as C_2H_2 (acetylene). For the CmC_{2n}^+ and $CmC_{2n}H^+$ species of particular interest, the compositional assignments were unambiguous.

Previous MPCA studies with lighter actinides and lanthanides[9–11] established that reproducible differences in complex ion abundances were evident, which could be understood in the context of the electronic configuration and energetics of the metal ion, An^+ or Ln^+. These earlier results provided strong evidence that

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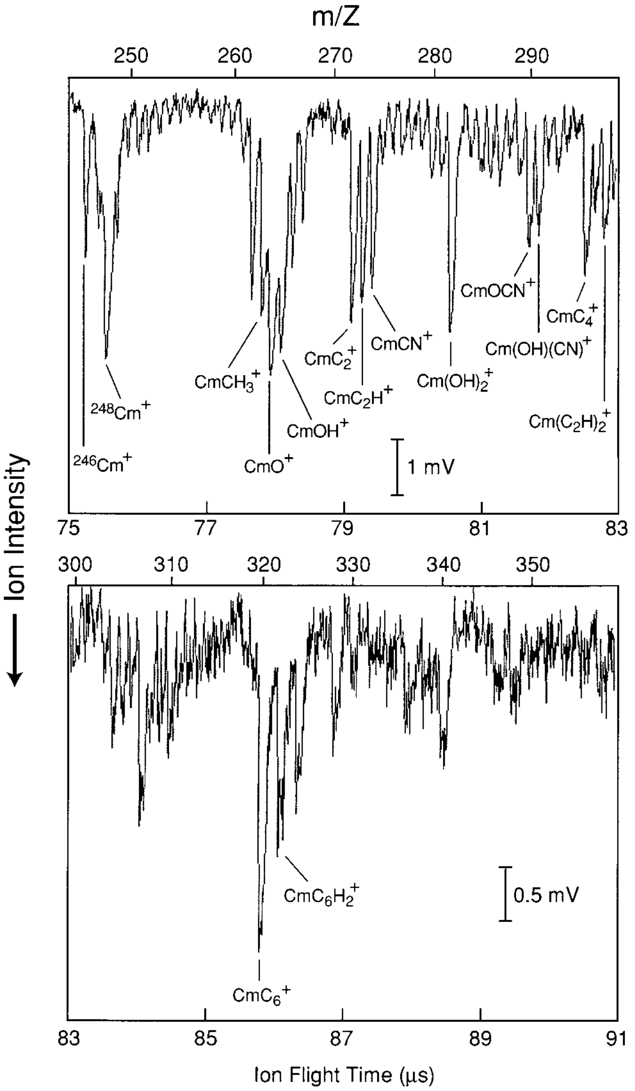

Figure 1. Laser ablation mass spectrum of small organocurium ions ($t_d = 50\ \mu$s). As discussed in the text, several of the peak assignments are speculative; for example, the "Cm(C$_2$H)$_2^+$" peak may more likely be Cm(C$_2$)(CN)$^+$.

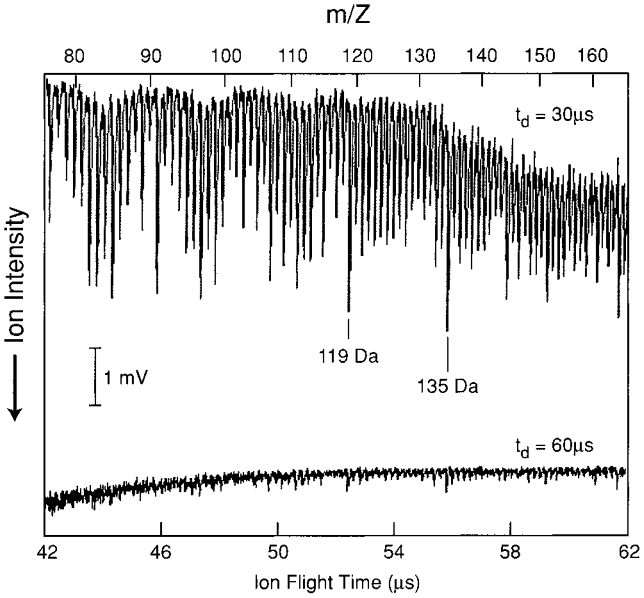

Figure 2. Laser ablation mass spectra of polymer fragment ions: (top) $t_d = 30\ \mu$s; (bottom) $t_d = 60\ \mu$s. The two spectra are superimposed with the same vertical intensity scales but different zero levels, which are approximated by the respective baselines; the relative peak intensities are given by the individual peak heights relative to these baselines.

Table 1. Configurations and Energies[a] for Ground [G], Monovalent[b] [I], and Divalent[c] [II] An^{+}[d]

An$^+$	An$^+$[G]	An$^+$[I]	ΔE[G→I]	An$^+$[II]	ΔE[G→II]
U$^+$	$5f^37s^2$	$5f^36d^17s^1$	3	$5f^36d^17s^1$	3
Np$^+$	$5f^46d^17s^1$	$5f^46d^17s^1$	0	$5f^46d^17s^1$	0
Pu$^+$	$5f^67s^1$	$5f^67s^1$	0	$5f^56d^17s^1$	104
Am$^+$	$5f^77s^1$	$5f^77s^1$	0	$5f^66d^17s^1$	245
Cm$^+$	$5f^77s^2$	$5f^87s^1$	25	$5f^76d^17s^1$	48
Bk$^+$	$5f^97s^1$	$5f^97s^1$	0	$5f^86d^17s^1$	147
Cf$^+$	$5f^{10}7s^1$	$5f^{10}7s^1$	0	$5f^96d^17s^1$	(~250)[c]

[a] ΔE values are promotion energies in kJ mol^{-1}. [b] Lowest energy configuration with at least one spin-unpaired non-5f valence electron. [c] Lowest energy configuration with at least two spin-unpaired non-5f valence electrons. [d] Most configurations and energies are from Fred and Blaise;[12] the estimate for Cf$^+$[II] is from Brewer.[13]

the observed MPCA chemistry is dominated by ground-state M$^+$. The promotion energies to obtain An$^+$ in electronic configurations suitable for covalent bond formation are given in Table 1 for the actinides U through Cf.[12,13] A "monovalent" An$^+$, denoted as "An$^+$[I]," is defined as an ion capable of forming a single covalent σ-type organometallic bond; and a "divalent" An$^+$, "An$^+$[II]," as being capable of forming two σ-type bonds. Implicit in Table 1 is the presumption that the 5f electrons cannot effectively participate in σ-type bonding, a premise established for C−H bond activation by transneptunium actinides from the results of gas-phase ion−molecule reaction studies.[1−3] The presumed necessity for promotion of ground-state Cm$^+$, from its closed-shell $7s^2$ configuration to a $6d^17s^1$ configuration, is based on the previously determined diminished capability of Cm$^+$ to activate hydrocarbons;[3] the inert character of the $7s^2$ configuration is also consistent with the low reactivity of ground-state Lu$^+$, which has a $4f^{14}6s^2$ valence shell configuration.[14−16]

The correlation between the promotion energies for U$^+$, Np$^+$, Pu$^+$, and Am$^+$ given in Table 1 and the organometallic product ion abundance distributions has been discussed previously in a somewhat different context.[1−3] In the present discussion, the presumed dominance of (polarized) covalent, rather than predominantly ionic, bonding is emphasized; the presumption of primarily covalent bonding character is consistent with the second and third ionization energies of curium (and other actinides), which are much larger than the electron affinities of even highly electronegative radical ligands.[3] The basic concept underlying the interpretation of the product ion abundance distributions is illustrated by the variations in the comparative abundances of the elementary complexes AnC$_2^+$ and AnC$_2$H$^+$.

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The latter complex is presumed to comprise a metal center attached to an acetylide radical through a single σ-type bond: $An^+{-}C{\equiv}CH$. This bonding configuration requires a single (non-5f) spin-unpaired valence electron at the metal center, a condition satisfied by the monovalent configurations given in Table 1, An^+[I]. Only U^+ and Cm^+ do not exhibit a monovalent ground state (i.e., $\Delta E[G{\to}I] > 0$); the value of $\Delta E[G{\to}I]$ for Cm^+ is nontrivial (25 kJ mol^{-1} for Cm^+ vs only 3 kJ mol^{-1} for U^+). The AnC_2^+ species are presumed to be represented as An^+ metal centers bonded to a dicarbide represented as C=C. This presumption is based primarily on a structual study of matrix-isolated CeC_2.[17] The geometry of these types of metal dicarbides is uncertain, but a linear structure has been postulated for most LnC_2 molecules,[17] whereas a T-shaped geometry has been proposed for YC_2.[18] Yttrium is a quasi-lanthanide, and the bonding in Y_3C_2 and $Y_3C_2^+$ has been assessed.[19] Regardless of the structure(s) of the actinide dicarbide species, the quasi-oxygen character of the C_2 moiety[20] (vide infra) implies formation of two bonds of indeterminate ionicity; this requires an actinide metal center possessing a divalent configuration with two non-5f valence electrons, the lowest energy of which are $[Rn]5f^{n-2}6d^17s^1$ for the An^+ included in Table 1. The promotion energies required to achieve the An^+[II] configurations, $\Delta E[G{\to}II]$, range from 0 for Np^+ to 245 kJ mol^{-1} for Am^+. In a comparison of Np^+ and Am^+, both should exhibit comparable propensities to attach to C_2H in the ablation plume (because $\Delta E[G{\to}I] = 0$ for both), whereas the large $\Delta E[G{\to}II]$ value for Am^+ should diminish the degree of attachment of Am^+ to C_2. This can be restated in terms of the following estimate for the ligand detachment energy: $D[An^+[II]{-}L] \approx D[Np^+{-}L] - \Delta E[G{\to}II]$. This approximate relationship assumes that the bonding between all An^+[II] species and a divalent ligand (e.g., C_2) are similar within this region of the actinide series and that the intrinsic bonding energy is approximated by $D[Np^+{-}L]$, because Np^+ exists in a divalent ground state.

The ablation plume is sufficiently energetic to effect significant actinide atom ionization. Given that actinide ionization energies are ~6 eV (=580 kJ mol^{-1}), it might be anticipated that thermochemical disparities significantly smaller than this—such as variations in promotion energies of $\lesssim$250 kJ mol^{-1}—might be obscured in processes occurring in the nascent plume environment. However, it has been clearly demonstrated that consistent and significant differences between $I\{An^+[II]{-}L_{II}\}/I\{An^+[I]{-}L_I\}$ (where L_{II} and L_I represent divalent and monovalent ligands, respectively) for different actinides were well-understood in the context of differences between the respective $\Delta E[G{\to}II]$ values. For example, $I[NpC_2^+]/I[NpC_2H^+] > 1$ vs $I[AmC_2^+]/I[AmC_2H^+] < 1$.[9,11] The more general validity of such a qualitative thermochemical interpretation of MPCA complex ion abundances was confirmed by studies with other actinides and several lanthanides.[10,11] The manifestation of thermochemically systematic chemistry in the ablation plume suggests that nucleation between An^+ and ablated radicals occurs primarily in a lower energy portion of the expanding ablation plume, after the initial and highly energetic ionization/fragmentation processes.

As is seen from the values in Table 1, the energetics of the Cm^+ ion are somewhat unique among the prevalent actinides. On the basis of the orbital-filling trend exhibited by the neighboring actinides, a $5f^87s^1$ ground state would be expected for Cm^+, but the stability afforded by the half-filled 5f subshell results instead in a $5f^77s^2$ ground-state configuration, 25 kJ mol^{-1} below the monovalent state, $5f^87s^1$, and 48 kJ mol^{-1} below the divalent state, $5f^76d^17s^1$. (In notable contrast, the ground state of homologous Gd^+ is "divalent" $[Xe]4f^75d^16s^1$.) The closed-valence-shell $7s^2$ electronic configuration is evidently chemically inactive,[3] and ground-state Cm^+ could accordingly be considered as an inert ion. However, both of the Cm^+ promotion energies, 25 and 48 kJ mol^{-1}, are minor compared with typical $M^+{-}C$ covalent bond energies, and behavior essentially similar to that of U^+ and Np^+ would be anticipated—i.e., a greater stability of the double-bonded divalent vs single-bonded monovalent complexes.

Although a covalent bonding model employed on the basis of the considerations discussed above provides good correlation with organoactinide speciation, it should be noted that qualitatively similar results regarding the comparative stabilities of "monovalent" and "divalent" actinide complexes are obtained by considering the variation in the third ionization energy, $IE[An^{2+}{\to}An^{3+}]$ (which is closely related to $\Delta E[I{\to}II] = \Delta E[G{\to}II] - \Delta E[G{\to}I]$), to predict the propensity to produce an ionic "divalent" complex ion, formally $\{An^{3+}{-}L_{II}{}^{2-}\}^+$. Specifically, the stabilities of $\{An^{3+}{-}L_{II}{}^{2-}\}^+$ relative to $\{An^{2+}{-}L_I{}^-\}^+$ should increase in the reverse order of the ionization energies: $IE[U^{2+}] < IE[Np^{2+}] < IE[Cm^{2+}] < IE[Pu^{2+}] < IE[Am^{2+}]$.[21] However, the second and third ionization energies of the actinides, typically ~12 and ~21 eV, respectively, are much larger than most $M^+{-}L$ bond dissociation energies;[22] even the unusually large $D[Ln{-}C_2]$ values are only ~6 eV.[23] Accordingly, a covalent bonding model such as that employed in the above discussion of promotion energies is considered most appropriate. Of course, a much greater degree of ionicity should be obtained for similar species in condensed-phase systems, where secondary coordination to solvent molecules or to neighboring lattice ions in a solid (i.e., the Madelung energy), as in $BaC_2(s)$ ($\sim Ba^{2+}C_2{}^{2-}$),[24] can effectively compensate for these ionization energies.

Some typical results in Figure 1 qualitatively confirm the expected behavior for the binding of Cm^+ to radical fragments in the ablation plume. The comparative intensities of the CmC_2^+, CmC_2H^+, and $CmCN^+$ peaks are very similar to the corresponding results obtained for Np but are in distinct contrast to those for Am. In

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particular, $I[CmC_2^+]/I[CmC_2H^+] > 1$ is in accord with the preferential formation of the divalent carbide over the monovalent acetylide; this result contrasts with $I[AmC_2+]/I[AmC_2H^+] < 1$. The amounts of $AnCN^+$ have been found to parallel that of the acetylide, in accord with a cyanide complex comprising a single bond: $An^+{-}C{\equiv}N$. These results for the most elementary complexes confirm the validity of the above interpretations and indicate significant differences between the organometallic chemistries of curium and americium. Specifically, solid divalent americium organometallic compounds may be isolable, but it is anticipated that divalent curium compounds should be substantially more unstable toward oxidation or disproportionation.

The preference for binary carbides over the monohydrido species was particularly pronounced for CmC_4^+ and CmC_6^+, again in correspondence with results for lighter actinides—NpC_4^+, NpC_6^+, AmC_4H^+, and AmC_6H^+ were dominant species for those representative systems. Whereas a significant amount of CmC_2H^+ was evident, the relative amount of CmC_4H^+ was minor; that C_4H was plentiful as a reactive radical in the ablation plume was established previously from the abundance of "monovalent" AmC_4H^+. Similarly, essentially no CmC_6H^+ formed in the presence of substantial CmC_6^+, again in sharp contrast to the corresponding americium chemistry, where $I[AmC_6H^+] \gg I[AmC_6^+]$[3]. The pseudo-oxygen concept has been postulated for the C_4 moiety,[25] as it had been previously for C_2,[26] and the present results suggest additionally an atomic oxygen-like character for the C_6 radical. In support of the latter concept, the amounts of AmC_{2n}^+ ($n = 1, 2, 3, ...$) paralleled the yields of directly ablated AnO^+: for example, $I[CmO^+] \approx I[Cm^+]$ and $I[CmC_{2n}^+] > I[CmC_{2n}H^+]$ vs $I[AmO^+] \ll I[Am^+]$ and $I[AmC_{2n}^+] < I[AmC_{2n}H^+]$. The pseudo-oxygen character of C_{2n} would suggest substantial ionic character of the $An{-}C_{2n}$ bond despite the applicability of a covalent bonding model.

In contrast to C_2, where the strong C=C bond can be presumed to remain intact (albeit perturbed) by bonding to the metal center, the structures of the larger carbide ligands are indeterminate. Thus, for polyvalent actinides, such as Np, which produced appreciable AnC_{2n}^+ for $n > 1$, it could be postulated that the larger binary carbides corresponded to a formally higher valence metal center bonded to more than one ligand, such as pentavalent Np in "$C_2{=}Np^+{=}C_2$." However, for Cm such a high valence state is practically inaccessible[27] and the C_{2n} moieties are considered to be polycarbon ligands. Simplistically, the larger curium carbide complexes might be considered to consist of a trivalent metal center bonded to a poly-ylide chain in a quasi-metallacyclic fashion: $Cm^+{-}\eta^2\text{-}\{{-}C{\equiv}C{-}C{\equiv}C{-}\}$; $Cm^+{-}\eta^2\text{-}\{{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}\}$; etc. The energy associated with formation of two covalent bonds between a "divalent" metal ion and either a dicarbide or tetracarbide moiety might be roughly comparable, but steric constraints would hinder the ability of the two terminal carbons of a longer C_4 chain to simultaneously bond to a single metal ion. For the C_4 molecule, two nearly degenerate structures have been proposed:[28] a linear chain and a planar rhombohedral ring. The CmC_4^+ species may involve bonding of the metal center to one end of a C_4 chain (in analogy to CeC_2), or to a C_4 ring, perhaps $Cm^+{-}\eta^4\text{-}C_4$ (formally $Cm^{3+}{-}\eta^4\text{-}C_4^{2-}$ in the extreme ionic limit). The relatively dramatic preference for CmC_4^+ over CmC_4H^+, despite the evident abundance of C_4H, would suggest that the $Cm^+{-}C_4$ bonding may be more robust than that for $Cm^+{-}C_2$. This can be rationalized on the basis of the more delocalized metal−carbon bonding involving four, rather than two, carbon atoms and/or of the existence of equivalent hybrid bonding structures. In the case of naked C_6, the cyclic form is evidently more stable than the linear form[25] and CmC_6^+ is probably reasonably represented as $Cm^+{-}\eta^6\text{-}C_6$ (formally $Cm^{3+}{-}\eta^6\text{-}C_6^{2-}$). It is evident that gas-phase and/or condensed-phase spectroscopic studies (e.g., of matrix-isolated complexes) would be invaluable in establishing the structure(s) and bonding in these transient complexes; only the net compositions and abundance distributions of product ions can be determined directly by MPCA mass spectrometry.

Figure 2 shows the m/z 80−160 Da segments of two mass spectra for positive ions ablated from the polyimide target, employing $t_d = 30\ \mu s$ (top spectrum) and $t_d = 60\ \mu s$ (bottom spectrum); the vertical axis zero is different for these two spectra and is approximated by their respective baselines (the vertical intensity scales are the same). These relatively low-mass ions did not complex with co-ablated curium-248 atoms or ions. The top spectrum reveals emission of ionized polyimide fragments with relatively high velocities; substantial amounts of fragment ions were also evident at masses higher and lower (m/z; $z = 1$) than those shown in Figure 2. The 119 and 135 Da peaks are identified in Figure 2 as particularly intense, but it was not practical to assign compositions to these or other constituents of the complex polyimide fragment ion spectra. These fragmentation spectra demonstrate the extensive severing of the polyimide chains and availability of a plethora of ablated radical species. The bottom, $t_d = 60\ \mu s$, spectrum reveals that very few polyimide fragment **ions** were ejected from the target with the relatively low velocities (energies) displayed by the primary detected $Cm^+{-}L$ product complexes (and clusters). The maximum intensities for both the polyimide fragment ions and the unreacted curium ions were for values of t_d substantially shorter than the maxima for the organocurium complex ions. This observation suggests that the organometallic complex ions produced and detected by the MPCA approach were formed by coalescence in the ablation plume of relatively low-energy curium (and curium oxide) ions with neutral polyimide radical fragments co-ablated with relatively low velocities. It is proposed that the evident coherent chemistry occurred in the relatively low energy, tail portion of the ablation plume; this concurs with the above-noted intuition based on energetic considerations.

This mechanistic interpretation is in accord with the undoubtedly exothermic nature of the postulated Cm^+−radical reactions and the exoergicity of the collisions of

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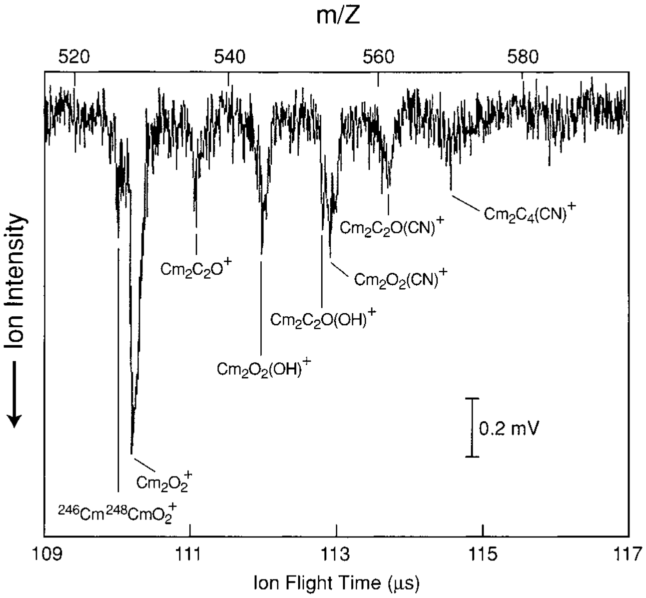

Figure 3. Laser ablation mass spectrum of small curium cluster ions ($t_d = 70$ μs). As discussed in the text, several of the peak assignments are speculative; for example, the "$Cm_2C_4(CN)^+$" peak could feasibly be nearly isobaric $Cm_2C_4(C_2H_2)^+$. The central point is the evident substitution of C_2 moieties for O atoms.

ablated ions with co-ablated neutral polymer fragments. It is probable that other, undetected, organocurium complexes were produced under higher energy conditions but possessed sufficient internal energies (due to both the collisional and exothermic reaction energies) that dissociation occurred prior to the <100 μs detection time scale of the MPCA experiments. The postulation that the detected complexes were produced by reaction of ablated Cm^+ (or CmO^+) ions with neutral polyimide fragments is furthermore consistent with the much greater energy necessary for ionization of the reactant organic fragments—for example, the ionization energy of Cm is 6.0 eV,[21] whereas that of C_2 is 12.1 eV.[29]

Curium Clusters. A primary impetus for selecting polyimide as a reactive matrix was that it has been well-established that vacuum laser ablation of this material produces abundant fullerenes, which are presumed to form by gas-phase nucleation in the ablation plume.[30] It was anticipated that some of the co-ablated An^+ might be encapsulated during fullerene growth, producing endohedral actinofullerenes. However, in the present studies with curium, only small amounts of C_{60}^+ were produced, and no CmC_{60}^+ or other curium fullerenes were detected.

Despite the low concentration of Cm in the targets, the polyimide ablation plume was sufficiently dense to produce measurable amounts of small clusters, comprising two or three Cm atoms, probably produced by coalescence. In Figure 3 is shown a mass spectrum of the identified clusters incorporating two Cm atoms. This mass spectrum was obtained using $t_d = 70$ μs; this relatively long delay resulted in nearly maximized cluster ion intensities and suggests a mechanism involving coalescence of multiple relatively low energy plume species. Clusters comprised of three Cm atoms apparent at very low intensities ($\lesssim 0.05$ mV) included $Cm_3O_4^+$, $Cm_3O_3C_2^+$, $Cm_3O_2C_4^+$, $Cm_3OC_6^+$, and $Cm_3C_8^+$. Assigning formal valence states of O^{2-}, OH^-, and CN^-, the average valence states of curium are +2.5 (i.e., a Cm^{II}/Cm^{III} mixed valence) in $Cm_2O_2^+$ and +3 in $Cm_2O_2(OH)^+$, $Cm_2O_2(CN)^+$, and $Cm_3O_4^+$. The propensity for curium to exist in the trivalent state is manifested clearly, in distinct contrast to the lighter actinides, where we have identified oxygen-rich clusters such as $Np_3O_8^+$, giving a formal average neptunium valence of +5.7. The results for curium illustrate its essential nature as a trivalent, lanthanide-like f element.

A fascinating aspect of the cluster mass spectra is the distinctive validation of the pseudo-oxygen character of the C_2 moiety, as discussed above (e.g., the similarity of the bonding in LnO^+ and LnC_2^+[23]). In the series of bis-Cm and tris-Cm clusters, systematic substitution of a dicarbide for oxygen is evident. The following homologous series of clusters illustrate this behavior: $Cm_2O_2^+$/$Cm_2C_2O^+$, $Cm_2O_2(OH)^+$/$Cm_2C_2O(OH)^+$, $Cm_2O_2(CN)^+$/$Cm_2C_2O(CN)^+$/$Cm_2C_4(CN)^+$, and $Cm_3O_4^+$/$Cm_3O_3C_2^+$/$Cm_3O_2C_4^+$/$Cm_3OC_6^+$/$Cm_3C_8^+$. In contrast to species such as CmC_4, where a C_4 moiety was assumed based on valence considerations, the systematic substitution in the clusters suggests discrete C_2 moieties. Sequential replacement of oxygens in $Cm_3O_4^+$ by dicarbides evidently results in a series of clusters terminating in the fully C_2-substituted cluster $Cm_3C_8^+$. Regardless of the indeterminate oxide, oxide–carbide and carbide cluster structures, the discrete substitution of dicarbide for oxygen provides a novel demonstration of the previously postulated chemical similarity of the C_2 and O moieties.

Future experimental and theoretical work should address the structure and bonding in these and larger oxide and carbide clusters. Such clusters offer a singular link between gas-phase molecular species and the solid state. The synthesis and spectroscopic characterization of these and larger actinide clusters should also serve to illuminate distinctive and complex behavior demonstrated by actinides in the condensed phase.

Conclusions

The MPCA technique has been developed into a unique and valuable approach for examining transuranic organometallic chemistry. Application of this method to scarce and/or radioactive actinides, such as Cm, is particularly significant in view of the difficulty in carrying out conventional condensed-phase organometallic chemistry with these elements. In this regard, the gas-phase species prepared by MPCA evidently represent the first σ-bonded organocurium complexes. The relative abundances of the singly bonded "monovalent" complexes, such as $Cm^+{-}C_2H$, and the doubly bonded "divalent" complexes, such as "$Cm^+{=}C_2$," were found to be in accord with the electronic configuration and energetics of the curium ion, Cm^+. The comparative MPCA results for Am and Cm suggest that it may be feasible to isolate divalent americium organometallic compounds but that divalent curium organometallics would be substantially more labile. The MPCA results for Cm and other transuranics should be complemented by future studies employing more sophisticated tech-

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niques, such as Fourier transform mass spectrometry, if/when appropriate instruments are configured to allow for safe handling of these isotopes. Such advanced studies should provide more lucid insights into the structures and bonding of the organoactinide complex ions.

Even small clusters comprising two or three curium atoms revealed the essential trivalent (lanthanide-like) behavior of Cm and illustrate the value of clusters as a link between the molecular and solid states of matter. Actinide clusters offer an avenue to elucidating the bonding of these unique series of elements, particularly the variable localized/itinerant character of the 5f electrons. Finally, the distinct sequential substitution of C_2 for O in clusters provides a novel demonstration of the pseudo-oxygen character of the dicarbide moiety.

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