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High-temperature transuranium organometallic species from laser ablation of actinide–polymer mixtures

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Abstract

Pulsed laser ablation of dispersions of f-element compounds in polymers produces novel 'high-temperature' organometallic complex ions. The M^+–L from reactions of metal ions (M^+) with polymer fragments (L) in the ablation plume are identified by time-of-flight mass spectrometry. Compositions and abundances of M^+–L from ablation of UO_2 and lanthanides in polyimide (PI) reflected distinctive f-element chemistries; we report here on ablation of $^{237}NpO_2$ and $^{242}PuO_2$ in PI. Primary products were Np^+-C_cH_h and Pu^+-C_cH_h with $1 \leq c \lesssim 20$–the characteristic complex ion compositions and abundances reveal distinctive chemistries; the transuranium results are compared with those for other f elements. Studies of lanthanides in polystyrene rather than PI excluded ^{14}N (isobaric with $^{12}CH_2$) as a potential ligand constituent, clarifying ion compositions. © 1998 Elsevier Science S.A.

Keywords: Neptunium organometallics; Plutonium organometallics; Actinide vaporization; Polymer ablation

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1. Introduction

The compositions, abundances and properties of high-temperature transition element vapor species provide differentiations which may be indiscernible in condensed phase chemistry. The disparate electronic configurations of f elements typically manifested as minor distinctions in condensed phase chemistry result in discrepant vapor chemistries. For example, monoxide dissociation energies (D^0[Ln–O]) vary by a factor of nearly two within the series (401 kJ mol^{-1} for YbO to 795 kJ mol^{-1} for LaO [1]) whereas the sesquioxide formation enthalpies vary by ~15% (826 kJ mol^{-1} for $EuO_{3/2}$ to 950 kJ mol^{-1} for $ErO_{3/2}$ [2]). Similarly, widely discrepant monoxide vapor stabilities are exhibited across the actinide series [3].

High-temperature chemistry has been studied in vapor plumes generated by pulsed laser ablation of inorganic solids [4]. In addition to producing typical high-temperature species, laser ablation generates novel species such as oxide clusters [5]. We developed laser ablation of metals in polymers to produce f-element organometallic species which are unknown or highly labile in the condensed phase; species compositions and abundances illuminate the metal's electronic structure and distinctive chemistry [6]. A dilute dispersion of an f-element compound in a polymer is ablated with a pulsed UV laser and the complex ions, M^+–L, produced by reactions of metal ions (M^+) with polymer fragments (L) are identified by time-of-flight mass spectrometry. This technique has illuminated high-temperature organometallic chemistries of lanthanides and U [6], and is suited to studying transuranium actinides on the milligram scale. We report here results for ablation of ^{237}Np and ^{242}Pu in polyimide (PI). Lanthanide results with polystyrene (PS) are included to clarify speciation.

2. Experimental

The instrumentation and techniques were described previously [5,6] except that the present experiments were the first to employ transuranics and the target region has been installed into an alpha-containment glovebox. The laser beam impinges on the target at ~90° incidence, focused to a ~0.5 mm^2 spot with a typical incident energy of ~1 mJ (~200 mJ cm^{-2}). Ablated material propagated from the target orthogonal to the mass spectrometer flight tube axis; after a selected delay, t_d, the positive ions in a ~0.3 cm^2 transverse cylinder of the ablation plume were injected into the flight tube by a +200 V pulse. By varying t_d it was possible to sample ablated ions with various velocities; the reported results correspond to delays of 35–45 μs.

Targets were prepared by mixing polymer and high-purity metal oxide powders (Ln_2O_3 or AnO_2) and com-

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pressing into pellets as described previously [6]; the pellet press was located in an alpha-containment glovebox. The polymer powders were commercial products (Aldrich): POLYIMIDE, poly[*N*,*N*′-(1,4-phenylene)-3,3′,4,4′-benzophenonetetracarboxylic imide/amic acid] ([-$C_{23}H_{10}O_5N_2$-]$_n$); POLYSTYRENE, dicarboxy terminated ([-$CH_2CH(C_6H_5)$-]$_n$; avg. M_w~100 000 Da). The target compositions are given as atomic percent metal relative to polymer carbon: La–Tm–PS=1.4% $LaO_{3/2}$+1.5% $TmO_{3/2}$+PS; Eu–Tb–PS=1.1% $EuO_{3/2}$+0.9% $TbO_{3/2}$+PS; Np–PI=1.3% $^{237}NpO_2$+PI; Pu-PI=0.8% $^{242}PuO_2$ (99.7% ^{242}Pu)+PI. The An–PI targets contained ~2 mg AnO_2.

3. Results and discussion

3.1. Lanthanides in polystyrene

An ablation mass spectrum for the La–Tm–PS target is shown in Fig. 1. Both La^+ and LaO^+ were abundant whereas Tm^+ appeared absent TmO^+. For the Eu–Tb–PS target, Eu^+ was dominant and EuO^+ absent whereas both Tb^+ and TbO^+ were comparably abundant. The distinctive Ln^+/LnO^+ yields reflected the monoxide stabilities–relevant D^0[Ln–O] are included in Table 1. The PS targets eliminated N as a constituent, allowing unambiguous assignment of ligands such as that at 26 Da which could be attributed to cyanide (C≡N) or acetylene (HC≡CH) from PI. Most Ln^+–L from PS corresponded to species from PI but Ln^+–L with L at 26 Da (Ln^+–{26}) were absent. While the Tm^+–{26} intensity from PI had been greater than that of Tm^+–C_2H, Fig. 1 reveals appreciable Tm^+-C_2H but nil Tm^+–{26} from PS; for Eu, the analogous comparison between PI and PS was obtained and it is evident that the 26 Da ligand was primarily $(C{\equiv}N)^-$.

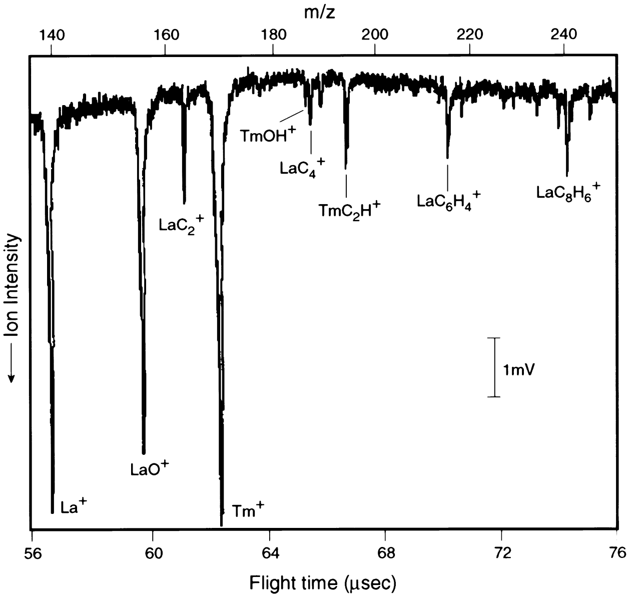

Fig. 1. Laser ablation mass spectrum for target La–Tm–PS.

Table 1
Oxide dissociation (D^0) and atom ionization energies (kJ mol^{-1})

	D^0[M–O][a]	Ionization energies[b]		
		$M^+ \to M^{2+}$	$M^{2+} \to M^{3+}$	$M^{3+} \to M^{4+}$
La	795	1067	1850	4819
Ce	790	1047	1949	3547
Eu	465	1018	2404	4110
Tb	693	1112	2114	3839
Ho	613	1139	2204	4101
Tm	508	1163	2285	4119
Th	891	1147	1930	2774
U	774	1148	1930	3146
Np	736	1129	1997	3242
Pu	703	1129	2104	3339
Am	550	1158	2161	3493

[a] Ln–O from Ref. [1]; An–O from Ref. [3].

[b] Ln^{n+} from Ref. [7]; An^{n+} from Ref. [8].

Both the Ln–PS and Ln–PI ablation product distributions indicated that high-temperature chemistry in the ablation plume reflected distinctive Ln electronic structures. In the case of PS ablation, predominantly trivalent Ln such as La and Tb produced primarily LnC_2^+ (~Ln^{3+}–C_2^{2-}) whereas lanthanides such as Eu and Tm, formed mainly LnC_2H^+ (Ln^{2+}–C_2H^-). The latter Ln were previously observed to react with CN from PI to yield $LnCN^+$ (~Ln^{2+}–CN^-) [6]. There was a close correspondence between the abundances of LnO^+ (~Ln^{3+}–O^{2-}) and LnC_2^+. The general trends are consistent with $M^{2+} \to M^{3+}$ ionization energies (Table 1).

3.2. Actinides in polyimide

Typical results for the Np–PI and Pu–PI targets are shown in Figs. 2 and 3. Before considering organometallic ions, it is worthwhile to compare AnO_x^+ abundances for An=Th, U, Np and Pu. Although the following relative yields are qualitative and somewhat dependent upon specific ablation conditions, regular distinctions between these An were apparent: $Th^+ < ThO^+$ ($<< ThO_2^+$/not detected); $U^+ \lesssim UO^+ \gtrsim UO_2^+$; $Np^+ \approx NpO^+ > NpO_2^+$; $Pu^+ \approx PuO^+ >> PuO_2^+$. The comparative AnO^+ yields are seen to be consistent with the D^0[An–O] given in Table 1; based upon Ln results [1] it is presumed that the values of D^0[An^+–O] parallel those of D^0[An–O], in accord with the AnO^+ abundances determined here. The large differences in AnO_2^+ abundances reflect the corresponding pentavalent oxide stabilities in condensed phase: $UO_2^+ > NpO_2^+ > PuO_2^+$ [7]. The absence of ThO_2^+ reflects that pentavalent Th is not feasible-$ThO_2^+ \approx Th^{5+}(O^{2-})_2$.

Although the yields of Pu^+–L were generally smaller than those of Np^+–L, the results for Np–PI and Pu–PI were generally similar. A central result was the relative yields of M^+–L for those small L which previously

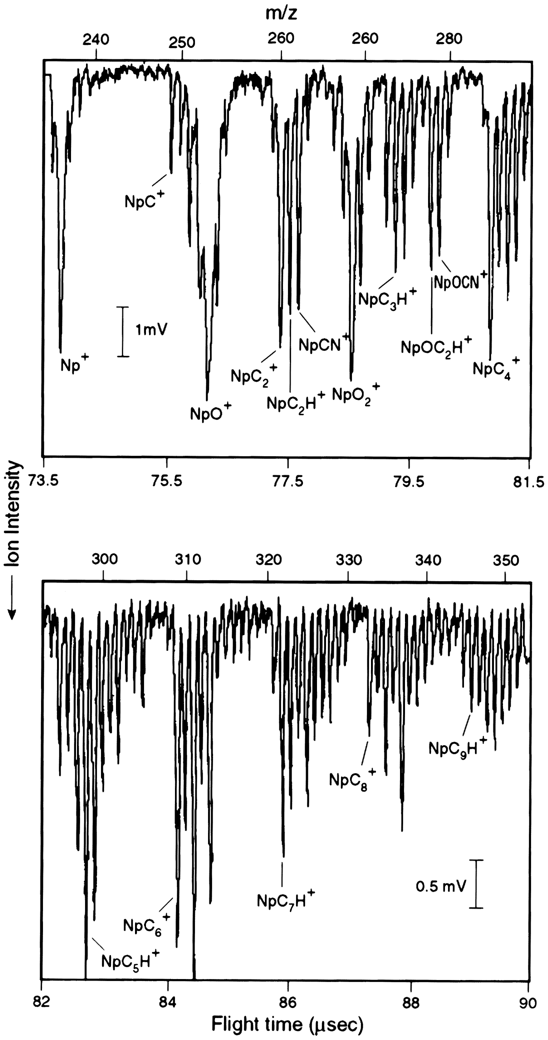

Fig. 2. Laser ablation mass spectrum for target Np–PI.

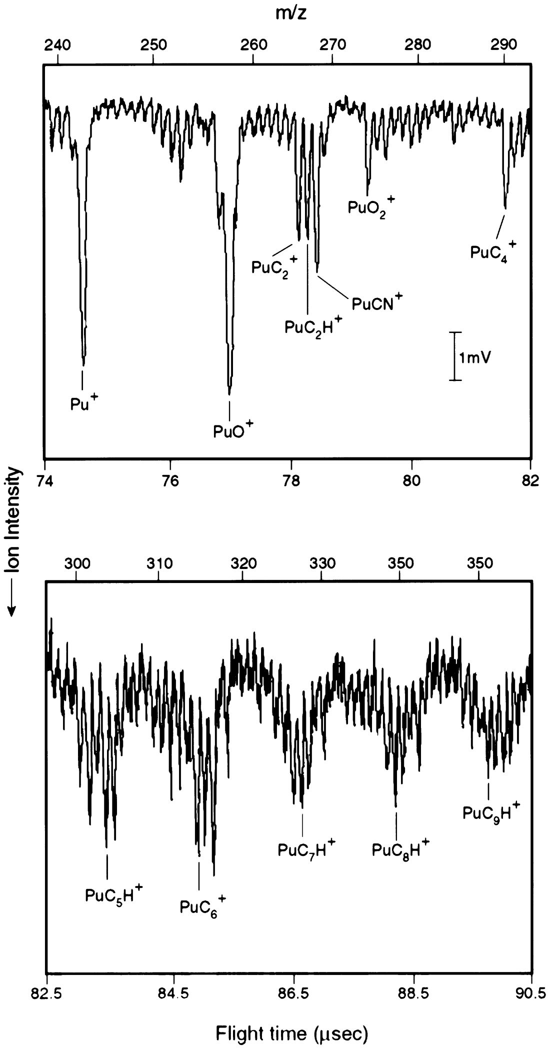

Fig. 3. Laser ablation mass spectrum for target Pu–PI.

provided coherent distinctions for Ln and U [6]; the following comparison with the U–PI results is illustrative: $UC_2^+ >> UC_2H^+ > UCN^+$ (similar to Ce) vs. $AnC_2^+ \approx AnC_2H^+ \approx AnCN^+$ [An=Np and Pu] (similar to Tb). In accord with the correlation between M–O and M–C_2 bonding [1], the lesser abundances of NpC_2^+ and PuC_2^+ compared with UC_2^+ was anticipated based upon the oxide dissociation energies in Table 1; the greater prevalence of trivalent UC_2^+ and divalent complexes for Np and Pu also correlates with the +2 to +3 ionization energies (Table 1). Although the distinctions between Np and Pu were relatively minor, NpC_2^+ appeared somewhat enhanced relative to PuC_2^+, in accord with the relative An^+–C_2 dissociation energies predicted from the D^0[An–O].

The ~280 Da region of the spectra in Figs. 2 and 3 suggest that species such as An^+–C_3H, An^+–OC_2H and An^+–OCN were significant for Np but minor for Pu. The greater stability of Np(IV) compared with Pu(IV) [7] might explain enhanced formation of species such as $\{O=Np^{IV}–C_2H\}^+$ and $\{O=Np^{IV}–CN\}^+$.

Additional $AnC_cH_h{}^+$ up to c~20 were especially abundant for Np. The average degree of hydrogenation (i.e., h) increased with c. The relatively intense peak corresponding to An^+–{124} (An=Np and Pu) could reasonably be attributed to An^+–$C_{10}H_4$, An^+ –$(C_8H_2)(CN)$ or An^+–$(C_6)(CN)_2$. However, the $AnC_c{}^+$ and AnC_cH^+ peaks are definitively assigned and the appearance of subsequent peaks at incremental mass units suggests a series of $AnC_cH_h{}^+$ for h=0, 1, 2, 3,.... A consistent observation was enhanced abundance of $AnC_c{}^+$ for even values of c (e.g., NpC_8^+) compared with AnC_cH^+ for odd-c (e.g., NpC_7H^+). The dominant structures of unmetallated $C_cH_h{}^+$ in this size range are monocyclic and linear, with hydrogenation stabilizing the latter [9]. Neutral LaC_c (c=2–6) are highly ionic, probably exhibiting quasi-metallocyclic 'fan' structures with essentially La–η^c–C_c coordination [10]. The substantially greater Ln–C_c dissociation energies for even-c [1] are consistent with the distinctively abundant AnC_2^+, AnC_4^+, AnC_6^+, AnC_8^+, etc. found here. The addition of a single H-atom may stabilize odd-c AnC_cH^+ by saturating a radical site. Some *bis*-Np species were also identified, the most prevalent of which were assigned as $Np^{II}Np^{III}O_2^+$, $Np^{II}Np^{III}OC_2^+$, $Np^{III}Np^{IV}O_3^+$ (or $Np^{II}Np^{III}C_4^+$) and $Np_2^{III}O_2(CN)^+$ (or $Np_2^{II}O(OCN)^+$).

4. Conclusion

Pulsed laser ablation of dispersions of Np and Pu oxides in polyimide has produced organometallic complexes whose compositions and abundance distributions reflect the distinctive chemistries of these first two transuranium actinides. Although the pentavalent oxide ions, NpO_2^+ and (minor) PuO_2^+ were detected, the $Np^+–C_cH_h$ and $Pu^+–C_cH_h$ chemistries appeared rather similar to those of trivalent lanthanides such as Tb and Ho. Experiments carried out with selected lanthanides in polystyrene identified the mass 26 Da ligand derived from polyimide as primarily cyanide, CN, rather than acetylene, C_2H_2; Np^+–CN and Pu^+–CN were comparably significant products, in contrast to minuscule yields of U^+–CN. In several regards the results reported here indicated significant disparities between the 'high-temperature' organometallic chemistries of Np/Pu versus U–it may be that the bonding in $U^+–C_cH_h$ species is substantially more covalent (perhaps involving 5f-orbitals) than in heavier $An^+–C_cH_h$.

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