



Formation of $[\text{U}^{\text{V}}\text{OF}_4]^-$ by collision-induced dissociation of a $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2)(\text{O}_2\text{C}-\text{CF}_3)_2]^-$ precursor

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ABSTRACT

Developing a comprehensive understanding of the reactivity of uranium species remains an important goal in areas ranging from the development of nuclear fuel processing methods to studies of the migration and fate of the element in the environment. Electrospray ionization (ESI) can provide relatively easy access to gas-phase complexes containing uranium in high oxidation states for subsequent studies of intrinsic structure and reactivity. We report here the formation of a superoxo-complex, $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2)(\text{O}_2\text{C}-\text{CF}_3)_2]^-$, which is created by ESI using “gentle” conditions (low sheath gas flow rate and low desolvation temperature). CID of $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2)(\text{O}_2\text{C}-\text{CF}_3)_2]^-$ causes elimination of O_2 , presumably with concomitant reduction of $\text{U}^{\text{VI}}\text{O}_2^{2+}$ to $\text{U}^{\text{V}}\text{O}_2^+$. Remarkably, subsequent CID of $[\text{U}^{\text{V}}\text{O}_2(\text{O}_2\text{C}-\text{CF}_3)_2]^-$ creates a species at m/z 330, which is attributed to formation of $[\text{U}^{\text{V}}\text{O}(\text{F})_4]^-$. A similar species is generated by multiple-stage CID in a linear ion trap, and collision-cell CID in a Fourier-transform ion-cyclotron resonance (FT-ICR) mass spectrometer, when initiated with the tris-trifluoroacetate complex $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{CF}_3)_3]^-$. High accuracy mass measurement using the FT-ICR instrument confirms the composition assignment for the species at m/z 330.

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1. Introduction

Developing a comprehensive understanding of the reactivity of uranium species [1] remains an important goal in the development of nuclear fuel processing methods [2] and in studies of the migration and fate of the element in the environment [3,4]. Electrospray ionization (ESI) can provide relatively easy access to gas-phase complexes containing uranium in high oxidation states [5]. Our group was among the first to use ESI to generate gas-phase complexes containing uranyl ion ($\text{U}^{\text{VI}}\text{O}_2^{2+}$) for studies of intrinsic structure and reactivity (i.e. outside of the influence of solvent or other condensed phase effects) in a species-specific fashion [6–14]. For example, complexes with $\text{U}^{\text{VI}}\text{O}_2^{2+}$ coordinated by ligands such as acetone (aco) or acetonitrile (acn) were produced by ESI for collision-induced dissociation (CID) and ion-molecule reaction experiments using tandem mass spectrometry [6,7]. Since

then, ESI has been used to create gas-phase uranyl species for a range of tandem mass spectrometry, ion mobility and anion photoelectron spectroscopy studies [15–39]. ESI and tandem mass spectrometry have also been used study and compare the reactivity of transuranic species [40–48].

More recent experiments in our laboratory [49–51] have demonstrated that the 2-D, linear ion trap (LIT) allows access to fragmentation pathways and reactions not observed in earlier studies with 3-D instruments. For example, our past studies of the dissociation behavior of gas-phase actinyl complexes using a 3-D ion trap were complicated by high yields of product ions obviously generated by collisions with background H_2O . Relatively high levels of H_2O in the ion trap (ca. 10^{-6} torr) creates hydrated ions, or leads to charge reduction reactions that form products such as $[\text{U}^{\text{VI}}\text{O}_2\text{OH}]^+$ and $[\text{U}^{\text{V}}\text{O}_2]^+$ and larger hydrated complexes containing these cations [6,7,41]. In a CID study of acetone-coordinated $\text{U}^{\text{VI}}\text{O}_2^{2+}$ performed with a 3-D ion trap, ligand addition reaction rates were so fast that complexes with 2 or 3 coordinating aco ligands hydrated to generate heterogeneous, tetra- or pentacoordinate complexes [6]. This prevented the detailed investigation of complex ions containing $\text{U}^{\text{VI}}\text{O}_2^{2+}$ and two or fewer ligands. How-

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ever, a more recent investigation of the fragmentation behavior of $U^{VI}O_2^{2+}$ complexes containing acn [49] demonstrated that the lower partial pressures of adventitious H_2O in the LIT allowed us to produce bare $U^{VI}O_2^{2+}$ by multiple-stage CID. More importantly, CID of $[U^{VI}O_2NC]^+$ created an $NU^{VI}O^+$ product ion via a putative cyanate intermediate. While $NU^{VI}O^+$ had previously been prepared in a “bottom-up” approach by insertion of U^+ into NO in an ion-molecule reaction [52], our experiments demonstrated that the species can also be created in a CID reaction. Similar experiments have now been conducted with aco-coordinated $U^{VI}O_2^{2+}$, and novel products such as $[U^{VI}O_2-HCO]^+$ and $[U^{VI}O_2-CH_2CH_3]^+$ have been identified using a combination of isotope labeling and high-resolution/high-accuracy mass measurements [50].

Our group has also used ESI, CID, and gas-phase ion-molecule reactions to create and characterize ions derived from precursors composed of $U^{VI}O_2^{2+}$ coordinated by formate or acetate ligands [51]. With the uranyl-formate system, CID of $[U^{VI}O_2(O_2CH)_3]^-$ caused decarboxylation and elimination of $CH_2=O$, ultimately to produce the oxo-hydride species $[U^{VI}O_2(O)(H)]^-$. With the uranyl-acetate system, our experiments allowed for a revision of the intrinsic dissociation pathways [53] for $[U^{VI}O_2(O_2CCH_3)_3]^-$. The primary fragmentation pathway for the intact precursor is elimination of acetyloxy radical, $CH_3CO_2^*$, with reduction of $U^{VI}O_2^{2+}$ to $U^VO_2^+$. Subsequent CID of $[U^VO_2(O_2CCH_3)_2]^-$ caused decarboxylation to generate $[U^VO_2(CH_3)(O_2CCH_3)]^-$. CID of $[U^VO_2(CH_3)(O_2CCH_3)]^-$ caused the elimination of CH_4 to create $[U^VO_2(O_2C=CH_2)]^-$, which subsequently fragmented to generate $[U^VO_2(O)]^-$.

The subject of this report is the dissociation of similar anionic complexes containing $U^{VI}O_2^{2+}$ or $U^VO_2^+$ and trifluoroacetate ligands. A previous study by Dau and Gibson focused on the competition between bond-breaking and bond making, with halide abstraction, during CID of actinyl ($U^{VI}O_2^{2+}$, $Np^{VI}O_2^{2+}$ and $Pu^{VI}O_2^{2+}$) complexes with halogenated acetate ligands, CX_3CO_2 ($X=F, Cl, Br$) in a 3-D quadrupole ion trap [54]. Most relevant to our own independent investigation, CID of $[U^{VI}O_2(O_2CCF_3)_3]^-$ complexes resulted exclusively in fluoride transfer and, presumably, elimination of difluoroacetolactone (CF_2CO_2) to create product ions such as $[U^{VI}O_2(F)(O_2C-CF_3)_2]^-$, $[U^{VI}O_2(F)_2(O_2C-CF_3)]^-$ and $[U^{VI}O_2(F)_3]^-$. Unlike our previous experiments with uranyl-acetate anions, in which CID of $[U^{VI}O_2(O_2C-CH_3)_3]^-$ at the MS/MS stage generated $[U^VO_2(O_2C-CH_3)_2]^-$ by elimination acetyloxy radical, fragmentation by loss of trifluoroacetyloxy radical from analogous species containing trifluoroacetate ligands, with associated production of $[U^VO_2(O_2C-CF_3)_2]^-$, was not observed by Dau and Gibson. Instead, using $-F$, $-Cl$ and $-Br$ substituted acetate, the conclusion drawn was that actinide-halide bond dissociation energies are sufficiently high that halide transfer is the dominant dissociation pathway during CID of $[An^{VI}O_2(O_2CCX_3)_3]^-$ where $An=U, Np$ and Pu and $X=F, Cl$ and Br .

In an extension of our work with uranyl-carboxylate anions, we report here the generation of an unusual precursor ion by ESI, and the subsequent CID of the species. Using relatively “gentle” ESI ion formation conditions, primarily lower sheath gas flow and capillary/desolvation temperatures than were employed in our previous investigation of uranyl-carboxylate anions, a species with formula $[U^{VI}O_2(O_2)(O_2CCF_3)_2]^-$ was generated. We found that CID of $[U^{VI}O_2(O_2)(O_2CCF_3)_2]^-$ creates $[U^VO_2(O_2CCF_3)_2]^-$, and subsequent collisional activation of this species leads to an unprecedented product ion with composition $[U^VO(F)_4]^-$. The composition assignment for the species, when generated independently by CID of $[U^{VI}O_2(O_2CCF_3)_3]^-$ in a Fourier-transform ion cyclotron resonance (FT-ICR) instrument, is supported by high-resolution, high-accuracy mass measurements.

2. Experimental methods

2.1. Sample preparation

Uranyl trifluoroacetate salt was prepared by combining ca. 2–3 mg of $U^{VI}O_3$ (Strem Chemicals, Newburyport MA), corresponding to approximately 7×10^{-6} to 1×10^{-5} moles, with a 2-fold mole excess of trifluoroacetic acid (Sigma Aldrich, St. Louis MO) and 400 μ L of deionized/distilled H_2O contained in a glass scintillation vial. The solutions were allowed to incubate on a hot plate at $70^\circ C$ for 12 h. The trifluoroacetate compound was synthesized because the salt is not commercially available. Caution: uranium oxide is radioactive (α - and γ -emitter), and proper shielding, waste disposal and personal protective gear should be used when handling the material.

When cooled, 20 μ L of the resulting solution was diluted with 800 μ L of 50:50 (by volume) H_2O /ethanol (EtOH) and used without further work up as the spray solution for ESI-MS. EtOH has been used in our most recent experiments to avoid any ambiguity when looking for potential molecular O_2 adducts to certain product ions [55–58]. With the limited mass measurement accuracy of the LIT, O_2 and CH_3OH adducts cannot be distinguished.

2.2. Linear ion trap mass spectrometry

ESI and CID experiments were performed on a ThermoScientific (San Jose, CA) LTQ-XL LIT mass spectrometer. The uranyl-trifluoroacetate spray solutions were infused into the ESI-MS instrument using the incorporated syringe pump at a flow rate of 5 μ L/min. In the negative ion mode, the atmospheric pressure ionization stack settings for the LTQ (lens voltages, quadrupole and octopole voltage offsets, etc.) were optimized for maximum transmission of the singly-charged ions anions such as $[U^{VI}O_2(O_2C-CF_3)_3]^-$ or $[U^{VI}O_2(O_2)(O_2C-CF_3)_2]^-$ to the ion trap mass analyzer by using the auto-tune routine within the LTQ Tune program. In contrast to our earlier studies using uranyl-formate or uranyl-acetate precursor anions [52], the sheath gas flow was set at 5 units (arbitrary to the ThermoFisher Scientific LTQ platform) rather than 15 units. We find that the higher flow rate maximizes the yield of tris-carboxylate anions. Our aim here was to probe the fragmentation of the $[U^{VI}O_2(O_2)(O_2C-CF_3)_2]^-$ ion, which is apparently produced in the ESI source in greater relative abundance using the lower sheath gas flow. In addition, to maximize the yield of the precursor, the capillary/desolvation temperature was decreased from 250° to $175^\circ C$.

Helium was used as the bath/buffer gas to improve trapping efficiency and as the collision gas for CID experiments. For CID, precursor ions were isolated using a width of 1.0–1.5 mass to charge (m/z) units. The exact value was determined empirically to provide maximum ion intensity while ensuring isolation of a single isotopic peak. To probe CID behavior in general, the (mass) normalized collision energy (NCE, as defined by ThermoScientific) was set between 5 and 18%, which corresponds to 0.075–0.27 V applied for CID with the current instrument calibration. The activation Q, which defines the frequency of the applied radio frequency potential, was set at 0.30 and the activation time employed was 30 ms.

To probe gas-phase reactions with background neutrals such as H_2O or O_2 , selected precursor ions were isolated using widths of 2–4 m/z units. The specific width used was chosen empirically to ensure maximum ion isolation efficiency. The ions were then stored in the LIT for periods as long as 10 s. For both CID and ion-molecule reaction experiments, the mass spectra displayed were created by accumulating and averaging at least 30 isolation, dissociation, and ejection/detection steps.

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