

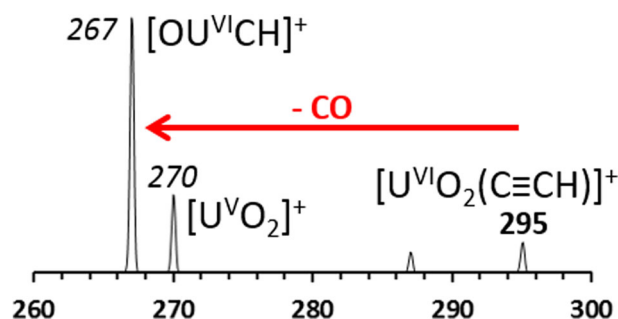
Gas-Phase Deconstruction of UO_2^{2+} : Mass Spectrometry Evidence for Generation of $[\text{OU}^{\text{VI}}\text{CH}]^+$ by Collision-Induced Dissociation of $[\text{U}^{\text{VI}}\text{O}_2(\text{C}\equiv\text{CH})]^+$

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Abstract. Because of the high stability and inertness of the $\text{U}=\text{O}$ bonds, activation and/or functionalization of UO_2^{2+} and UO_2^+ remain challenging tasks. We show here that collision-induced dissociation (CID) of the uranyl-propiolate cation, $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})]^+$, can be used to prepare $[\text{U}^{\text{VI}}\text{O}_2(\text{C}\equiv\text{CH})]^+$ in the gas phase by decarboxylation. Remarkably, CID of $[\text{U}^{\text{VI}}\text{O}_2(\text{C}\equiv\text{CH})]^+$ caused elimination of CO to create $[\text{OU}^{\text{VI}}\text{CH}]^+$, thus providing a new example of a well-defined substitution of an “yl” oxo ligand of $\text{U}^{\text{VI}}\text{O}_2^{2+}$ in a unimolecular reaction. Relative energies for candidate structures based on density functional theory calculations suggest that the $[\text{OU}^{\text{VI}}\text{CH}]^+$ ion is a uranium-methyldiyne product, with a $\text{U}=\text{C}$ triple bond composed of one σ -bond with contributions from the $\text{U } d f$ and $\text{C } s p$ hybrid orbitals, and two π -bonds with contributions from the $\text{U } d f$ and $\text{C } p$ orbitals. Upon isolation, without imposed collisional activation, $[\text{OU}^{\text{VI}}\text{CH}]^+$ appears to react spontaneously with O_2 to produce $[\text{U}^{\text{VI}}\text{O}_2]^+$.

Keywords: Uranyl ion, Collision-induced dissociation, Ion trap mass spectrometry, Oxo ligand substitution, Density functional theory

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Introduction

While there is growing interest in methods to activate and/or functionalize UO_2^{2+} and UO_2^+ [1–3], these transformations remain challenging because of the high (thermodynamic) stability and (kinetic) inertness of the $\text{U}=\text{O}$ bonds. Despite this, it has been demonstrated that activation and functionalization of $\text{U}=\text{O}$ bonds can be achieved in the condensed phase using a combination of coordination by Lewis acids and reductive silylation [4–15], or by other means [16–

18]. In the gas phase, recent experiments have shown that the $\text{U}=\text{O}$ bonds of UO_2^{2+} can be activated and substituted, primarily through the use of collision-induced dissociation (CID) [19–23]. For example, we have shown that NUO^+ can be created by rearrangement and fragmentation of $[\text{UO}_2(\text{N}\equiv\text{C})]^+$, which was itself generated by dissociation of a $[\text{UO}_2(\text{N}=\text{C}-\text{CH}_3)]^{2+}$ precursor [19]. In similar studies, Gibson and coworkers demonstrated that CID of $[\text{UO}_2(\text{N}_3)\text{Cl}_2]^-$ creates the activated ion $[\text{UO}(\text{NO})\text{Cl}_2]^-$ by elimination of N_2 [20], and that $[\text{UO}_2(\text{NCO})\text{Cl}_2]^-$ will dissociate by elimination of CO_2 to leave $[\text{UONCl}_2]^-$ [21]. More recent experiments have demonstrated that CID of uranyl complexes with octadentate catecholamide ligands can cause $\text{U}=\text{O}$ bond cleavage [22], and that $[\text{UO}(\text{F})_4]^-$ is the dominant product ion generated by CID of $[\text{UO}_2(\text{O}_2\text{C}-\text{CF}_3)_2]^-$ [23].

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Recently, the gas-phase dissociation reactions of a series of $[\text{AnO}_2(\text{O}_2\text{C}-\text{R})_3]^+$, $\text{An} = \text{U}, \text{Np}, \text{Pu}$, precursors were investigated [24]. For precursors containing U, decarboxylation products with general composition $[(\text{R})\text{AnO}_2(\text{O}_2\text{C}-\text{R})_2]^+$, species which include discrete U–C organouranyl bonds, were created when $\text{R}=\text{CH}_3$, C_6H_5 , C_6F_5 , $\text{CH}_3\text{C}\equiv\text{C}$. In contrast, it was only for $\text{R}=\text{C}_6\text{F}_5$ and $\text{CH}_3\text{C}\equiv\text{C}$ that similar species were observed when investigating precursors that contained Np and Pu. The formation of organometallic products was confirmed using infrared multiple-photon photodissociation spectroscopy, and the intrinsic stability of the organoactinyl bonds was investigated by measuring relative gas-phase hydrolysis rates.

We have continued to explore the intrinsic unimolecular reactions of gas-phase organo-uranyl complexes [25]. We report here a study that involved CID of the uranyl-propiolate cation, $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{C}-\text{H})]^+$. CID of $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{C}-\text{H})]^+$ was used to prepare the organometallic species $[\text{UO}_2(\text{C}\equiv\text{CH})]^+$ by decarboxylation. Surprisingly, we found that the dominant product ion generated by CID of $[\text{U}^{\text{VI}}\text{O}_2(\text{C}\equiv\text{CH})]^+$ is $[\text{U}^{\text{VI}}\text{OCH}]^+$, which must be created by the elimination of CO. Experimental data to support the proposed dissociation reaction pathway, including high-accuracy mass to charge ratio (m/z) measurements, and preliminary quantum chemical calculations to probe possible structures, chemical bonding, and reaction energetics are presented below.

Experimental Methods

Sample Preparation

Methanol (CH_3OH) and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) were purchased from Sigma-Aldrich Chemical (St. Louis, MO) and used as received. The sample used to prepare gas-phase $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})]^+$ was created by combining 2–3 mg of $\text{U}^{\text{VI}}\text{O}_3$ (Strem Chemicals, Newburyport, MA), corresponding to approximately 7×10^{-6} to 1×10^{-5} mol, with a 2-fold mole excess of propiolic acid (Sigma-Aldrich, St. Louis, MO) and 400 μL of deionized/distilled H_2O in a glass scintillation vial. The solutions were allowed to incubate on a hot plate at 70 °C for 12 h. *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 μL of the resulting solution was diluted with 800 μL of 90:10 (by volume) $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ or $\text{H}_2\text{O}/\text{CH}_3\text{CH}_2\text{OH}$ (same proportions) and used without further work up as the spray solution for electrospray ionization (ESI).

ESI and CID experiments were performed on a ThermoScientific (San Jose, CA) LTQ-XL linear ion trap (LIT) mass spectrometer. Solutions for ESI were infused into the instrument using the incorporated syringe pump at a flow rate of 5 $\mu\text{L}/\text{min}$. In the positive ion mode, the auto-tune routine within the LTQ Tune program was used to optimize the atmospheric pressure ionization stack settings for the instrument

(lens voltages, quadrupole and octopole voltage offsets, etc.) to achieve maximum transmission of singly charged ions such as $[\text{UO}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})(\text{H}_2\text{O})_2]^+$ and $[\text{UO}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})(\text{CH}_3\text{OH})_2]^+$ to the LIT. Helium was used as the bath/buffer gas to improve trapping efficiency and as the collision gas for CID experiments.

For multiple-stage (MS^n) CID experiments to probe fragmentation and ion-molecule reaction (IMR) pathways [26], precursor ions were isolated using a width of 1.0 to 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, 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 a 30-ms activation time was used.

To probe gas-phase reactions of selected precursor ions with background neutrals (primarily H_2O and O_2 [27–29]), ions were isolated using widths of 1–2 m/z units. Here too, the specific width was chosen empirically to ensure maximum ion isolation efficiency. The ions were then stored in the LIT for periods ranging from 1 ms to 10 s. While we have shown that the levels of adventitious H_2O in the 2-D LIT, under normal operating conditions, is lower than in 3-D ion traps [19, 30, 31], there is still a sufficient partial pressure to permit an investigation of IMRs, especially when using long isolation times. When examining IMRs, our intent was not to measure or report rates or rate constants, but to identify the *pathways* by which ions react with neutrals such as H_2O or O_2 in the LIT. The levels of these neutral species in the LIT are too low to allow a rigorous examination of H_2O addition rates to specific uranyl complexes for comparison to earlier studies, and our instrument is not configured to allow controlled addition of neutral reagents for IMR. For both CID and IMR experiments, the mass spectra displayed were created by accumulating and averaging at least 30 isolation, dissociation, and ejection/detection steps.

High-resolution/high-accuracy measurements were performed on a ThermoScientific (San Jose, CA) LTQ-Orbitrap Elite mass spectrometer using experimental conditions and settings similar to those outlined above for the LTQ-XL instrument. With the Orbitrap instrument, the experiments were performed with the 120,000 resolution setting, NCE values of 8–16%, activation Q setting of 0.25, and a 10-ms activation time. Mass spectra were collected for 1 min at each MS^n stage.

Density Functional Theory Calculations

Geometry optimizations for potential product ion structures were performed using the B3LYP [32–34], PBE0 [35, 36], and M06-2X [37] functionals, the MWB60 pseudopotential and associated basis set on U, and the 6-311+G(d,p) basis set

on all other atoms. In all cases, an ultrafine integration grid was used. Vibrational frequency calculations were used to determine whether optimized structures were true minima (i.e., no imaginary frequencies) and for zero-point and thermal correction of electronic energies. The Gaussian 09 software package [38] was used for all calculations. NBO 5.9, as integrated in the Gaussian 09 software, was used for natural bond orbital (NBO) and natural localized molecular orbital (NLMO) calculations to examine bonding orbital interactions [39].

Results and Discussion

Collision-Induced Dissociation of Water- and Alcohol-Coordinated $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})]^+$

The initial goal of this study was to determine whether $[\text{U}^{\text{VI}}\text{O}_2(\text{C}\equiv\text{CH})]^+$ could be synthesized in the gas phase by decarboxylation (an approach used successfully in prior investigations of metal-carboxylate complexes [24, 40–44]), and to probe the dissociation and IMR reactivity of the species. The ESI mass spectrum generated using a solution created by digestion of UO_3 with propiolic acid is shown in Figure 1. The solvent mixture used in this case was 90:10 $\text{H}_2\text{O}/\text{CH}_3\text{OH}$, and the most abundant positively charged ions generated were $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})(\text{H}_2\text{O})_2]^+$, $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})(\text{H}_2\text{O})(\text{CH}_3\text{OH})]^+$, and $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})(\text{CH}_3\text{OH})_2]^+$ at m/z 375, 389, and 403, respectively. The remaining cations observed in the m/z 250–370 region of the ESI spectrum are H_2O and MeOH adducts to $[\text{U}^{\text{VI}}\text{O}_2(\text{OH})]^+$ and $[\text{U}^{\text{VI}}\text{O}_2(\text{OCH}_3)]^+$ and their CID pathways were investigated in an earlier study [45].

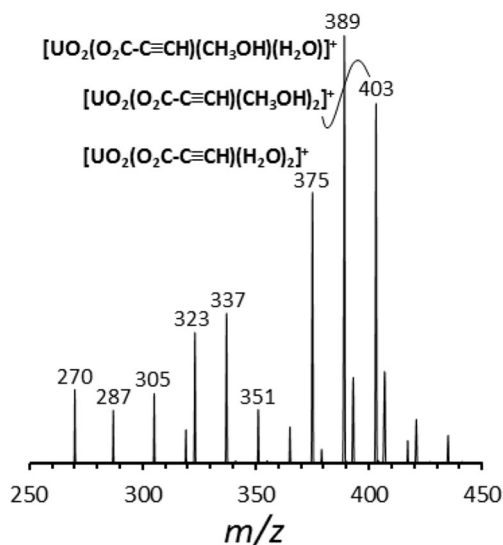
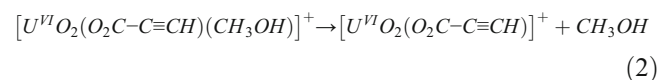
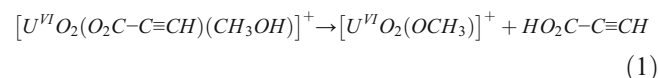


Figure 1. Electrospray ionization mass spectrum generated using spray solution of $[\text{UO}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})_2]$ in 90:10 (v/v) $\text{H}_2\text{O}/\text{CH}_3\text{OH}$. Compositions of the principal species germane to this study are labeled. Species in the m/z region of 250–370 correspond to H_2O and CH_3OH -coordinated $[\text{UO}_2]^+$, $[\text{UO}_2(\text{OH})]^+$, and $[\text{UO}_2(\text{OCH}_3)]^+$

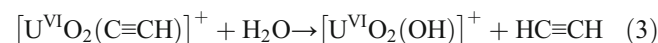
The CID of $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})(\text{H}_2\text{O})(\text{CH}_3\text{OH})]^+$ (data not shown) and $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})(\text{CH}_3\text{OH})_2]^+$ (Figure S1b of the supporting information) led to formation of $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})(\text{CH}_3\text{OH})]^+$ by elimination of an H_2O or MeOH ligand, respectively. In both cases, subsequent CID of $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})(\text{CH}_3\text{OH})]^+$ (MS^3 stage, Figure S1c of the supporting information) produced $[\text{U}^{\text{VI}}\text{O}_2(\text{OCH}_3)]^+$ by intra-complex proton transfer and elimination of propiolic acid (reaction 1), as well as $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})]^+$ by elimination of CH_3OH (reaction 2).



The tendency to eliminate propiolic acid over the remaining alcohol ligand was greater for CID of $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})(\text{CH}_3\text{CH}_2\text{OH})]^+$ (Figure S2c of the supporting information).

CID of $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})(\text{H}_2\text{O})_2]^+$ at m/z 375 generated the highest yield of $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})]^+$, and is therefore used to summarize the results of the MS^n CID experiments (Figure 2). As shown in Figure 2a, b, CID of $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})(\text{H}_2\text{O})_2]^+$ caused elimination of single H_2O ligands in sequential steps (MS/MS and MS^3 stages, respectively) to generate $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})]^+$ at m/z 339. Subsequent CID of $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})]^+$ (MS^4 stage, Figure 2c) generated peaks initially assigned as $[\text{U}^{\text{VI}}\text{O}_2(\text{C}\equiv\text{CH})]^+$ at m/z 295, and $[\text{U}^{\text{VI}}\text{O}_2(\text{OH})]^+$ at m/z 287.

The $[\text{U}^{\text{VI}}\text{O}_2(\text{C}\equiv\text{CH})]^+$ ion at m/z 295 was isolated, independently, for IMR in the LIT for periods ranging from 1 ms to 1 s (MS^5 stage, Figure S3a–d of the supporting information). It is important to note that during the isolation step, all ionized species except the one chosen for storage are resonantly ejected from the ion trap. The appearance of peaks other than the isolated ion identifies IMR products. The isolation and storage of $[\text{U}^{\text{VI}}\text{O}_2(\text{C}\equiv\text{CH})]^+$ in the LIT led to production of $[\text{U}^{\text{VI}}\text{O}_2(\text{OH})]^+$ at m/z 287. The neutral eliminated in the reaction is assumed to be acetylene (reaction 3), which indicates a gas-phase IMR with background H_2O . Therefore, it is likely that the $[\text{U}^{\text{VI}}\text{O}_2(\text{OH})]^+$ product that appears in the CID spectrum of $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})]^+$ (Figure 2c) is generated by hydrolysis of $[\text{U}^{\text{VI}}\text{O}_2(\text{C}\equiv\text{CH})]^+$ after its creation by decarboxylation. This general pattern in reactivity is consistent with our earlier study of the formation of uranyl-organometallic complexes [24].



In our previous study, CID of the positively charged organometallic uranyl species such as $[\text{U}^{\text{VI}}\text{O}_2(\text{CH}_3)]^+$ and $[\text{U}^{\text{VI}}\text{O}_2(\text{CH}_2\text{CH}_3)]^+$ generated $[\text{U}^{\text{VI}}\text{O}_2]^+$ by elimination of (neutral) methyl and ethyl radicals, respectively [25]. In the

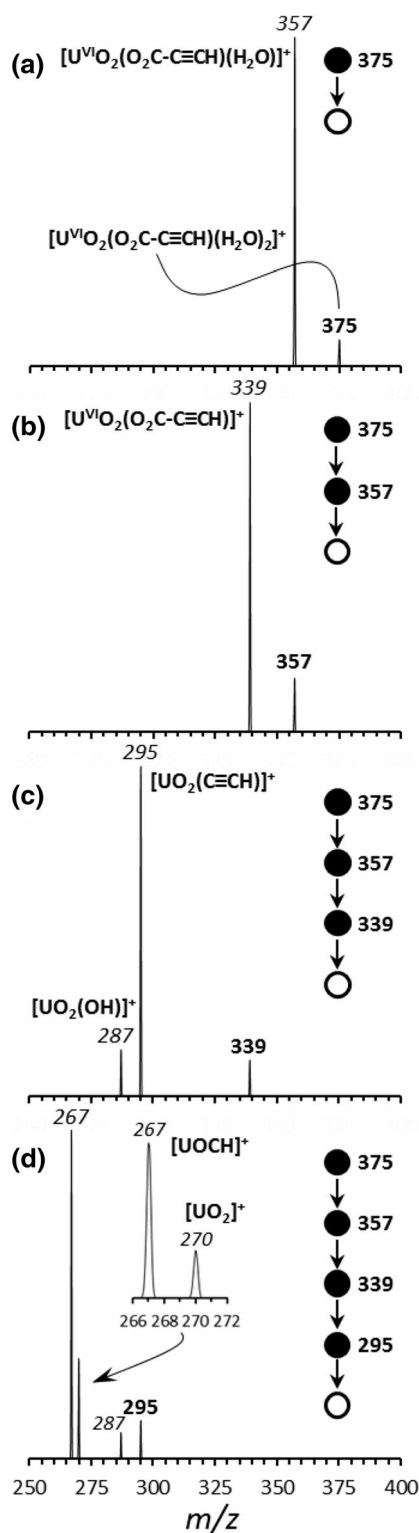


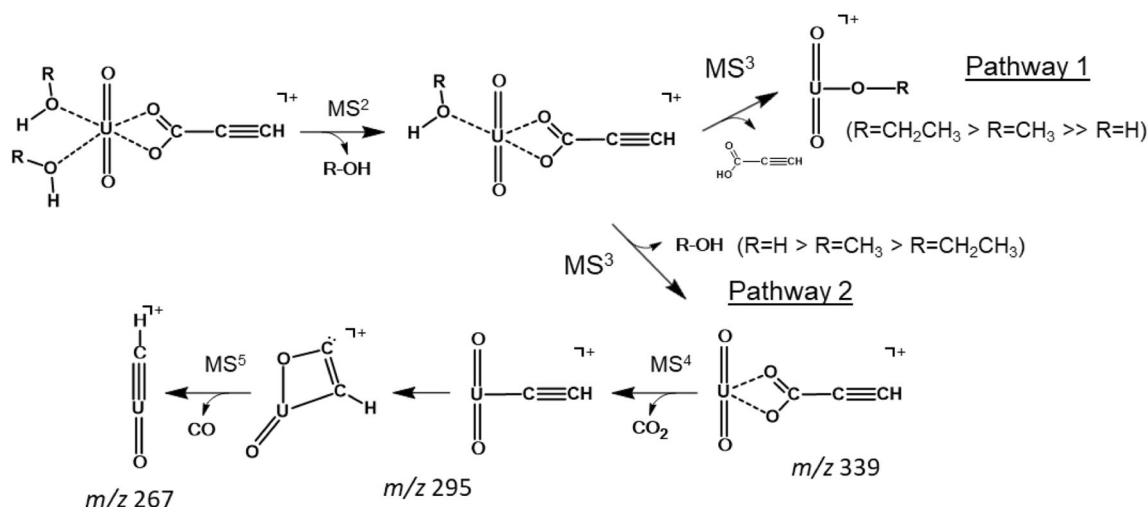
Figure 2. Multiple-stage CID spectra initiated with $[\text{UO}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})(\text{H}_2\text{O})_2]^+$: (a) CID (MS^2 stage) of $[\text{UO}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})(\text{H}_2\text{O})_2]^+$, (b) CID (MS^3 stage) of $[\text{UO}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})(\text{H}_2\text{O})_2]^+$, (c) CID (MS^4 stage) of $[\text{UO}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})]^+$, and (d) CID (MS^5 stage) of $[\text{UO}_2(\text{C}\equiv\text{CH})]^+$. For the spectra, the circles and arrows illustrate the MS^n sequence/pathway. In each spectrum, the bold peak label indicates the precursor selected for CID whereas labels in italics represent the products from dissociation or ion-molecule reactions as indicated in the text

present set of experiments, however, subsequent CID of $[\text{U}^{\text{VI}}\text{O}_2(\text{C}\equiv\text{CH})]^+$ at m/z 295 (MS^5 stage, Figure 2d) generated a peak at m/z 267, along with $[\text{U}^{\text{V}}\text{O}_2]^+$ and $[\text{U}^{\text{IV}}\text{O}_2(\text{OH})]^+$ at m/z 270 and 287, respectively. The ion at m/z 267 was initially assigned as $[\text{UOCH}]^+$, which would be formed by the elimination of CO upon collisional activation of $[\text{U}^{\text{VI}}\text{O}_2(\text{C}\equiv\text{CH})]^+$.

The LIT does not have sufficient mass measurement accuracy to unambiguously establish molecular formulae for the ions at m/z 267 and 239. However, the LTQ-Orbitrap instrument is capable of resolving powers greater than 100,000 ($m/\Delta m$), and accuracies in the 1–5-ppm range. Accurate masses measured with the LTQ-Orbitrap are compared to theoretical monoisotopic masses for a range of possible precursor and product ion compositions in Table S1 of the supporting information. For the species at nominal m/z 339, assumed to be $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})]^+$, the accurate m/z value differs from the theoretical mass for the corresponding molecular formula of $[\text{C}_3\text{HO}_4\text{U}]$ by 0.200 mDa (0.590 ppm error) and supports the composition assignment. The same is true for the ion at nominal m/z 295, assumed to be $[\text{UO}_2(\text{C}\equiv\text{CH})]^+$ for which the measured mass differs from the theoretical mass by 0.300 mDa (1.017 ppm error) for the molecular formula $[\text{C}_2\text{HO}_2\text{U}]$. In addition, the difference in measured mass between $[\text{C}_3\text{HO}_4\text{U}]$ and $[\text{C}_2\text{HO}_2\text{U}]$ is 43.9899 u compared to the theoretical mass for CO_2 of 43.9898 (0.100 mDa difference, 2.273 ppm error). This provides additional support for a dissociation reaction that involves elimination of CO_2 from $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})]^+$ to create $[\text{U}^{\text{VI}}\text{O}_2(\text{C}\equiv\text{CH})]^+$. The accurate mass measurements also support the composition assignments for the m/z 287, 286, and 270 ions ($[\text{U}^{\text{VI}}\text{O}_2(\text{OH})]^+$, $[\text{U}^{\text{VI}}\text{O}_2(\text{O})]^+$, and $[\text{U}^{\text{V}}\text{O}_2]^+$, respectively).

The accurate mass measurement for the ion at nominal m/z 267 differs from the theoretical mass for a composition of $[\text{UOCH}]^+$ by only 0.400 mDa (1.498 ppm error). Furthermore, the difference in measured masses of $[\text{U}^{\text{VI}}\text{O}_2(\text{C}\equiv\text{CH})]^+$ and $[\text{UOCH}]^+$ is 27.9950 u compared to a theoretical mass for CO of 27.9949 (0.100 mDa, 3.572 ppm error). Clearly, the accurate mass measurements support the hypothesis that sequential CID steps cause the decarboxylation of $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})]^+$ to create $[\text{U}^{\text{VI}}\text{O}_2(\text{C}\equiv\text{CH})]^+$ and, more importantly, subsequent elimination of CO to leave $[\text{UOCH}]^+$.

Given the established compositions of the precursor and product ions, we can speculate on the general MS^n CID pathways initiated with the $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})(\text{H}_2\text{O})_2]^+$ precursor, and by extension, the alcohol-coordinated analogues. Scheme 1 shows a proposed sequence of steps. At the MS/MS stage, CID causes the elimination of a single H_2O or ROH ($\text{R}=\text{CH}_3$ or CH_2CH_3) ligand. Elimination of an alcohol ligand competes with intra-complex proton transfer and elimination of (neutral) propiolic acid at the MS^3 stage. The loss of propiolic acid is most favored for complexes that include $\text{CH}_3\text{CH}_2\text{OH}$, less so for analogues that contain CH_3OH and is not observed



Scheme 1. Reaction pathway to production of $[\text{OUCH}]^+$ by multiple-stage CID of $[\text{UO}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})(\text{R}-\text{OH})_2]^+$ ($\text{R}=\text{H}$, CH_3 , or CH_2CH_3)

for $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})(\text{H}_2\text{O})_2]^+$. We note that in these experiments, the tendency to eliminate neutral propionic acid and retain hydroxide or alkoxide follows the relative trend in gas-phase acidity, $\text{CH}_3\text{CH}_2\text{OH} > \text{CH}_3\text{OH} > \text{H}_2\text{O}$ [46, 47]. Upon loss of the second H_2O or ROH ligand (MS^3 stage), subsequent CID of $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})]^+$ causes decarboxylation to generate $[\text{U}^{\text{VI}}\text{O}_2(\text{C}\equiv\text{CH})]^+$. We propose that elimination of CO from $[\text{U}^{\text{VI}}\text{O}_2(\text{C}\equiv\text{CH})]^+$ may occur by rearrangement and nucleophilic attack by an “yl” oxo ligand.

Computed Structures for $[\text{OUCH}]^+$

The composition assignment of $[\text{OUCH}]^+$ leads to the intriguing suggestion that a uranium-methyldiyne (i.e., $-\text{U}\equiv\text{CH}$) species is generated by CID of $[\text{U}^{\text{VI}}\text{O}_2(\text{C}\equiv\text{CH})]^+$. Formation of

similar species, such as (neutral) $[\text{F}_3\text{U}^{\text{VI}}\text{CH}]$, has been reported by Andrews, Li, and coworkers in experiments that involved reactions of laser-ablated U atoms with trihalomethanes or carbon tetrafluoride [48]. Following deposition of gas-phase species into an Ar matrix at 8 K, annealing and irradiation with UV light, a range of products were identified using infrared spectroscopy and density functional theory (DFT) calculations. Beyond data from vibrational spectra, support for generation of a methyldiyne in the matrix-isolation studies was provided by quantum mechanical calculations and NLMO, which suggest the formation of a triple bond between uranium and carbon: one σ -bond utilizing the $\text{U } df$ and $\text{C } sp$ hybrid orbitals, and two π -bonds utilizing the $\text{U } df$ and $\text{C } p$ orbitals [48].

Despite the information provided by the MS^n CID patterns and accurate mass measurements in the present study, the

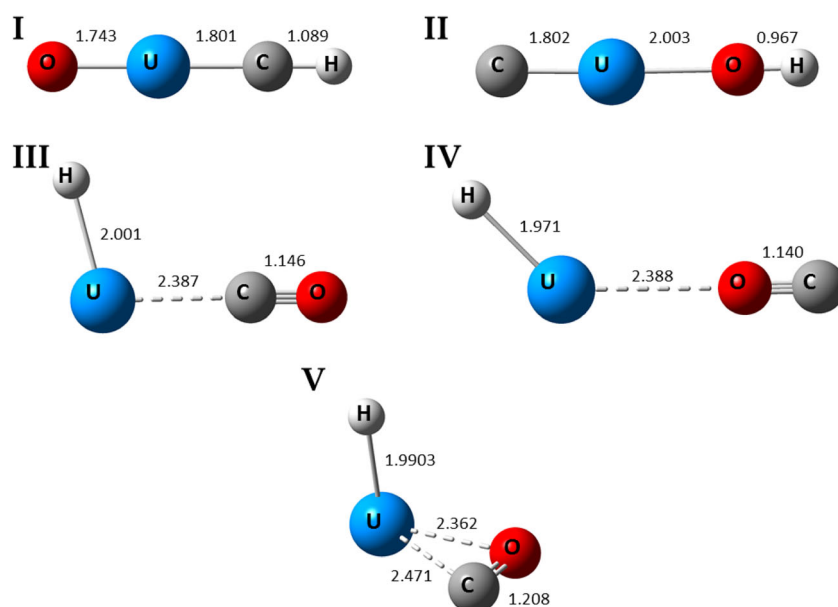


Figure 3. Possible structures for product ion at $m/z\ 267$, with composition $[\text{OUCH}]$. Structures were generated from calculations at the B3LYP/MWB60/6-11+G(d,p) level of theory. Bond lengths are shown in angstroms

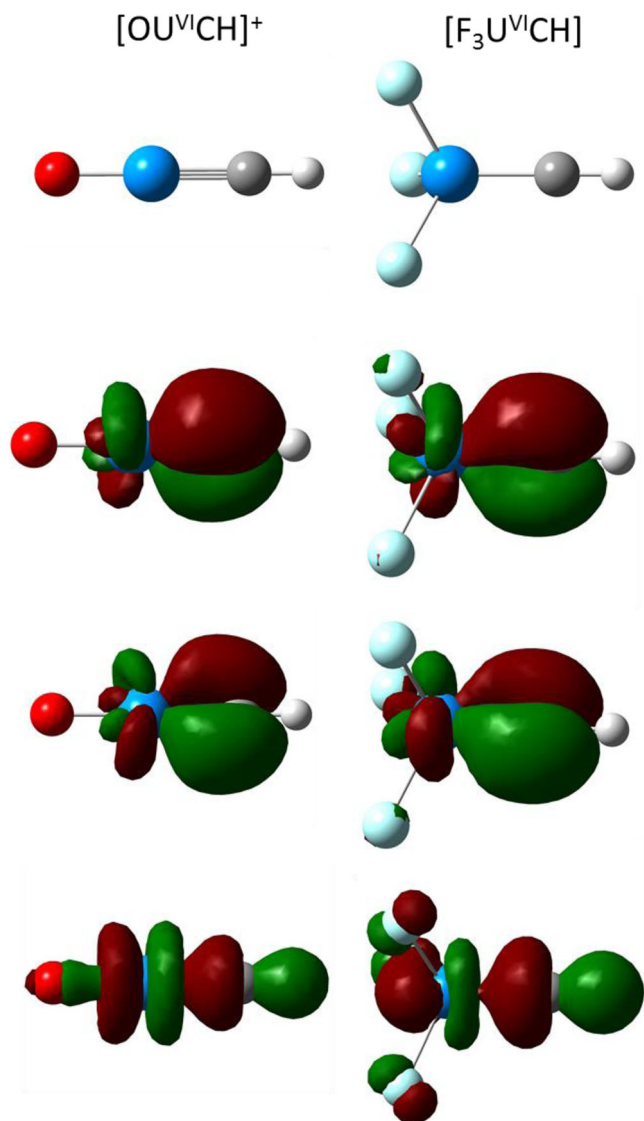


Figure 4. Bonding orbitals for $[\text{OU}^{\text{VI}}\text{CH}]^+$ and $[\text{F}_3\text{U}^{\text{VI}}\text{CH}]$, generated at the B3LYP/MWB60/6-11+G(d,p) level of theory

structure of the ion at nominal m/z 267 is not known. Therefore, DFT calculations were used to predict possible connectivity and structures for the product ion, and 5 minima were identified (structures **I**–**V** in Figure 3). Structure **I** is the methylidyne structure with connectivity $[\text{O}-\text{U}-\text{C}-\text{H}]$. The connectivity of structure **II** is instead $[\text{C}-\text{U}-\text{O}-\text{H}]$. Structures **III** through **V** are best described as $[\text{U}-\text{H}]^+$ coordinated to CO: structures **III** and **IV** are end-on complexes with coordination of U by either

O or C, while structure **V** is an η^2 complex with CO bound side-on.

The electronic energies, zero-point corrections, and relative energies in kilojoules/mole for the respective structures, modeled in both the singlet and triplet spin states, are provided in Table S2 of the supporting information. The computed energy for the $[\text{O}-\text{U}-\text{C}-\text{H}]$ composition/structure is significantly lower in energy than the other minima identified, regardless of the functional used. The calculations also suggest that the singlet state is lowest in energy for the $[\text{O}-\text{U}-\text{C}-\text{H}]$ composition (structure **I**) while the triplet state is favored for the $[\text{C}-\text{U}-\text{O}-\text{H}]$ and $[\text{H}-\text{U}-\text{CO}]$ species (structures **II** through **V**). We tentatively conclude, therefore, that the ion at m/z 267 corresponds to $[\text{O}-\text{U}-\text{C}-\text{H}]^+$, with the caveat that any potential barriers to the rearrangements necessary to generate the respective species have been neglected in our argument. However, based on the calculated relative energies, we feel that it is reasonable to assume that the $[\text{OU}^{\text{VI}}\text{CH}]^+$ ion adopts the linear geometry of structure **I**.

We next examined the (calculated) molecular orbitals and atomic charges for $[\text{OU}^{\text{VI}}\text{CH}]^+$. Of particular interest was the evidence for a U-C triple bond, and correlation between the bonding in $[\text{OUC}]^+$ to similar structures identified by Andrews and coworkers [48]. As noted above, the (neutral) species $[\text{F}_3\text{U}^{\text{VI}}\text{CH}]$ is proposed to include a U-C triple bond, and it was noted by Andrews and Li that strong inductive effects of the fluoride ligands support the positive charge on U, which stabilizes the U(VI) oxidation state and, in turn, the bonding to the methylidyne ligand. The molecular orbitals for $[\text{OU}^{\text{VI}}\text{CH}]^+$ and $[\text{F}_3\text{U}^{\text{VI}}\text{CH}]$, calculated here using the same functional and basis set to facilitate direct comparison, are shown in Figure 4.

The bonding patterns for the two species are nearly identical at the level of theory used, including formation of a triple bond by σ -bonding involving the U $df\sigma$ and C $sp\sigma$ hybrid orbitals, and two π -bonds between the U $d\pi$ and C $p\pi$ orbitals. A comparison of the natural charges on U and C, the Wiberg natural bond order (BO_w), NBO occupancies, and NLMO compositions are shown in Table 1. The electron contributions from carbon and uranium to form the U-C σ -bonding NLMO, 53 and 45%, respectively, indicate a higher degree of covalent character in $[\text{OU}^{\text{VI}}\text{CH}]^+$ than in $[\text{F}_3\text{U}^{\text{VI}}\text{CH}]$ (71 and 29%, respectively). The slightly higher bond order in $[\text{OU}^{\text{VI}}\text{CH}]^+$ is likely due to the higher occupancy of the two π -bonding orbitals, provided by favorable overlap with the p -bonding orbitals of the oxo ligand. In addition, the stabilizing inductive effect attributed to the fluoride ligands in $[\text{F}_3\text{U}^{\text{VI}}\text{CH}]$ is provided in the case of

Table 1. Natural Charges on Uranium (q_U) and Carbon (q_C), Wiberg Natural Bond Order (BO_w) for the U-C Bond, Occupancies of the U-C NBOs, and the Contributions of Both Uranium and Carbon to the Bonding NLMOs. Hybridization Values for Uranium Are Normalized with Respect to the d-Orbital Contributions

	q_U	q_C	BO_w		NBO occupancy	NLMO contributions & hybrids	
$[\text{OU}=\text{CH}]^+$	2.04	− 0.61	2.83	σ	1.87	53% ^a C ($s^1 p^{0.80}$)	45% ^a U ($s^{0.06} p^{0.09} d^{1.00} f^{2.92}$)
				π	1.97	55% C ($p^{1.00}$)	45% U ($p^{0.03} d^{1.00} f^{1.77}$)
$[\text{F}_3\text{U}=\text{CH}]$	1.89	− 0.41	2.78	σ	1.95	71% C ($s^1 p^{0.62}$)	29% U ($s^{0.12} d^{1.00} f^{0.57}$)
				π	1.88	46% C ($p^{1.00}$)	54% U ($p^{0.01} d^{1.00} f^{4.41}$)

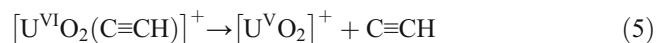
^aA significant (2%) delocalization contribution from the -yl oxygen brings the total to 100%

Table 2. Computed Gibbs Free Energies for Reactions 4–7. Calculations Were Performed Using the B3LYP, M06-2X, and PBE0 Functionals, MWB60 Pseudopotential and Basis Set on U, and 6-311+G(d,p) Basis Set on C, H, and O

	ΔG (kJ/mol)		
	B3LYP	M06-2X	PBE0
$[\text{U}^{\text{VI}}\text{O}_2(\text{C}\equiv\text{CH})]^+ \rightarrow [\text{U}^{\text{V}}\text{O}_2]^+ + \text{C}\equiv\text{CH}$	253.3	255.1	231.8
$[\text{U}^{\text{VI}}\text{O}_2(\text{C}\equiv\text{CH})]^+ \rightarrow [\text{OU}^{\text{VI}}\text{CH}]^+ + \text{CO}$	215.1	165.8	213.2
	ΔG (kJ/mol)		
	B3LYP	M06-2X	PBE0
$[\text{OU}^{\text{VI}}\text{CH}]^+ + \text{O}_2 \rightarrow [\text{U}^{\text{V}}\text{O}_2]^+ + \text{OCH}$	− 604.2	− 555.7	− 596.5
$[\text{OU}^{\text{VI}}\text{CH}]^+ + \text{H}_2\text{O} \rightarrow [\text{U}^{\text{V}}\text{O}_2]^+ + \text{CH}_3$	− 279.1	− 217.4	− 260.1

$[\text{OU}^{\text{VI}}\text{CH}]^+$ by the oxo ligand, as indicated by the small, but significant, contribution to the U-C σ -bonding NLMO.

As noted above, our previous study showed that CID of $[\text{U}^{\text{VI}}\text{O}_2(\text{CH}_3)]^+$ and $[\text{U}^{\text{VI}}\text{O}_2(\text{CH}_2\text{CH}_3)]^+$ generated $[\text{U}^{\text{V}}\text{O}_2]^+$ by elimination of (neutral) methyl and ethyl radicals, respectively [25]. Therefore, another consideration in the present study was competition between rearrangement of $[\text{U}^{\text{VI}}\text{O}_2(\text{C}\equiv\text{CH})]^+$ and loss of CO to create $[\text{OU}^{\text{VI}}\text{CH}]^+$ (reaction 4) and direct ejection of $\text{C}\equiv\text{CH}$ radical to leave $[\text{U}^{\text{V}}\text{O}_2]^+$ (reaction 5), especially because a peak corresponding to $[\text{U}^{\text{V}}\text{O}_2]^+$ appears in Figure 2d at ca. 20% relative intensity.



The computed Gibbs free energies for reactions 4 and 5 are provided in Table 2. As expected, both reactions are predicted to be endergonic. However, the computed energies suggest that reaction 4 requires less energy and should be favored over reaction 5. Therefore, the DFT results are consistent with the experimental observation that rearrangement and loss of CO is favored over elimination of $\text{C}\equiv\text{CH}$ radical.

Apparent ion-molecule reactions of $[\text{OU}^{\text{VI}}\text{CH}]^+$

The isolation, without imposed collisional activation, of $[\text{OU}^{\text{VI}}\text{CH}]^+$ was investigated to determine the susceptibility of the species to reactions with neutrals in the ion trap. The LIT is not currently configured to allow the controlled introduction of neutral reagents for accurate measurements of ion reaction rates. Previous studies done by our group and others have demonstrated that gas-phase organometallic species, including those that contain U^{VI} and U^{V} , will undergo hydrolysis reactions [30, 31, 42–44], and there is a pronounced tendency for U^{V} species to add molecular oxygen [28, 49–51]. Both H_2O and O_2 are present in sufficient quantities as background gases to probe general trends in reactivity.

Product ion spectra generated by isolation and storage of $[\text{OU}^{\text{VI}}\text{CH}]^+$ for 10 ms, 100 ms, and 1 s are shown in Figure 5a–c. At 10-ms reaction time, the only product ion observed above baseline was $[\text{U}^{\text{V}}\text{O}_2]^+$ at m/z 270. At 100-ms reaction time, the intensity of $[\text{U}^{\text{V}}\text{O}_2]^+$ increased, and a minor peak at m/z 255 was also observed. The ion at m/z 255 is consistent with formation of $[\text{U}^{\text{II}}(\text{OH})]^+$ or $[\text{U}^{\text{IV}}(\text{O})(\text{H})]^+$ and elimination of $[\text{OCH}_2]$. The $[\text{U}^{\text{V}}\text{O}_2]^+$ product was the base peak at 1000 ms isolation time, and a minor peak (< 5% relative intensity) corresponding to formation of $[\text{U}^{\text{VI}}\text{O}_2(\text{OH})]^+$ was also observed.

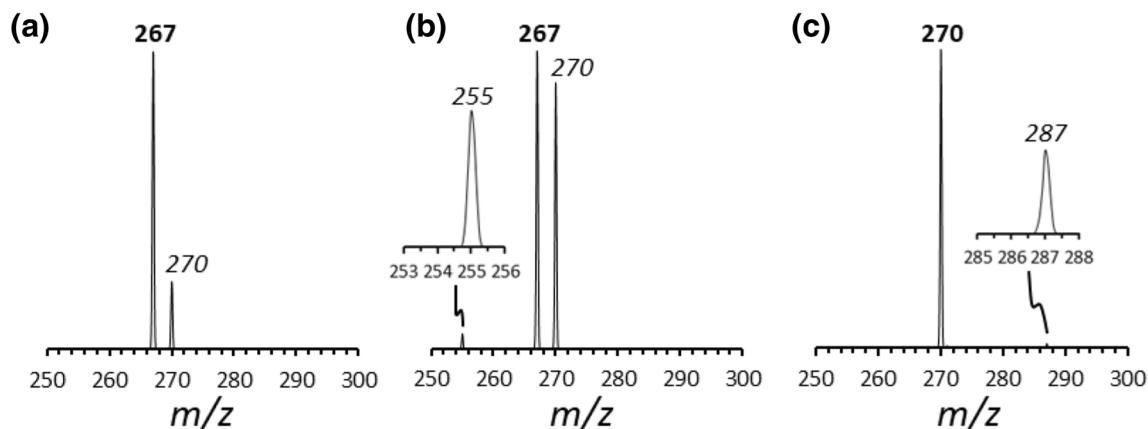
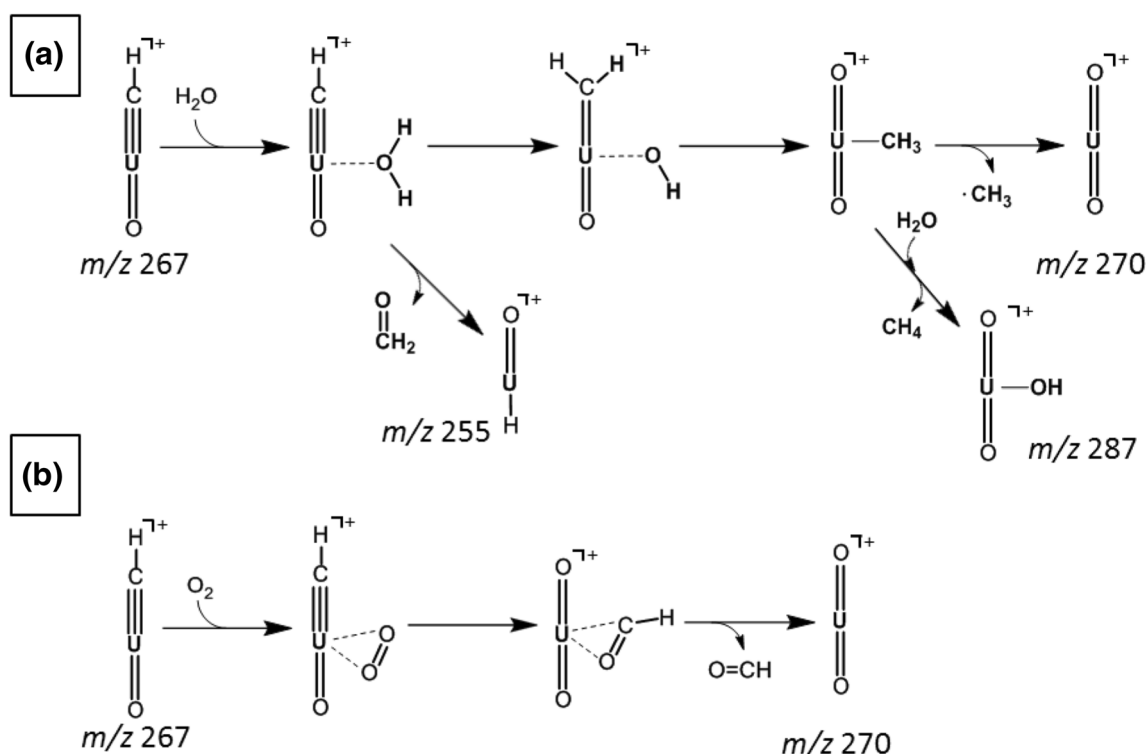
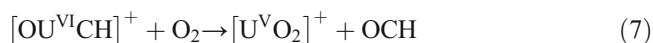
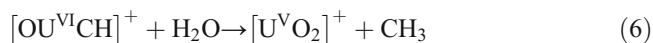


Figure 5. Product ion spectra generated by isolating $[\text{OU}^{\text{VI}}\text{CH}]^+$, without imposed collisional activation for (a) 10 ms, (b) 100 ms, and (c) 1000 ms. During isolation period, the $[\text{OU}^{\text{VI}}\text{CH}]^+$ ion reacts with adventitious H_2O and/or O_2 in the linear ion trap. In each spectrum, the bold peak label indicates the precursor selected for isolation whereas labels in italics represent the products from ion-molecule reactions



Scheme 2. Proposed pathways for ion-molecule reaction between $[\text{OUCH}]^+$ and (a) background H_2O and (b) background O_2

Reasonable pathways to explain the apparent reaction of $[\text{OU}^{\text{VI}}\text{CH}]^+$ with H_2O (reaction 6) or O_2 (reaction 7) to generate $[\text{U}^{\text{VO}}\text{O}_2]^+$ are provided in Scheme 2.



In pathway A (reaction 6), addition of H_2O to $[\text{OU}^{\text{VI}}\text{CH}]^+$, followed by consecutive H transfer steps might yield the organometallic species $[\text{UO}_2(\text{CH}_3)]^+$, which would then either undergo elimination of methyl radical to leave UO_2^+ or hydrolysis to create $[\text{UO}_2(\text{OH})]^+$. In pathway B (reaction 7), addition of O_2 to $[\text{OU}^{\text{VI}}\text{CH}]^+$, subsequent generation of a formyl anion, and then elimination of OCH radical would also furnish $[\text{U}^{\text{VO}}\text{O}_2]^+$. The computed free energies for reactions 6 and 7 are provided in Table 2. While the DFT calculations suggest that both pathways should be spontaneous, the reaction with O_2 is significantly more exergonic. Furthermore, the calculations strongly suggest that O_2 addition leads spontaneously to oxidation of the methynyl group to create the formyl anion (structure VI in Figure S4), whereas H_2O addition merely creates a hydrate (structure VII in Figure S4).

The likelihood that reaction pathway A contributes to the formation of $[\text{U}^{\text{VO}}\text{O}_2]^+$ can be tested, in part, by probing the IMR of $[\text{U}^{\text{VI}}\text{O}_2(\text{CH}_3)]^+$, which can be generated independently using CID of $[\text{U}^{\text{VI}}\text{O}_2(\text{OCH}_2\text{CH}_3)]^+$ [25]. Isolation of $[\text{U}^{\text{VI}}\text{O}_2(\text{CH}_3)]^+$ for periods ranging from 10 ms to 10 s (MS^4

stage, Figure S5 of the supporting information) leads to formation of $[\text{U}^{\text{VO}}\text{O}_2(\text{H}_2\text{O})]^+$ and hydrates of the product. The $[\text{U}^{\text{VO}}\text{O}_2]^+$ ion at m/z 270 is observed at only 10% relative intensity, and a peak corresponding to $[\text{U}^{\text{VI}}\text{O}_2(\text{OH})]^+$ at m/z 287 is not detected above baseline. Preliminary calculations of reaction energetics (Table S3) suggest that while hydrolysis (reaction 8) should be favored thermodynamically, the barrier for proton transfer to create CH_4 is higher than the energy required to eliminate the methyl radical directly (reaction 9).



The data generated by independent isolation and reaction of $[\text{U}^{\text{VI}}\text{O}_2(\text{CH}_3)]^+$ is inconsistent with participation of the species as an intermediate in the IMR of $[\text{OU}^{\text{VI}}\text{CH}]^+$ with H_2O . If pathway A was to contribute significantly to the reactivity of $[\text{OU}^{\text{VI}}\text{CH}]^+$, we would expect a peak corresponding to $[\text{U}^{\text{VO}}\text{O}_2(\text{H}_2\text{O})]^+$ at m/z 288 to be present in the product ion spectrum. Because $[\text{U}^{\text{VO}}\text{O}_2]^+$ is the dominant product ion observed, we conclude instead that the formation of $[\text{U}^{\text{VO}}\text{O}_2]^+$ from $[\text{OUCH}]^+$ is due to reaction with O_2 in the ion trap. While the mechanism remains speculative without isotopic labeling to confirm reactions with H_2O over O_2 , and comprehensive quantum chemical modeling of the reaction pathways is beyond the scope of this report, our preliminary experiments demonstrate

that the alkylidyne species, if generated, is very reactive in the gas phase and open the door for further studies.

Conclusions

In summary, we have shown that CID of $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{CC}\equiv\text{CH})]^+$ can be used to prepare the organometallic species $[\text{U}^{\text{VI}}\text{O}_2(\text{C}\equiv\text{CH})]^+$ by decarboxylation. High-accuracy m/z measurements demonstrate conclusively that subsequent CID of $[\text{U}^{\text{VI}}\text{O}_2(\text{C}\equiv\text{CH})]^+$ caused elimination of (neutral) CO to furnish $[\text{OU}^{\text{VI}}\text{CH}]^+$, thus providing another example of the substitution of an oxo ligand of uranyl ion in a unimolecular gas-phase reaction. Relative energies for various candidate structures based on DFT calculations suggest that the $[\text{OU}^{\text{VI}}\text{CH}]^+$ ion is a uranium-methyldyne product, demonstrating one rare instance of a $\text{U}\equiv\text{C}$ triple bond. To the best of our knowledge, there is only one other report of the synthesis of such a species [42].

One limitation of the present study is the lack of clear structural information to support the proposed formation of an alkylidyne species. The DFT calculations provide circumstantial information about the most probable structure, and a reasonable reaction pathway (Scheme 1) involves intramolecular nucleophilic attack by the “yl” oxo ligand of UO_2^{2+} on the C-atom of the alkynyl ligand to leave $[\text{OU}^{\text{VI}}\text{CH}]^+$ as a product.

DFT calculations of $[\text{OU}^{\text{VI}}\text{CH}]^+$ and $[\text{F}_3\text{U}^{\text{VI}}\text{CH}]$ [42] were performed here at the same level of theory to allow direct comparison. The bonding patterns for the two species are nearly identical at the level of theory used. The $\text{U}\equiv\text{C}$ triple bond formed is composed of one σ -bond with contributions from the U df and C sp hybrid orbitals, and two π -bonds with contributions from the U df and C p orbitals. NBO occupancies and NLMO compositions were used in a preliminary probe of chemical bonding. NLMO calculations show electron contributions from carbon and uranium to be 53 and 45%, respectively, indicating a higher degree of covalent character in $[\text{OU}^{\text{VI}}\text{CH}]^+$ than in $[\text{F}_3\text{U}^{\text{VI}}\text{CH}]$ (71 and 29%, respectively). We speculate that the slightly higher bond order in $[\text{OU}^{\text{VI}}\text{CH}]^+$ is likely due to the higher occupancy of the two π -bonding orbitals, provided by favorable overlap with the p orbitals of the oxo ligand. In addition, the oxo ligand of $[\text{OU}^{\text{VI}}\text{CH}]^+$ appears to provide a stabilizing inductive effect to the complex.

Computed Gibbs free energies also suggest that reaction of $[\text{OU}^{\text{VI}}\text{CH}]^+$ with either H_2O or O_2 to create $[\text{U}^{\text{V}}\text{O}_2]^+$ should be spontaneous. However, the reaction is significantly more exergonic for O_2 addition, and the calculations strongly suggest that spontaneous oxidation of the methynyl group to create a formyl anion occurs. Based on this, and data from independent measurements that rules out a presumed intermediate on the pathway for reaction with H_2O , we conclude that the formation of $[\text{U}^{\text{V}}\text{O}_2]^+$ from $[\text{OU}^{\text{VI}}\text{CH}]^+$ is due to reaction with O_2 in the ion trap. However, because of the appearance of a minor peak corresponding to $[\text{UOH}]^+$ at m/z 255, spontaneous reactions of $[\text{OU}^{\text{VI}}\text{CH}]^+$ with H_2O cannot be ruled out altogether. A

more comprehensive computational examination of the reaction pathways, including the formation of $[\text{UOH}]^+$, is beyond the scope of this study and will be reported at a later date.

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