# Elucidating Protactinium Hydrolysis: The Relative Stabilities of $PaO_2(H_2O)^+$ and $PaO(OH)_2^+$

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**ABSTRACT:** It is demonstrated that the gas-phase oxo-exchange of $PaO_2^+$ with water is substantially faster than that of $UO_2^+$, indicating that the Pa−O bonds are more susceptible to activation and formation of the bis-hydroxide intermediate, $PaO(OH)_2^+$. To elucidate the nature of the water adduct of $PaO_2^+$, hydration of $PaO_2^+$ and $UO_2^+$, as well as collision induced dissociation (CID) and ligand-exchange of the water adducts of $PaO_2^+$ and $UO_2^+$, was studied. The results indicate that, in contrast to $UO_2(H_2O)^+$, the protactinium oxo bis-hydroxide isomer, $PaO(OH)_2^+$, is produced as a gas-phase species close in energy to the hydrate isomer, $PaO_2(H_2O)^+$. CID behavior similar to that of $Th(OH)_3^+$ supports the assignment as $PaO(OH)_2^+$. The gas-phase results are consistent with the spontaneous hydrolysis of $PaO_2^+$ in aqueous solution, this in contrast to later $AnO_2^+$ (An = U, Np, Pu), which forms stable hydrates in both solution and gas phase. In view of the known propensity for Th(IV) to hydrolyze, and previous gas-phase studies of other $AnO_2^+$, it is concluded that the stabilities of oxo-hydroxides relative to oxide hydrates decreases in the order: Th(IV) > Pa(V) > U(V) > Np(V) > Pu(V). This trend suggests increasing covalency and decreasing ionicity of An−O bonds upon proceeding across the actinide series.
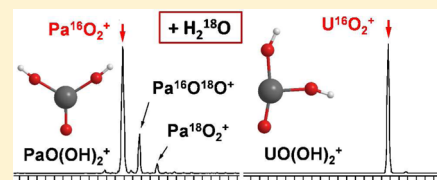
## INTRODUCTION

Differences in chemistry among the actinide elements can be largely attributed to the varying participation of 6d and 5f orbitals/electrons in bonding.[1−4] Located between thorium and uranium, protactinium is formally the first actinide with 5f electron occupancy, which renders understanding its chemistry particularly important to reveal 5f electron participation in bonding.[4−8] Experiments with protactinium pose particular challenges of paucity, high radiotoxicity, and unknown reactivity.[9,10] Overcoming these obstacles has resulted in important chemistry, such as the synthesis of the organo-metallic complexes $Pa(C_5H_5)_4$ and $Pa(C_8H_8)_2$.[11,12] The oxidation state Pa(V) is dominant;[13−15] absent complexing agents, Pa(V) is rapidly hydrolyzed in aqueous solution, followed by the formation of colloids and polymers with unpredictable induction times.[9,10,16,17] This behavior presents challenges in studying the speciation of Pa(V) in solution, including irreproducible results and precipitation.[18−21]

To simplify the reactivity of Pa(V), hydrolysis studies are typically performed at trace concentrations. The following anions, in order of complexation strength, have been employed to stabilize aqueous Pa(V): $F^- > SO_4^{2-} > NO_3^- \approx Cl^- > ClO_4^-$.[22] However, hydrolysis is generally unavoidable.[16,23] Referring to the early reviews by Guillaumont et al.,[16,24] as well as more recent solvent extraction[25,26] and capillary diffusion[27] studies, proposed hydrolytic species include $PaO(OH)^{2+}$, $PaO(OH)_2^+$, $Pa(OH)_5$, and $Pa(OH)_6^-$, which were inferred based on the assumption of $PaO_2^+$ in aqueous solution.[28] Different estimation methods[29,30] applied in these speciation analyses resulted in uncertainties as to the hydrolytic Pa species, largely due to the uncertainty regarding the presence of $PaO_2^+$

versus $PaO^{3+}$. Although $PaO_2^+$ is stable in the gas phase,[4,31] it has not been identified in solution, whereas several complexes containing $PaO^{3+}$ have been identified. The first crystal structure demonstrating a Pa−O bond was $(NEt_4)_2(PaOCl_5)$.[32] Guillaumont has suggested that the absorption band at 200−210 nm is due to the Pa−O bond in $PaO(OH)_2^+$ and $PaO(OH)^{2+}$.[33] Almost 40 years later, an X-ray absorption study confirmed the mono-oxo bond in $PaO(SO_4)_3^{3-}$ present in a 13 M $H_2SO_4$ solution.[34] Oxalate and diethylenetriaminepentaacetate can also form complexes containing Pa−O bonds.[35,36] The use of HF as the complexing medium eliminated all Pa−O bonds,[22,34,37] forming the stable complex $K_2PaF_7$. Other work has reported crystal structures of $(NH_4)_2PaF_7$, $Rb_2PaF_7$, $Cs_2PaF_7$, $Na_3PaF_8$, $(Me_4N)_2(H_3O)PaF_8$, and $(Me_4N)Pa_6$.[38] Extended X-ray absorption fine structure spectra suggested the possibility of the hydrate $PaF_7(H_2O)^{2-}$ in very dilute HF solutions.[39]

Theoretical studies have also examined essential aspects of the chemistry of Pa.[40−42] The calculated structure of $PaO_2^+$ is linear and its electronic structure is similar to those of higher linear actinides, where the 5f orbital contribution to bonding is important.[3,4,40,41,43] It has been suggested that the apparent instability of $PaO_2^+$ in solution may be related to a more negative charge on the $O_{yl}$ of $PaO_2^+$ than on that of $UO_2^{2+}$[40−42] and later $AnO_2^+$ (An = U, Np).[41] $PaO_2^+$ is a closed-shell species without nonbonding valence electrons at the metal to reduce the polarization of the O atoms. The negative charge on the $O_{yl}$ in $PaO_2^+$ may result in a distinctively strong apical interaction

with the hydrogen atoms of water molecules, an effect not expected for $UO_2^{2+}$.[41,42] The prediction is thus that $PaO_2^+$ should more readily protonate to produce $PaO(OH)_2^+$ and $Pa(OH)_4^+$. Four stable hydrate structures have been proposed, including $PaO_2(H_2O)_5^+$, $Pa(OH)_4(H_2O)_2^+$, $PaO(OH)_2(H_2O)_4^+$, and $Pa(OH)_4(H_2O)_3^+$.[40−42] However, the energetics for the conversion of $PaO_2(H_2O)^+$ to $PaO(OH)_2^+$ have not been reported.

Although complexing agents can stabilize reactive Pa in aqueous solution, these environments do not reflect the interaction of Pa(V) with water; hydrolysis reactions of Pa(V) occur too rapidly and result in too many possible species to allow assignments of rates and products.[25] Without experimental results at the molecular level, theoretical predictions of stable aqueous protactinium species, especially the hydrate structures, cannot be validated. It is evident that speciation of aqueous Pa(V) remains inconclusive.[17] At a molecular level in the gas phase, where complications due to solvation are eliminated, it is possible to obtain definitive insights into reactions of Pa(V) with water, notably to differentiate hydration from hydrolysis. Gas phase results are furthermore amenable to accurate modeling by theory. Previous gas-phase experiments have resulted in species such as $PaS^+$,[44] complexes of $PaO^+/PaO_2^+$ with hydrocarbons,[31,45] and $PaO_2^{2+}$ in which the indeterminate oxidation state is Pa(V) or lower.[46] The formation and thermodynamic characterization of small protactinium oxide molecules have been reported. Measured pressures of Pa(g), PaO(g), and $PaO_2$(g) yielded the bond energies D[Pa-O] and D[OPa-O].[47] Oxidation reactions of $PaO^+$ to $PaO_2^+$ established a limit for the bond dissociation energy, D[OPa$^+$-O] $\geq$ 751 kJ/mol.[31,46] Among the characterized $AnO_2^{0/+/2+}$ (An = Pa, U, Np, Pu, Am), the mean bond enthalpy of $PaO_2^+$ is the highest;[48] both Pa−O bonds are strong.[43,48−52] It is thus seemingly enigmatic that in the condensed phase, protactinium evidently appears as mono-oxo rather than a dioxo species;[8,17] $PaO_2^+$ exhibits strong Pa−O bonds that are unusually susceptible to activation, as in hydrolysis.[8,31,44−46,48]

The central goal of the work reported here was to examine the stability of $PaO_2^+$ upon the addition of a water molecule. This is a means to evaluate at the most fundamental level the relative stabilities of the two potential water-addition products, the hydrate $PaO_2(H_2O)^+$ and the bis-hydroxide, $PaO(OH)_2^+$. The results are compared with those for other $AnO_2^+$, particularly $UO_2^+$, with Th(IV), and with the aqueous solution chemistry of Pa(V). Although $UO_2^{2+}$ is much more prevalent than $UO_2^+$, the latter species is known to exist in solution[53,54] and solid state.[55] Furthermore, electrospray ionization (ESI) of $UO_2^{2+}$ solutions in the absence of a stabilizing strongly basic ligand[56,57] results in only monopositive gas species, primarily reduced $U^VO_2^+$ and hydrolyzed $U^{VI}O_2(OH)^+$.[58,59] The propensity of $UO_2^{2+}$, which is very stable in solution, to reduce to $UO_2^+$ upon ESI is due to electron-transfer from a neutral solvent molecule to the dipositive uranyl ion upon desolvation. Ligation of $UO_2^{2+}$ by more basic ligands than water, such as acetonitrile, can stabilize dipositive uranyl from solution to gas, but bare $UO_2^{2+}$ is not accessible by ESI. In contrast to reduced $UO_2^+$, the Th(IV) oxidation state is retained upon ESI by hydrolysis to produce monopositive ions, primarily $Th^{IV}(OH)_3^+$ as in the present work. The different ESI behaviors of U(VI) and Th(IV) reflects the accessibility of the U(V) oxidation state but not the Th(III) oxidation state. Studying the gas-phase chemistry of $PaO_2^+$ and $UO_2^+$ allows comparison of the behavior of these two actinides under the same conditions of speciation and charge state.

## ■ EXPERIMENTAL SECTION

*Caution! The Pa-231 isotope employed in this work is highly radiotoxic. All experiments were conducted in laboratories designed for handling such radiologically hazardous materials.*

$PaO_2^+$ and $UO_2^+$, as well as their water-addition products and $Th(OH)_3^+$, were produced by ESI using methanol/ethanol solutions containing 200 μM of the actinide. A 10 mM $UO_2(ClO_4)_2$ at pH 2 was diluted with methanol to prepare the ESI solution. To produce $Th(OH)_3^+$, the ESI solution was prepared from a stock solution of 0.46 mM $Th(ClO_4)_4$ in 1.2 mM $HClO_4$ at pH 2.9. The $^{231}$Pa solution, recently purified from its decay daughters, was prepared by the dissolution of 1.7 mg of $(NH_4)_2PaF_7$(cr) in 1 M HF to produce a stock solution 22 mM in $^{231}$Pa.[38,60] The Pa solution for ESI was prepared by dilution of this stock solution with methanol/ethanol. The actinide isotopes (>99%) were U-238 ($t_{1/2} \approx 4 \times 10^9$ y), Pa-231 ($t_{1/2} \approx 33,000$ y), and Th-232 ($t_{1/2} \approx 1.4 \times 10^{10}$ y). The experiments were performed using an Agilent 6340 quadrupole ion trap mass spectrometer (QIT/MS) with a $MS^n$ collision induced dissociation (CID) capability. Ions in the trap can undergo ion−molecule reactions by applying a reaction time of up to 10 s; as no excitation is applied, observed reactions occur at the trap temperature of ∼300 K.[61] A particular ion is isolated in the QIT after ejection of all other ions and reacted with gases in the trap for a known time, prior to mass analysis of the products and any remaining reactant ion. The variable experiment time frame is selected to provide sufficient product abundance while still retaining some reactant and acquiring high-quality mass spectra for reactions having different efficiencies and using different reagent pressures. The ESI source region of the QIT/MS is inside of a radiological-containment glovebox, as described elsewhere.[56] Mass spectra were obtained in the positive ion accumulation and detection mode using the following instrumental parameters: solution flow rate, 60 μL/h; nebulizer gas pressure, 15 psi; capillary voltage offset and current, −6 kV and ca. 20 nA; end plate voltage offset and current, −500 V and ca. 200 nA ; dry gas flow rate, 4 l/min; dry gas temperature, 325 °C; capillary exit, 141.7 V; skimmer, 26.3 V; octopole 1 and 2 DC, 15.75 and 3.13 V; octopole RF amplitude, 58.3 $V_{pp}$; lens 1 and 2, −4.8 V and −65.2 V; and trap drive, 216.8 (the trap drive is a dimensionless instrumental parameter). High-purity nitrogen for nebulization and drying in the ion transfer capillary was supplied from the boil-off of a liquid nitrogen Dewar. The background water pressure in the ion trap is estimated as ∼10$^{−6}$ Torr;[62] reproducibility of hydration rates of $UO_2(OH)^+$[58] confirm that the background water pressure remained constant to within <10%. The helium buffer gas pressure in the trap is constant at ∼10$^{−4}$ Torr. The ion trap has been modified to allow for the introduction of reagent gases through a leak valve.[56] The CID experiments were performed using ca. 0.5 V; this energy is an instrumental parameter that provides an indication of relative ion excitation, not ion energetics. CID under these low-energy conditions is a muticollisional process in which the ion is heated by sequential collisions with many helium atoms.

The pressure of $H_2^{18}O$ (Aldrich, 99% $^{18}O$) introduced into the trap relative to the background $H_2^{16}O$ pressure was determined from the ratio of $U^{16}O_2(^{16}OH)^+/U^{16}O_2(^{18}OH)^+$. This approach is based on work that showed the oxo-exchange rate of $U^{16}O_2(^{16}OH)^+$ reached near-equilibrium within <100 ms and can thus be used to obtain the $H_2^{18}O/H_2^{16}O$ pressure ratio.[63] The employed $H_2^{18}O/H_2^{16}O$ ratio was ca. 1:2. Like the $H_2^{18}O$, the $CH_3CN$ reagent was introduced into the trap from a reservoir in which the liquid had been degassed by repeated freeze−vacuum−thaw cycles. The $CH_3CN$ pressure was not known, but experiments were carried out using essentially constant reagent pressures to allow for direct comparison of results for different ions.
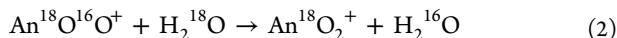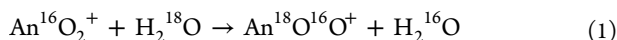
## ■ RESULTS AND DISCUSSION

The goals were to study oxo-exchange reactions of PaO$_2^+$ and UO$_2^+$ with water and to evaluate the relative stabilities of the isomers PaO$_2$(H$_2$O)$^+$ and PaO(OH)$_2^+$. Reactions were performed for unknown but invariant water pressures, as described above, such that the results can be directly compared despite the fact that reaction rate constants cannot be derived. The oxo-exchange and water addition reactions were performed using AnO$_2^+$ produced by ESI. The CID and acetonitrile experiments were performed using the water-adduct ions produced by ESI. It should thus be remarked that the structures, or distribution of structures, for species produced by gas-phase water addition may be different from those produced by association with water during ESI.

**Oxo-Exchange of PaO$_2^+$ and UO$_2^+$ with H$_2$O.** Previous studies revealed a significant difference in oxo-exchange efficiencies of the AnO$_2^+$ ions (An = U, Np, and Pu) with water.[63,64] In the present work, the comparative exchange rates of PaO$_2^+$ and UO$_2^+$ were determined. In Figure 1 is shown a
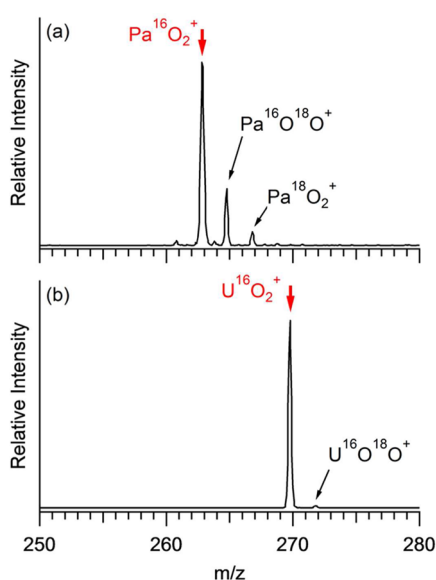


**Figure 1.** Mass spectra acquired after 0.5 s exposure to a constant H$_2^{18}$O pressure for (a) Pa$^{16}$O$_2^+$ and (b) U$^{16}$O$_2^+$. Exchange of the first and second O$_{yl}$ is apparent for PaO$_2^+$, reactions 1 and 2, whereas only very minor exchange of one O$_{yl}$, reaction 1, is observed for UO$_2^+$.

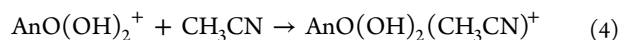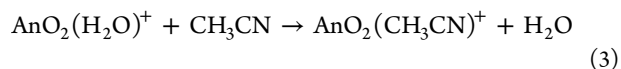mass spectrum acquired after reacting Pa$^{16}$O$_2^+$ and U$^{16}$O$_2^+$ with H$_2^{18}$O under the same conditions. The sequential exchange reactions 1 and 2 are readily apparent for An = Pa, whereas only a minuscule exchange product due to reaction 1 is seen for An = U.

$$An^{16}O_2^+ + H_2^{18}O \rightarrow An^{18}O^{16}O^+ + H_2^{16}O \quad (1)$$

$$An^{18}O^{16}O^+ + H_2^{18}O \rightarrow An^{18}O_2^+ + H_2^{16}O \quad (2)$$

From the results in Figure 1, it is evident that PaO$_2^+$ exchanges at least an order of magnitude faster than UO$_2^+$. Previous work showed that the corresponding oxo-exchange rate for UO$_2^+$ is faster than those for NpO$_2^+$ and PuO$_2^+$,[63] such that the following ordering of exchange rates has now been established, where NpO$_2^+$ and PuO$_2^+$ cannot be differentiated because exchange was not detected for either: PaO$_2^+$ > UO$_2^+$ > NpO$_2^+$/PuO$_2^+$.

Oxo-exchange of AnO$_2^+$ with H$_2$O proceeds through the following steps:[63] (a) exothermic addition of H$_2$O to produce the hydrate AnO$_2$(H$_2$O)$^+$; (b) a transition state (TS) in which a hydrogen atom is being transferred from H$_2$O to an O$_{yl}$; (c) formation of a bis-hydroxo intermediate, AnO(OH)$_2^+$; (d) reversal of the process, which ultimately results in AnO$_2^+$ and H$_2$O where an O$_{yl}$ and the O atom of water have been exchanged. The exchange rate is determined by the TS barrier between the hydrate and the bis-hydroxide intermediate. It was previously found that differences in exchange behavior could be traced to decreasing stability of AnO(OH)$_2^+$ relative to AnO$_2$(H$_2$O)$^+$ from An = U to Np to Pu. In a continuation of this trend, the results for PaO$_2^+$ suggest that PaO(OH)$_2^+$ is more stable than UO(OH)$_2^+$ and raise the possibility that the bis-hydroxide PaO(OH)$_2^+$ is lower in energy than the alternative PaO$_2$(H$_2$O)$^+$ hydrate isomer, which would contrast with later AnO$_2$(H$_2$O)$^+$.[58,59,63,64] The experiments described below were carried out to evaluate this possibility, where the peak corresponding to the addition of one water molecule to PaO$_2^+$ is identified as PaO$_3$H$_2^+$.

**Water Replacement by Acetonitrile.** Thermal reactions of hydrates/hydroxides with molecules exhibiting a higher gas-phase basicity than water, such as acetonitrile, can differentiate between isomers. The gas basicities of water and acetonitrile are 660 and 748 kJ/mol, respectively.[65] For a hydrate, H$_2$O can be replaced by the stronger base CH$_3$CN (reaction 3), whereas for a hydroxide only ligand addition is observed (reaction 4). This approach has previously been employed to assign the tris-hydroxide, Th(OH)$_3^+$, rather than the alternative hydrate structure, ThO(OH)(H$_2$O)$^+$.[66]

$$AnO_2(H_2O)^+ + CH_3CN \rightarrow AnO_2(CH_3CN)^+ + H_2O \quad (3)$$

$$AnO(OH)_2^+ + CH_3CN \rightarrow AnO(OH)_2(CH_3CN)^+ \quad (4)$$

In Figure 2 are shown mass spectra acquired after exposure of UO$_2$(H$_2$O)$^+$ and PaO$_3$H$_2^+$ to the same (unknown) pressure of CH$_3$CN for 40 ms. The reactant ions were isolated from the ESI mass spectrum. It is apparent that the dominant channel for
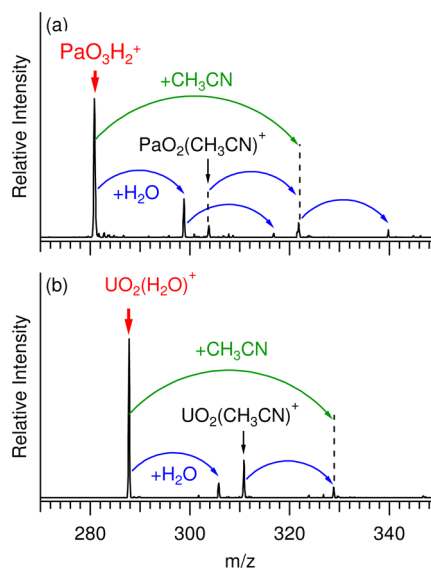


**Figure 2.** Mass spectra acquired after 40 ms of exposure to CH$_3$CN for (a) PaO$_3$H$_2^+$ and (b) UO$_2$(H$_2$O)$^+$.

$UO_2(H_2O)^+$ is reaction 3, with lesser contributions due to the addition of a $H_2O$ or $CH_3CN$ molecule. In contrast, for $PaO_3H_2^+$ the dominant processes are the addition of $H_2O$ and $CH_3CN$. The appearance of a weak peak corresponding to $PaO_2(CH_3CN)^+$ indicates that reaction 3 does occur as a minor channel. These results suggest that the $PaO_3H_2^+$ peak comprised a mixture of $PaO(OH)_2^+$ and lesser $PaO_2(H_2O)^+$. Comparison of Figure 2a and b reveals that $PaO_3H_2^+$ adds acetonitrile at least as efficiently as does $UO_2(H_2O)^+$, indicating comparable affinities of the two cations for this base. The greater rate of substitution in the case of $UO_2(H_2O)^+$ can therefore not be attributed to a difference in intrinsic affinities for acetonitrile. The appearance of some $PaO_2(CH_3CN)^+$ in Figure 2a suggests that the hydrate and hydroxide structures, $PaO_2(H_2O)^+$ and $PaO(OH)_2^+$, are close in energy and that both are produced during ESI of $PaO_2^+$.

**Water Addition to $UO_2^+$ and $PaO_2^+$.** Another experimental evaluation of the nature of $PaO_3H_2^+$ was performed by a reaction of $UO_2^+$ and $PaO_2^+$ with ca. $10^{-6}$ Torr background water at constant pressure, with the results shown in Figure 3.
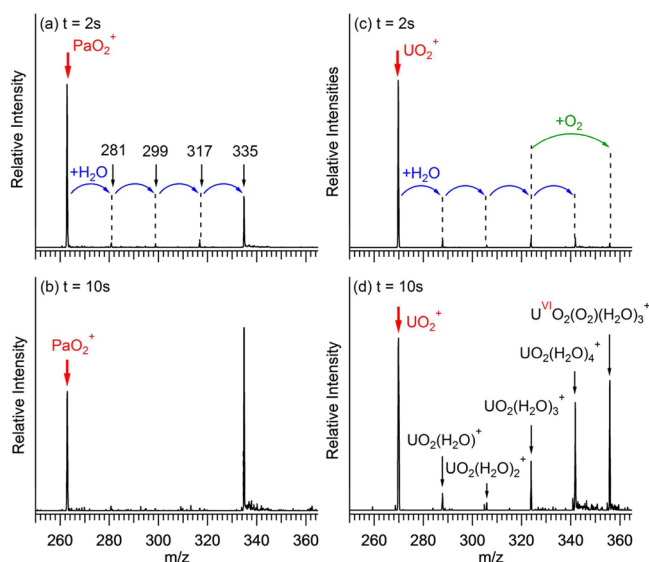


**Figure 3.** Mass spectra acquired for (a,b) $PaO_2^+$ and (c,d) $UO_2^+$ after the reaction with background in the ion trap for 2 and 10 s. After 2 s, intermediate hydrates are observed for both, whereas after 10 s only the terminal tetrahydrate is observed in the case of $PaO_2^+$.

Both $PaO_2^+$ and $UO_2^+$ add up to four water molecules but with very different kinetics. Referring to Figure 3b and d, it is apparent that after the longest accessible reaction time of 10 s, neither $PaO_2^+$ nor $UO_2^+$ has fully reacted with the background water. The striking difference between these two spectra is the absence of any intermediate species for $PaO_2^+$, in distinct contrast to the intermediate hydrates $UO_2(H_2O)_{1-3}^+$. This suggests that the initial $H_2O$-addition product for $PaO_2^+$, $PaO_3H_2^+$, adds water much more rapidly than does $UO_2(H_2O)^+$. The apparent explanation for this disparity is that $PaO_3H_2^+$ is (primarily) $PaO(OH)_2^+$, which adds three more water molecules rapidly such that no intermediates are observed. This interpretation is substantiated by the previous report that $UO_2(OH)^+$ hydrates much more rapidly than does $UO_2^+$, with water addition facilitated by stabilization of the nascent hydrate due to energy dissipation by the hydroxide ligand.[58]

Referring to Figure 3, the previously reported $O_2$-addition process to yield $UO_2(O_2)(H_2O)_3^+$ corresponds to the oxidation of U(V) to U(VI).[58] Similar oxidation of Pa(V) is not viable except under extreme conditions and was not observed here. It should be remarked that the present results do not reveal whether the addition of a second $H_2O$ molecule to $PaO(OH)_2^+$ yields $PaO(OH)_2(H_2O)^+$ or $Pa(OH)_4^+$.

**Collision Induced Dissociation of Hydrates and Hydroxides.** CID results for $Th(OH)_3^+$, $PaO_3H_2^+$, and $UO_2(H_2O)^+$ are shown in Figure 4. These species were
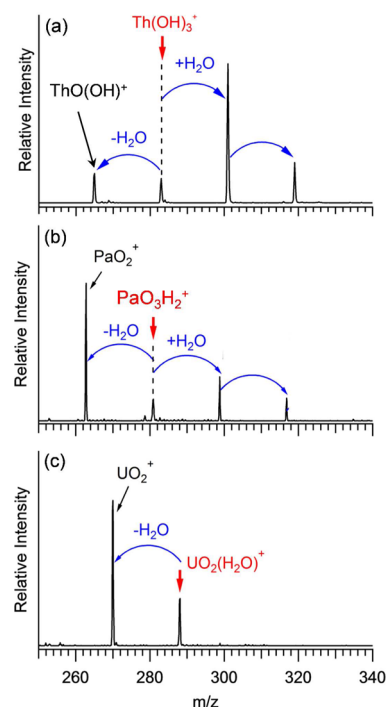


**Figure 4.** Mass spectra acquired after applying a CID voltage of 0.5 V to (a) $Th(OH)_3^+$, (b) $PaO_3H_2^+$, and (c) $UO_2(H_2O)^+$. The water-addition products are not due to CID but rather result from a reaction with background water during the CID time frame of 40 ms.

isolated from the ESI mass spectrum for CID. The CID process occurs during a ca. 40 ms period such that addition of water to the parent or product ions can occur. The sole observed pathway for $UO_2(H_2O)^+$ is elimination of $H_2O$. This process is indicative of dehydration because $UO_2^+$ is known to add water inefficiently.[58] For both $Th(OH)_3^+$ and $PaO_3H_2^+$, elimination of $H_2O$ and addition of one and two $H_2O$ molecules are observed; this addition reaction is not a CID process but rather a reaction with background water in the ion trap during the CID time frame. The structural assignment of $Th(OH)_3^+$ as a tris-hydroxide rather than $ThO(OH)(H_2O)^+$ has been discussed previously.[66] Elimination of $H_2O$ from $Th(OH)_3^+$ can be attributed to an energetic rearrangement to yield $ThO(OH)^+$, a previously identified species.[66] For $Th(OH)_3^+$, the dominant CID pathway is sequential addition of water to produce $Th(OH)_3(H_2O)^+$ and $Th(OH)_3(H_2O)_2^+$, processes kinetically facilitated by the hydroxyl groups that serve to stabilize nascent hydrates for collisional cooling prior to dissociation.[58] The CID behavior of $PaO_3H_2^+$ is clearly disparate from that of $UO_2(H_2O)^+$ and is generally similar to that of $Th(OH)_3^+$. In particular, the addition of one and two $H_2O$ molecules is observed, which suggests $PaO(OH)_2^+$ rather
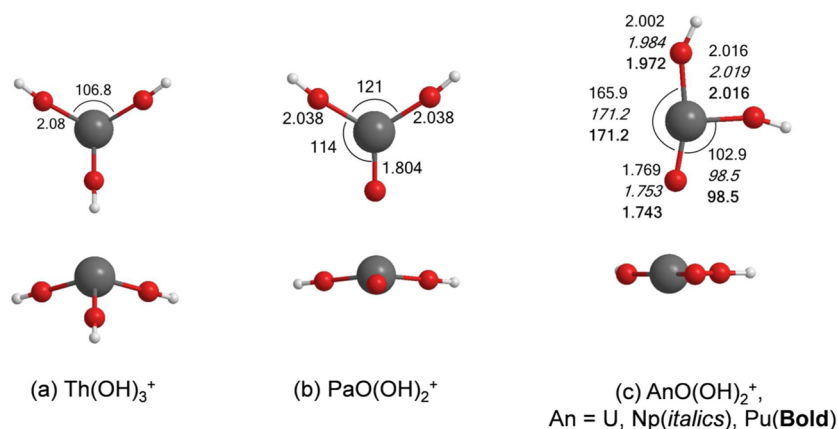
**Figure 5.** Optimized geometric parameters of (a) Th(OH)$_3^+$, PaO(OH)$_2^+$, and (c) AnO(OH)$_2^+$ for U, Np (*italics*), and Pu (**bold**), from refs 41, 63, and 66.

than PaO$_2$(H$_2$O)$^+$. The H$_2$O-elimination channel is more pronounced for PaO$_3$H$_2^+$ than for Th(OH)$_3^+$ such that it is feasible that the PaO$_3$H$_2^+$ peak comprised a mixture of PaO(OH)$_2^+$ and PaO$_2$(H$_2$O)$^+$, an issue further addressed below. The key conclusion from the CID results is that a significant fraction of the PaO$_3$H$_2^+$ peak produced by ESI corresponds to PaO(OH)$_2^+$, whereas CID of the water-addition product in the case of uranyl shows evidence for only UO$_2$(H$_2$O)$^+$.

**Comparative Stabilities and Structures of Actinide Oxides and Hydroxides.** The oxo-exchange, acetonitrile-displacement, hydration, and CID results together provide convincing evidence that the energies of the two isomers, PaO$_2$(H$_2$O)$^+$ and PaO(OH)$_2^+$, are similar such that the two structures can coexist in the gas phase. In contrast, AnO$_2$(H$_2$O)$^+$ is significantly lower in energy than AnO(OH)$_2^+$ for An = U, Np, and Pu. The previously computed energetics for isomerization (reaction 5) are as follows, with the values for An = U, Np, and Pu from ref 63: 48, 84, and 117 kJ/mol, respectively.

$$AnO_2(H_2O)^+ \rightarrow AnO(OH)_2^+ \qquad (5)$$
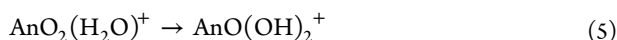
For these computed energies, there is a clear and regular trend toward decreasing stability of the bis-hydroxide relative to the hydrate upon proceeding across the actinide series from U to Pu. To the best of our knowledge, the energy for reaction 5 has not been reported for An = Pa; such a challenging computation is beyond the scope of the present experimental study. It would certainly be desirable to have a computed value for the hydrolysis reaction (reaction 5) for the case of An = Pa. The experimental results for CID and acetonitrile substitution of PaO$_3$H$_2^+$ formed by ESI, as well as for water-addition to PaO$_2^+$ in the gas phase, indicate that the gas-phase addition of H$_2$O to PaO$_2^+$ produces primarily the bis-hydroxide isomer, PaO-(OH)$_2^+$. With the assumption that the internal temperature of ions in the trap is ~300 K, the ion kinetic energy is ca. 4 kJ/mol. The ions furthermore possess some indeterminate internal energy that may be available to enable slightly endothermic reactions. The evidence that PaO(OH)$_2^+$ and PaO$_2$(H$_2$O)$^+$ coexist in the ion trap thus suggest that reaction 5 is nearly thermoneutral, to within ca. 10 kJ/mol. The conversion of the An(V) hydrates to the hydroxides, reaction 5, are substantially endothermic, by at least ca. 50 kJ/mol, for the later AnO$_2^+$. The current results thus place Pa(V) at a turning point in the actinide series with regard to the relative stabilities of the

hydrate and hydroxide isomers, AnO$_2$(H$_2$O)$^+$ and AnO(OH)$_2^+$. Hydrolysis of Th(IV) is contrastingly highly exothermic, with the energy for the hydrolysis of ThO(OH)$^+$ to Th(OH)$_3^+$ computed to be −260 kJ/mol.[66]

The result that an An═O bond is more readily activated to produce two An−OH bonds, despite increasing BDE[An-O], can be attributed to increasing covalency of the An═O bonds, or conversely decreasing ionicity, of the An−OH bonds, upon proceeding across the actinide series from Th to Pu.[63] This interpretation is consistent with ground state structures for ThO(OH)$_2$, PaO(OH)$_2^+$, UO(OH)$_2^+$, NpO(OH)$_2^+$, and PuO(OH)$_2^+$ shown in Figure 5.[41,63,66] For the U, Np, and Pu oxide hydroxides, the structures are similar and the O-An-OH bond angles are close to linear, which is indicative of covalent character. However, for the Th and Pa hydroxides the structures are close to triangular, which is indicative of ionic character. On the basis of the greater stabilities of the hydroxides of Th and Pa, and the structures of the hydroxides, it is inferred that the An−OH bonds exhibit predominantly ionic character for Th and Pa, and more covalent character for U, Np, and Pu.

## ■ CONCLUSIONS

It was established that gas-phase exchange with water of the oxo ligand of PaO$_2^+$ occurs much more rapidly than for UO$_2^+$. This establishes a continuation of the rate trend previously demonstrated for UO$_2^+$, NpO$_2^+$, and PuO$_2^+$. This trend is seemingly enigmatic given that it contrasts with decreasing An−O bond dissociation energies from Pa to Pu and has been attributed to increasing An-O bond covalency from Pa to Pu, which results in greater resistance to disruption of the An−O bonds to produce the two An−OH bonds in the exchange intermediate. It would be desirable to study the relative oxo-exchange rate of AmO$_2^+$ to determine if this trend continues beyond Pu.

The oxide bond dissociation energies (BDEs), which decrease substantially from Pa to Pu (and further decrease to Am), are the experimentally measurable bond energies. Differences in the intrinsic bond dissociation energies (IBDEs) between the actinide oxides may be much smaller, as has recently been discussed.[57] Given that it is the IBDE which best indicates the bonding disruption that occurs during processes such as oxo-exchange, in which no bond is discretely broken, the apparent "enigma" of more facile oxo-exchange for those AnO$_2^+$ with higher BDEs is not necessarily enigmatic.

The propensity for oxo-exchange is evidently affected by other more subtle factors, such as the degree of covalency/ionicity of the disrupted An−O and created An−OH bonds.

The result that oxo-exchange is relatively facile for $PaO_2^+$ suggests that the energy of the $PaO(OH)_2^+$ exchange intermediate relative to the $PaO_2(H_2O)^+$ association product is lower than that for later $AnO_2(H_2O)^+$ (An = U, Np, and Pu). Given that $PaO_2^+$ readily hydrolyzes in aqueous solution whereas the later $AnO_2^+$ do so only at much higher pH, the question arises as to whether the energy of gas-phase $PaO(OH)_2^+$ is lower than that of the $PaO_2(H_2O)^+$ isomer. This possibility was evaluated by comparing the hydration of $UO_2^+$ and $PaO_2^+$, with the conclusion that the initial water-addition products are very different, evidently $UO_2(H_2O)^+$ and $PaO(OH)_2^+$, a result consistent with solution behavior. The comparative structures of $UO_2(H_2O)^+$, the water adduct of $PaO_2^+$, and $Th(OH)_3^+$ produced by ESI were assessed by collision induced dissociation and ligand-exchange. The essential conclusion was that a substantial fraction of the Pa species was $PaO(OH)_2^+$, with possibly a lesser amount of the $PaO_2(H_2O)^+$ isomer, suggesting that the two structures are close in energy. This present observation of hydrolysis versus hydration behaviors of $PaO_2^+$ places Pa(V) between Th(IV) and later actinide(V) in the overall trend of increasing stabilities of hydrates relative to hydroxides: Pa is a turning point in the actinide series. The gas-phase results are consistent with the rapid hydrolysis of $PaO_2^+$ in aqueous solution, in contrast to the stable aqua ions of the later $AnO_2^+$.

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**Notes**
The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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