Elucidation of the Collision Induced Dissociation Pathways of Water and Alcohol Coordinated Complexes Containing the Uranyl Cation

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Multiple-stage tandem mass spectrometry was used to characterize the dissociation pathways for complexes composed of (1) the uranyl ion, (2) nitrate or hydroxide, and (3) water or alcohol. The complex ions were derived from electrospray ionization (ESI) of solutions of uranyl nitrate in H₂O or mixtures of H₂O and alcohol. In general, collisional induced dissociation (CID) of the uranyl complexes resulted in elimination of coordinating water and alcohol ligands. For undercoordinated complexes containing nitrate and one or two coordinating alcohol molecules, the elimination of nitric acid was observed, leaving an ion pair composed of the uranyl cation and an alkoxide. For complexes with coordinating water molecules, MSⁿ led to the generation of either [UO₂²⁺OH⁻] or [UO₂²⁺NO₃⁻]. Subsequent CID of [UO₂²⁺OH⁻] produced UO₂²⁺. The base peak in the spectrum generated by the dissociation of [UO₂²⁺NO₃⁻], however, was an H₂O adduct to UO₂²⁺. The abundance of the species was greater than expected based on previous experimental measurements of the (slow) hydration rate for UO₂²⁺ when stored in the ion trap. To account for the production of the hydrated product, a reductive elimination reaction involving reactive collisions with water in the ion trap is proposed. (J Am Soc Mass Spectrom 2003, 14, 1205–1214) © 2003 American Society for Mass Spectrometry

The speciation and reactivity of uranium is a topic of sustained interest because species-dependent chemistry [1] controls processes ranging from nuclear fuel processing [2] to mobility and fate in the geologic subsurface [3, 4]. The solution chemistry of uranium is dominated by the uranyl dication, UO₂²⁺, which is known to form complexes with a range of ligands [1]. Specific interaction with solvent will significantly influence the physico-chemical behavior of the uranyl ion and its complexes, and this has motivated investigations of complex composition and stability using infrared spectroscopy and extended X-ray absorption fine structure [5–11]. Unfortunately, explicit control over the interactions of solvent and non-solvent ligands with the uranyl ion is difficult, which

makes the study of species-dependent uranium behavior complicated. To gain a better understanding of the intrinsic interactions between different uranyl species and solvent, we have begun an investigation of uranyl-anion complexes in the gas phase using ion-trap mass spectrometry (IT-MS). Several recent reports have demonstrated that intrinsic metal and metal complex chemistry can be investigated by the (controlled) addition of reagent gas to an ion trap [12–22], or by way of the presence of H₂O and other small molecule contaminants within the He bath gas used to collisionally cool ions and improve trapping efficiency [23–25]. The reactions of uranium ions in the gas phase have been the subject of several earlier investigations. Studies by Gibson [26–29], and by Schwarz and coworkers [30] have probed the reactions between U⁺ and UO⁺ and organic compounds such as alkanes and alcohols. Armentrout and Beauchamp [31] investigated the oxidation of U⁺ using small molecules such as O₂, CO, CO₂, COS, and

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D₂O. Subsequent studies by Duckworth and coworkers [32], Schwarz and coworkers [33], and Gibson [34] also demonstrated the tendency for oxidation of U⁺ using small molecules.

The early studies emphasized reactivity of U cations in low oxidation states. However, uranium in the environment occupies higher oxidation states, principally IV and VI. Complex ions containing U in the higher states can be generated using ESI, and the method has been used in prior investigations to generate the gas-phase uranyl ion for analysis by mass spectrometry and ion mobility-mass spectrometry [35–38]. Combining ESI with an IT-MS would enable investigation of intrinsic reactivity of individual U species. Because gas-phase speciation can be complex, the CID and tandem mass spectrometry capabilities of the IT-MS are invaluable for elucidating the composition and structure of gas-phase ions. Presented here is a study in which ESI was used to produce gas-phase ions from solutions containing uranyl nitrate in solvent systems ranging from pure H₂O to mixtures of H₂O and alcohol. Multiple-stage tandem mass spectrometry was then used to determine the CID pathways for the various complex ions generated. These fundamental studies identify the analytical behavior of uranyl under ESI conditions, and establish the ground work for the analytical and intrinsic studies of more complex uranyl-bearing uranyl systems. The behavior is important for analyte recognition, which is key to understanding geochemical transport and solubilization behavior.

Experimental

Uranyl nitrate hexahydrate, UO₂(NO₃)₂·6H₂O was purchased from Fluka/Sigma-Aldrich (St. Louis, MO) and used as received. Methanol (MeOH), ethanol (EtOH), 1,1-*d*₂ ethyl alcohol (*d*₂EtOH), 2,2,2-*d*₃ ethyl alcohol (*d*₃EtOH), ethyl-*d*₅ alcohol (*d*₅EtOH) and *n*-propanol (*n*-PrOH) were purchased from Aldrich Chemical (St. Louis, MO) and used as received. A stock solution (1 × 10^{−3} M) of UO₂(NO₃)₂·6H₂O was prepared by dissolving the appropriate amount of solid material in deionized H₂O.

ESI mass spectra were collected using a Finnigan LCQ-Deca ion-trap mass spectrometer (ThermoFinnigan Corporation, San Jose, CA). The uranyl nitrate stock solution and water:alcohol solutions were infused into the ESI-MS instrument using the incorporated syringe pump at a flow rate of 3–5 μl/min. The atmospheric pressure ionization stack settings for the LCQ (lens voltages, quadrupole and octapole voltage offsets, etc.) were optimized for maximum ion transmission to the ion trap mass analyzer by using the auto-tune routine within the LCQ Tune program. Following the instrument tune, the spray needle voltage was maintained at +5 kV and the N₂ sheath gas flow at 25 units (arbitrary to the LCQ instrument, corresponding to approximately .375 liters/min). To ensure maximum yield of solvated uranyl cation complexes, the capillary (desolvation)

Figure 1. ESI mass spectra generated from UO₂(NO₃)₂ dissolved in (a) 50:50 MeOH/H₂O, (b) 90:10 MeOH/H₂O, and (c) deionized H₂O. UO₂(NO₃)₂ concentration in each case was 1 mM, capillary desolvation temperature 115 °C.

temperature was maintained between 110 °C and 130 °C. The ion trap analyzer was operated at a pressure of ~1.5 × 10^{−5} torr. Helium gas, admitted directly into the ion trap, was used as the bath/buffer gas to improve trapping efficiency and as the collision gas for CID experiments.

CID experiments were performed by setting the isolation width between 5 and 12 u (depending on the species), the activation Q (as labeled by instrument manufacturer, used to adjust the *q* value for the resonant excitation of the precursor ion during the CID portion of the experiment) at .3 and the activation amplitude at 10–20% (of 5 V). In all cases, activation times for CID were 30 ms.

Results and Discussion

Our initial experiments involved the generation of ESI spectra from solutions containing uranyl nitrate in solvent mixtures containing different relative proportions of H₂O and MeOH. These trials were undertaken to assess the influence of the composition of the solvent system on the production of ion signal by ESI, and to qualitatively probe the preference of the uranyl cation to be coordinated by H₂O or MeOH within gas-phase complexes. Figure 1 shows the ESI mass spectra generated from UO₂(NO₃)₂ dissolved in 50:50 MeOH/H₂O

(Figure 1a), 90:10 H₂O/MeOH (Figure 1b), and pure deionized H₂O (Figure 1c). The dominant species observed in the mass spectra derived from the mixed MeOH/water solvent systems was one at mass to charge ratio (m/z) 428, consistent with a composition that included a single UO_2^{2+} cation, one nitrate anion and three coordinating MeOH molecules [$\text{UO}_2^{2+}(\text{NO}_3^-)(\text{MeOH})_3$]. An analogous species, with MeOH replaced by H₂O, was observed at m/z 386 in the spectrum of uranyl nitrate dissolved in deionized H₂O, [$\text{UO}_2^{2+}(\text{NO}_3^-)(\text{H}_2\text{O})_3$]. This spectrum also contained a less abundant ion at m/z 341 in which nitrate was replaced by hydroxide, [$\text{UO}_2^{2+}(\text{OH}^-)(\text{H}_2\text{O})_3$]. In the ESI spectrum produced from the sample with high MeOH content, a prominent peak was observed at m/z 397, consistent with the formation of a complex with composition including UO_2^{2+} , MeO^- , and three coordinating MeOH molecules, [$\text{UO}_2^{2+}(\text{MeO}^-)(\text{MeOH})_3$]. Also present within the low mass region of the spectrum were complex ions containing UO_2^{2+} , either nitrate or MeO^- , and 1 or 2 coordinating H₂O or MeOH molecules.

Larger polyatomic species were observed at m/z 822 in Figure 1a and at m/z 780 in Figure 1c, and are consistent with the addition of an $\text{UO}_2(\text{NO}_3)_2$ unit to the species at 428 and 386, respectively. In the spectrum shown in 1a, a third prominent peak was observed at m/z ~762. This peak was unusually wide, with pronounced tailing to the low mass side and a significant chemical mass shift [39, 40]. These observations are consistent with the formation of a weakly bound complex. Attempts to isolate the species for a higher resolution scan, and thus better determine the m/z value were not successful, presumably because of the instability of the complex. Several compositions are possible for this mass assignment, and identification remains tentative. Additionally, large polyatomic ions (not shown in Figure 1) were observed at m/z 1095, 1156, 1457, and 1851. These ions have tentative compositions consistent with $[(\text{UO}_2)_3(\text{NO}_3)(\text{MeO})(\text{MeOH})_6]^+$, $[(\text{UO}_2)_3(\text{NO}_3)_3(\text{MeOH})_5]^+$, $[(\text{UO}_2)_4(\text{NO}_3)_3(\text{MeO})(\text{MeOH})_5]^+$, and $[(\text{UO}_2)_5(\text{NO}_3)_5(\text{MeO})(\text{MeOH})_5]^+$.

For the H₂O/MeOH mixed solvent system, the peaks at m/z 428 and 822 remained the predominant ions observed when the relative proportion of alcohol was reduced to 5%. The persistence of the MeOH-solvated complex ions suggests that UO_2^{2+} has a higher affinity for alcohol molecules than for H₂O, which is consistent with the tendency for the former to be stronger electron donors to metal ions [41]. In general, the greatest influence of decreasing MeOH content in the spray solvent system was an observed decrease in intensity of the peak at m/z ~762, and analogous species observed when using the other alcohols.

Proposed compositions for the major species generated by ESI of uranyl nitrate dissolved in 50:50 ROH/H₂O (ROH = methanol, ethanol, and *n*-propanol) are provided in Table 1. In most cases, the assigned compositions were supported by MSⁿ CID except for those

Table 1. Compositions of prominent ions observed in the ESI mass spectra of uranyl nitrate sprayed from alcohol/water solutions

Alcohol	m/z	Composition
Methanol	333	$[\text{UO}_2^{2+}(\text{MeO}^-(\text{MeOH}))]$
	365	$[\text{UO}_2^{2+}(\text{MeO}^-(\text{MeOH})_2)]$
	397	$[\text{UO}_2^{2+}(\text{MeO}^-(\text{MeOH})_3)]$
	364	$[\text{UO}_2^{2+}(\text{NO}_3^-(\text{MeOH}))]$
	396	$[\text{UO}_2^{2+}(\text{NO}_3^-(\text{MeOH})_2)]$
	428	$[\text{UO}_2^{2+}(\text{NO}_3^-(\text{MeOH})_3)]$
	762	Unidentified
	822	$[(\text{UO}_2^{2+})_2(\text{NO}_3^-)_3(\text{MeOH})_3]$
	361	$[\text{UO}_2^{2+}(\text{EtO}^-(\text{EtOH}))]$
	407	$[\text{UO}_2^{2+}(\text{EtO}^-(\text{EtOH})_2)]$
Ethanol	452	$[\text{UO}_2^{2+}(\text{EtO}^-(\text{EtOH})_3)]$
	378	$[\text{UO}_2^{2+}(\text{NO}_3^-(\text{EtOH}))]$
	424	$[\text{UO}_2^{2+}(\text{NO}_3^-(\text{EtOH})_2)]$
	470	$[\text{UO}_2^{2+}(\text{NO}_3^-(\text{EtOH})_3)]$
	864	$[(\text{UO}_2^{2+})_2(\text{NO}_3^-)_3(\text{EtOH})_3]$
	369	$[\text{UO}_2^{2+}(n\text{PrO}^-(n\text{PrOH}))]$
	449	$[\text{UO}_2^{2+}(n\text{PrO}^-(n\text{PrOH})_2)]$
	509	$[\text{UO}_2^{2+}(n\text{PrO}^-(n\text{PrOH})_3)]$
<i>n</i> -Propanol	393	$[\text{UO}_2^{2+}(\text{NO}_2^-(n\text{PrOH}))]$
	452	$[\text{UO}_2^{2+}(\text{NO}_2^-(n\text{PrOH})_2)]$
	512	$[\text{UO}_2^{2+}(\text{NO}_2^-(n\text{PrOH})_3)]$
	906	$[(\text{UO}_2^{2+})_2(\text{NO}_3^-)_3(n\text{PrOH})_3]$
	305	$[\text{UO}_2^{2+}(\text{OH}^-(\text{H}_2\text{O}))]$
	323	$[\text{UO}_2^{2+}(\text{OH}^-(\text{H}_2\text{O})_2)]$
	341	$[\text{UO}_2^{2+}(\text{OH}^-(\text{H}_2\text{O})_3)]$
	350	$[\text{UO}_2^{2+}(\text{NO}_3^-(\text{H}_2\text{O}))]$
No alcohol	368	$[\text{UO}_2^{2+}(\text{NO}_3^-(\text{H}_2\text{O})_2)]$
	386	$[\text{UO}_2^{2+}(\text{NO}_3^-(\text{H}_2\text{O})_3)]$
	780	$[(\text{UO}_2^{2+})_2(\text{NO}_3^-)_3(\text{H}_2\text{O})_3]$

unstable species that did not survive the ion isolation step required for the dissociation experiment. Trials attempted using solutions containing *n*-butanol were plagued by significant precipitation of solids within the fused silica transport capillary used in the ESI instrument. Therefore, an investigation of butanol coordinated uranyl complexes was not conducted.

Figure 2 shows, as representative examples for the alcohol containing complexes, multiple stage CID spectra initiated with the dissociation of the species at m/z 428, $[\text{UO}_2^{2+}(\text{NO}_3^-(\text{MeOH})_3)]^+$, generated from ESI of uranyl nitrate in 50:50 MeOH/H₂O. The dissociation spectra produced at each CID stage were complex, containing both product ions from fragmentation reactions, and H₂O adducts to those product ions formed by association reactions with adventitious H₂O present as a contaminant in the He buffer/bath gas (H₂O adducts are identified with an asterisk in figures). In general, the H₂O adducts can be identified by characteristic peak tails and chemical mass shifts (shifts of ~.2–.3 u lower than expected mass). In addition, the adducts were identified in our experiments by isolating expected product ions in the ion trap for periods of 100–300 ms, without an imposed activation amplitude. During the isolation step, all ionized species except the one chosen for storage are resonantly ejected from the ion trap. The appearance of peaks 18 u higher than the isolated ion is

Figure 2. Multiple stage CID spectra initiated with the dissociation of the $[\text{UO}_2^{2+}(\text{NO}_3)(\text{MeOH})_3]^+$ complex ion derived from $\text{UO}_2(\text{NO}_3)_2$ dissolved in 50:50 MeOH/ H_2O . Peaks marked with an asterisk indicate H_2O adducts formed from reaction of the CID products with adventitious water in the IT-MS.

indicative of the formation of H_2O adducts [23–25]; the abundance of the adducts increased as the isolation and storage time was extended. The formation of abundant H_2O adducts indicates that several of the uranyl complex ions show a significant tendency to accept ligands via gas-phase association reactions in the ion trap. The reaction kinetics for the addition of one or more H_2O ligands to UO_2^+ and related species generated by ion-induced sputtering of solid UO_3 was recently investigated [42]. While beyond the scope of the present study, the reaction kinetics for the addition of H_2O ligands to the various CID products generated from the alcohol coordinated complexes containing UO_2^{2+} were also investigated and will be the subject of a separate report [43].

The multiple-stage dissociation pathways for the CID of m/z 428 $[\text{UO}_2^{2+}(\text{NO}_3)(\text{MeOH})_3]^+$ are shown in Scheme 1. CID (MS/MS or MS^2) caused the loss of 32 u, consistent with the elimination of a single MeOH molecule. Subsequent CID (MS^3) of $[\text{UO}_2^{2+}(\text{NO}_3)(\text{MeOH})_2]^+$ at m/z 396, caused the elimination of a second MeOH molecule to produce $[\text{UO}_2^{2+}(\text{NO}_3)(\text{MeOH})]^+$ at m/z 364. A second minor dissociation pathway involved the loss of 95 u, consistent with the elimination of MeOH and HNO_3 , to produce an ion at m/z 301. CID of the ion at m/z 364 (MS^4) primarily caused the elimination of

Scheme 1. MS^n pathways for the dissociation of $[\text{UO}_2^{2+}(\text{NO}_3)(\text{MeOH})_3]^+$. Product ion intensities are reported relative to base peak at each CID stage. In some stages, H_2O adducts to product ions were the base peaks.

HNO_3 to generate a product ion at m/z 301, with a minor pathway corresponding to the loss of MeOH to produce $[\text{UO}_2^{2+}(\text{NO}_3)]^+$ at m/z 332. The ion at m/z 301 corresponds to an ion-pair composed of the uranyl cation and a deprotonated MeOH molecule, $[\text{UO}_2^{2+}(\text{MeO}^-)]$, consistent with previously reported tendencies for lanthanide and actinide species to form alkoxide complexes [44–46].

The MS^n experiments suggest that the species at m/z 428 may have a composition of either $[\text{UO}_2^{2+}(\text{NO}_3)(\text{MeOH})_3]^+$ or $[\text{UO}_2^{2+}(\text{CH}_3\text{O}^-)(\text{HNO}_3)(\text{MeOH})_2]^+$. A significant ion population with the latter composition might be expected to eliminate HNO_3 at any CID stage because of a weaker interaction between HNO_3 and UO_2^{2+} vis-à-vis NO_3^- and UO_2^{2+} . The preferred elimination of nitric acid at the MS^4 stage might instead suggest that the complex ion has the former composition, and that a proton is transferred from a coordinating alcohol molecule to the nitrate anion during the dissociation reaction. Such a proton transfer process is not without precedent, and has been recently reported for gas-phase alcohol complexes incorporating Pb^{2+} [47]. The strong tendency to form alkoxide species, noted above, may be a driving force for the apparent proton transfer step and subsequent elimination of HNO_3 .

CID of $[\text{UO}_2^{2+}(\text{MeO}^-)]$ at m/z 301 (MS^5) caused the elimination of 31 u, presumably via the elimination of a methoxy radical, to generate the reduced uranyl cation, UO_2^+ , at m/z 270. A prominent peak at m/z 288 was also observed in the product ion spectrum generated at the

Scheme 2. MS^n pathways for the dissociation of $[UO_2^{2+}(NO_3^-)(EtOH)_3]^+$. Product ion intensities are reported relative to base peak at each CID stage. In some stages, H_2O adducts to product ions were the base peaks.

MS^5 CID stage, suggesting the formation of a hydrated, reduced uranyl ion with formula $UO_2^+ \cdot H_2O$. The generation of this species is discussed further in the next section.

The multiple stage dissociation pathways for the species $[UO_2^{2+}(NO_3^-)(EtOH)_3]^+$ and $[UO_2^{2+}(NO_3^-)(n\text{-}PrOH)_3]^+$ are shown in Schemes 2 and 3, respectively. In general, the MS^n results were similar to those exhibited by $[UO_2^{2+}(NO_3^-)(MeOH)_3]^+$, including the eventual formation of alkoxide-containing complexes with composition $[UO_2^{2+}(EtO^-)]$ and $[UO_2^{2+}(n\text{-}PrO^-)]$ at m/z 315 and 329, respectively. One notable difference was the observation of an increased tendency to eliminate HNO_3 at an earlier (MS^3) stage. Based on the relative intensities of product ions as provided in Schemes 2 and 3, the tendency to lose HNO_3 , relative to the loss of an alcohol molecule, at earlier stages followed the trend $n\text{-}PrOH > EtOH > MeOH$. If the loss of HNO_3 from the gas-phase complexes involves transfer of a proton from ROH to the nitrate anion, this trend is consistent with the known acidities of the alcohols in the gas phase [48, 49]: Acidity increases, in general, with the size of the alkyl group.

A second major difference observed for complexes incorporating EtOH and $n\text{-}PrOH$ was the appearance of fragmentation pathways that appeared to involve cleavage of C–C bonds within an alcohol ligand. For example, at the MS^5 stage, fragmentation pathways

corresponding to the loss of 15 u ($\cdot CH_3$) from the complexes containing EtOH and to the loss of 15 and 29 u ($\cdot C_2H_5$) from the complexes containing $n\text{-}PrOH$ were observed. For the EtOH-containing complex, the mass of the neutral eliminated shifted by three units (loss of 18 u) when the d_3 - and d_5 -EtOH were used in the spray solvent. The loss of 15 u was observed, however, when the d_2 -EtOH was used. These results indicate that the reaction pathway involves the elimination of an intact methyl group following C–C bond cleavage. For the complex containing EtOH, a product ion at m/z 285 was also generated by the CID (MS^5) of $[UO_2^{2+}(CH_3CH_2O^-)]$. CID generated the same product ion when d_2 -EtOH (CH_3CD_2OH) was used in the spray solvent. The product ion mass shifted, however, to m/z 288 when d_3 -EtOH (CD_3CH_2OH) was used. These observations suggest that the product ion is generated by insertion into the C–C bond to form $[UO_2-CH_3]^+$ (m/z 285) by the elimination of CH_2O as a neutral. A similar product ion was not observed following the CID of $[UO_2^{2+}(n\text{-}PrO^-)]$.

A third difference was the appearance at the MS^5 stage of a product ion at m/z 287, which corresponds to the formula $[UO_2^{2+}(OH^-)]$. Subsequent CID caused the elimination of 17 u to produce m/z 270 (UO_2^+). The formation of m/z 287 from, for example, $[UO_2^{2+}(EtO^-)]^+$ suggests the transfer of an H atom from the alkyl group to the oxygen atom, with the elimination of an alkene

Scheme 3. MSⁿ pathways for the dissociation of $[\text{UO}_2^{2+}(\text{NO}_3^-)(n\text{PrOH})_3]^+$. Product ion intensities are reported relative to base peak at each CID stage. In some stages, H_2O adducts to product ions were the base peaks.

neutral as depicted in Scheme 4. A common observation in previous studies of the reactions between gas-phase U^+ and alkanes was a tendency toward dehydrogenation [26–30], albeit with the elimination of H_2 to form unsaturated neutrals. The product ion at m/z 287 was also observed when the d_2 -EtOH was used to generate

Scheme 4. Proposed reaction to generate m/z 287 from $[\text{UO}_2^{2+}(\text{EtO}^-)]^+$.

the uranyl complex, but was not observed when the d_3 -EtOH and d_5 -EtOH were used. Transfer from the methyl group of the ethoxy moiety would involve a D atom for the d_3 - and d_5 -versions of the alcohols, and would shift the mass of the product ion to 288, which is isobaric with the H_2O adduct to the m/z 270 product and the $[\text{UO}_2\text{-CD}_3]^+$ product. However, generation of the m/z 287 product was the principal pathway observed following CID of $[\text{UO}_2^{2+}(n\text{-PrO}^-)]$, and the pathways to produce m/z 270 and 288 (the principal reaction products generated from the complex containing methoxide) were not observed. Therefore, this observation, and the trials with d -labeled EtOH, support a dissociation pathway involving H-transfer.

An alternative pathway for the formation of the m/z 287 product ion from the uranyl-alkoxy precursor ions might involve a reactive collision with an H_2O molecule within the ion trap via the reaction:

Such a reaction pathway is plausible based on recent experiments that have demonstrated that CID within ion trap instruments involves a significant number of activating collisions between precursor ions and small molecules such as N_2 and H_2O present as contaminants within the He bath gas [50, 51]. The reaction shown above would involve the ultimate elimination of EtOH, with a proton extracted from the H_2O collision partner, and retention of the hydroxyl group by the uranyl ion. Were such a process to occur, with H_2O in the ion trap as the source of the hydroxyl moiety, one might expect the product at m/z 287 to be observed following CID of all complexes regardless of the identity of the alkoxy group and the extent of deuterium label (with the caveat that the relative proton affinities of hydroxide and the alkoxides, and the affinity of the uranyl ion for the same species, may play a role in determining the probability of observing this pathway). Therefore, the experimental results described here do not support this mechanism.

As the size of the alcohol increased, so too did the tendency to form a complex containing UO_2^{2+} , alkoxide and coordinating alcohol ligands by ESI (Table 1), with general formula $[UO_2^{2+}(RO^-)(ROH)_3]^+$. For complex ions derived from MeOH or EtOH (Schemes not shown), MS^n caused successive elimination of alcohol molecules to generate the $[UO_2^{2+}(RO^-)]^+$. Subsequent CID of $[UO_2^{2+}(RO^-)]^+$ produced spectra qualitatively and quantitatively similar to those reported above. The $[UO_2^{2+}(n\text{-}PrO^-)(n\text{-}PrOH)_3]^+$ complex was sufficiently unstable/labile to prohibit its isolation in the gas phase for CID experiments. It seems reasonable to assume, however, that similar CID behavior would be observed were isolation of the species possible.

The MS^n spectra obtained for the CID of the species at m/z 386, $[UO_2^{2+}(NO_3^-)(H_2O)_3]^+$ generated from the aqueous solution of $UO_2(NO_3)_2$ are shown in Figure 3. The MS/MS , MS^3 , and MS^4 CID stages initiated with the ion at m/z 386 caused the successive elimination of coordinating H_2O molecules to leave the uranyl-nitrate ion pair, $[UO_2^{2+}(NO_3^-)]^+$ at m/z 332. Subsequent CID of this species produced ions at m/z 270 and 288. In this case, m/z 288 is consistent (based on mass) with the formation of the hydrated, reduced uranyl ion, $UO_2^+ \cdot H_2O$. No plausible mechanism to explain the loss of 44 u can be proposed starting from $[UO_2^{2+}(NO_3^-)]^+$ (m/z 332). CID of the peak at m/z 288 (spectrum not shown) caused the elimination of 18 u, consistent with the loss of a H_2O molecule, forming UO_2^+ at m/z 270. Figure 4 shows the mass spectrum that was a result of the isolation and storage of UO_2^+ in the ion trap for a period of 1 second without imposed collisional activation. Because only the ion at m/z 270 was isolated for storage in the ion trap, the m/z 288 peak observed in Figure 4 is an H_2O adduct to m/z 270 formed by an association reaction in the gas phase. However, the intensity of m/z 288 (<5% relative to m/z 270) is vastly lower than the peak at the same m/z that was an apparent product ion generated by the CID of

Figure 3. Multiple stage CID spectra initiated with the dissociation of the $[UO_2^{2+}(NO_3^-)(H_2O)_3]^+$ complex ion derived from $UO_2(NO_3)_2$ dissolved in deionized H_2O . Peaks marked with an asterisk indicate H_2O adducts formed from reaction of the CID products with adventitious water in the IT-MS.

$[UO_2^{2+}(NO_3^-)]$ shown in Figure 3d. The activation time used to dissociate $[UO_2^{2+}(NO_3^-)]$ in the MS^n experiments was 30 msec, considerably less than the isolation and storage time used to produce the H_2O adduct to UO_2^+ observed in Figure 4. Therefore, it is unlikely that m/z 288 observed following CID of $[UO_2^{2+}(NO_3^-)]$ results from a slow, serial addition of H_2O to the m/z 270 (UO_2^+) product ion. This conclusion is supported by a recent

Figure 4. Mass spectrum generated by the isolation and storage of UO_2^+ (m/z 270) in the ion trap for 1 s. The peak at m/z 288 is an H_2O adduct formed by an association reaction in the ion trap during the storage period.

investigation that demonstrated slow hydration rates for the reduced uranyl ion produced by ion induced sputtering of solid UO_3 [42]. We propose instead that the product may be generated via the reaction:

in which an energetic collision with H_2O in the ion trap mass spectrometer causes the formation of an activated ternary complex, rapidly followed by the reductive elimination of an NO_3 radical (with electron transfer to the uranyl ion) to leave the hydrated, reduced uranyl ion. Noting again the recent experiments that have demonstrated activating collisions between precursor ions and small molecules such as N_2 and H_2O (He bath gas contaminants) [50], such a process is plausible. The presence of numerous, abundant H_2O adducts in the MS^n experiments show that significant levels of H_2O are present within the He bath gas within the ion trap (Figures 2 and 3). In addition, isolation of the species at m/z 332, $[\text{UO}_2^{2+}(\text{NO}_3^-)]$, followed by storage in the ion trap for 1 second produced an intense hydrated complex (spectrum not shown), which supports the proposition that an activated reactive complex might also be formed during the CID experiment. As noted earlier, the formation of the H_2O adduct to UO_2^+ was also observed following the CID of $[\text{UO}_2^{2+}(\text{MeO}^-)]^+$ and of $[\text{UO}_2^{2+}(\text{EtO}^-)]^+$ species; these adducts likely arise via a similar process.

MS^n spectra for $[\text{UO}_2^{2+}(\text{OH}^-)(\text{H}_2\text{O})_3]^+$, at m/z 341, derived from ESI of the $\text{UO}_2(\text{NO}_3)_2$ solution in pure deionized H_2O are shown in Figure 5. As with the nitrate-bearing ion at m/z 386, the MS/MS , MS^3 , and MS^4 CID stages caused the successive elimination of coordinating H_2O molecules; the ultimate end product in this case was $[\text{UO}_2^{2+}(\text{OH}^-)]^+$ at m/z 287. Subsequent CID of this ion caused the elimination of 17 u, attributed to a hydroxyl radical, to generate the reduced uranyl ion, UO_2^+ at m/z 270. Unlike the CID of the species at m/z 301 and 332 discussed above, the dissociation of the peak at m/z 287 did not result in the formation of the hydrated, reduced uranyl ion at m/z 288. This suggests that if a mechanism for the production of the peak at m/z 288 proceeds as proposed above, the formation of the activated complex may be assisted or stabilized by the presence of the nitrate or alkoxide anions in the UO_2^{2+} -anion pair, but not by hydroxide.

The CID of the higher mass ions at m/z 762 and 822 observed following ESI of uranyl nitrate in $\text{H}_2\text{O}/\text{MeOH}$, and similar species generated from the other alcohols, was also examined. Regardless of the alcohol, MS/MS and MS^3 caused the elimination of alcohol molecules. For the complex ion at m/z 822 generated from MeOH , and similar complexes containing the other alcohols, CID at the MS^3 and MS^4 stages generated a product ion via the elimination of a stoichiometric $\text{UO}_2(\text{NO}_3)_2$ unit. The prominence of this CID path-

Figure 5. Multiple stage CID spectra initiated with the dissociation of the $[\text{UO}_2^{2+}(\text{OH}^-)(\text{H}_2\text{O})_3]^+$ complex ion derived from $\text{UO}_2(\text{NO}_3)_2$ dissolved in deionized H_2O .

way increased with the size of the alcohol molecule within the complex. The CID product ions generated from the higher-mass complex ions showed a high tendency to hydrate in the ion trap, and at high MS^n stages (i.e., $>\text{MS}^3$) the product ion mass spectra were dominated by H_2O adducts. In many cases, the intensities of CID product ions were only 1–5% relative to their associated H_2O adducts. The diminished product ion intensities precluded the investigation of subsequent CID stages, and the generation of complete MS^n schemes for the higher mass complexes was not possible.

Conclusions

To the best of our knowledge, this is the first demonstration that ESI can be used to generate gas-phase complexes composed of the UO_2^{2+} , hydroxide or nitrate, and coordinating H_2O and alcohol molecules: species relevant to the study of the interaction between uranyl complexes and solvent. The combination of ESI and IT-MS should therefore be a useful tool for characterizing the intrinsic chemistry of the coordinated uranyl ion. For species in which the complex contained the nitrate anion and coordinating alcohol molecules, multiple CID stages caused the elimination of two alcohol molecules and nitric acid to leave an ion pair composed

of the uranyl ion and an alkoxide anion. ESI of a solution containing uranyl nitrate in deionized H₂O resulted in the production of complexes containing the uranyl ion, either nitrate or hydroxide, and coordinating H₂O molecules. Multiple stage CID of the species incorporating hydroxide generated [UO₂²⁺(OH[−])] via the elimination of the coordinating H₂O molecules, and ultimately the reduced uranyl ion. Multiple-stage CID of the species incorporating nitrate instead generated an apparent hydrated, reduced uranyl ion, UO₂⁺·H₂O, which we propose is the result of the formation of an activated, ternary complex including an H₂O molecule during the final dissociation reaction.

Regardless of the coordinating anion, ESI produced gas-phase uranyl complexes that contained three solvent molecules, whether alcohol or H₂O. Work by Vachet and Callahan [14] has suggested that the nitrate anion, within gas-phase transition metal complexes, is primarily a bidentate ligand. The acceptance of three additional ligands by the uranyl-nitrate ion pair is consistent with a hypothesis that ESI produces a gas-phase complex with a pentagonal bipyramidal conformation reminiscent of the structure of uranyl complexes in the solution phase [5–11]. The fact that the uranyl-hydroxide containing complex ion, as generated by ESI, also incorporated a maximum of 3 additional H₂O ligands is therefore interesting. The hydroxide anion is a monodentate ligand, and the acceptance of 3 H₂O ligands to produce the peak at *m/z* 341 suggests that the gas-phase complex adopts an octahedral conformation (i.e., with three H₂O ligands joining an hydroxide ligand in the equatorial coordination plane). Isolation and storage of the peak at *m/z* 341 for 10 s failed to produce a complex with 1 additional H₂O molecule, demonstrating that the complex is highly resistant to the addition of a fifth equatorial ligand. The behavior in the gas phase is therefore in stark contrast to the structure of uranyl complexes in solution.

Currently we are in the process of investigating the intrinsic hydration reaction rates of the uranyl cation-anion pairs to assess the discrepancies observed between the species generated here by ESI and those from solution phase investigations. In addition, we have also begun an investigation of the most probable gas-phase conformations of the coordinated uranyl ions using ab-initio calculations, which should shed considerable light on the thermodynamic factors that guide the stability of these complexes.

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