

# Production and Collision Induced Dissociation of Gas-Phase, Water and Alcohol Coordinated Uranyl Complexes Containing Halide or Perchlorate Anions

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## 1. Introduction

To improve the understanding of intrinsic uranium chemistry, and in particular the chemistry of species in higher oxidation states, we and others have been exploring the use of electrospray ionization to generate mono-positive uranyl-ligand cations for subsequent gas phase studies. In this study, ESI was used to generate mono-positive gas-phase complexes containing the uranyl ion and OH<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> or ClO<sub>4</sub><sup>-</sup> and coordinated by solvent molecules. The multiple-stage collision-induced dissociation (CID) pathways of the complexes were then investigated using ion-trap mass spectrometry.

## 2. Experiment

The ESI and CID experiments were conducted using a Finnigan LCQ-Decaa ion-trap mass spectrometer. UO<sub>2</sub>Cl<sub>2</sub>, UO<sub>2</sub>Br<sub>2</sub>, UO<sub>2</sub>I<sub>2</sub> and UO<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> were prepared by combining solid UO<sub>3</sub> and the respective strong acids. 1 mM stock solutions for ESI were prepared by dissolving an appropriate amount of uranyl salt (uranyl halide or perchlorate) in distilled/deionized H<sub>2</sub>O.

Ion formation was carried out at atmospheric pressure at ~25°C. The ion trap mass spectrometer was operated at a pressure of ~1.5 x 10<sup>-5</sup> Torr. Helium was used as the bath (to assist collisional cooling and ion trapping) and collision (for activation of accelerated precursor ions) gas. CID was executed using ion isolation widths of 3-8 mass units, depending on the particular complex isolated, activation amplitudes of 10-20% (of 5V) and activation times 30 msec. ESI can be used to generate gas-phase complexes with general formula [UO<sub>2</sub>A(S)<sub>3</sub>]<sup>+</sup>, where A=Cl, Br, I or ClO<sub>4</sub><sup>-</sup>, S=H<sub>2</sub>O, CH<sub>3</sub>OH or CH<sub>3</sub>CH<sub>2</sub>OH.

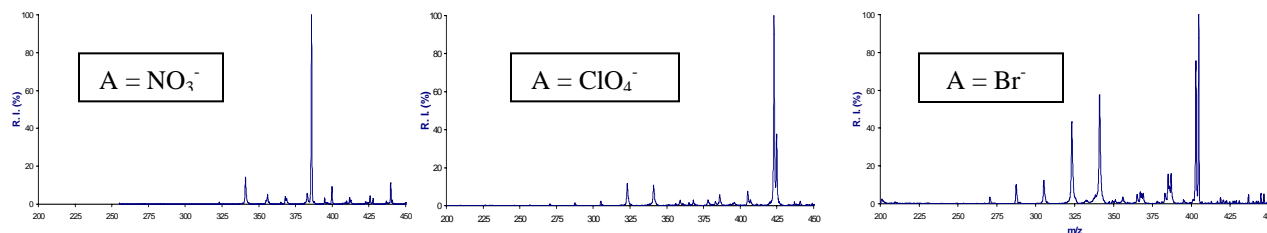
## 3. Results and Discussion

The ESI mass spectra can be generated using the solutions prepared by dissolving the uranyl perchlorate and uranyl bromide solids in deionized H<sub>2</sub>O. Solution, whether its uranyl chloride or iodide complex all generate abundant singly charged complexes with the general formula of [UO<sub>2</sub>A(H<sub>2</sub>O)<sub>n</sub>]<sup>+</sup>, where A corresponded to the respective anions including (hydroxide) and n = 1-3. When multiple-stage CID were performed on complexes with the general formula with A being bromide, chloride, and perchlorate similar observation were seen. Only the bromide and perchlorate complexes showed a tendency to generate the bare [UO<sub>2</sub>ClO<sub>4</sub>]<sup>+</sup> species. In general the observed trend with respect to the formation of the uranyl-anion complex does not correlate with calculations of UO<sub>2</sub>-A bond distances or coordination energies with in bis-complexes.

Uranyl-halide complexes can also coordinate with alcohols to be further investigated by multiple-stage CID. The loss of HCl and HBr from the [UO<sub>2</sub>Cl(H<sub>2</sub>O)]<sup>+</sup> and [UO<sub>2</sub>Br(H<sub>2</sub>O)]<sup>+</sup> respectively, to form [UO<sub>2</sub>OH]<sup>+</sup> suggested the possibility of an intra-complex proton-transfer form bound H<sub>2</sub>O to Cl or Br. Such a proton-transfer process is not without precedent, and has been observed during the CID of gas-phase alcohol complexes incorporating Pb<sup>2+</sup>. The apparent elimination of HA, rather than H<sub>2</sub>O, in the present experiments is somewhat counterintuitive given the relative strengths of HClO<sub>4</sub>, HCl, HBr, and H<sub>2</sub>O as acids. To explore further the possible influence of relative acidity and strength of donation by O-containing ligands on the tendency to eliminate HA from the gas-phase complexes, we generated uranyl-halide complexes coordinated by methanol or ethanol from solutions of the uranyl-halide compounds dissolved in 50:50 mixtures of H<sub>2</sub>O and respective alcohols. Because the gas-phase acidities (Δ<sub>acid</sub>G<sub>298</sub>) are 1571.1 and 1557.7 kJ/mol for CH<sub>3</sub>OH and CH<sub>3</sub>CH<sub>2</sub>OH (again compared to 1605.3kJ/mol for H<sub>2</sub>O<sup>11</sup>), we reasoned that the tendency for intra-complex proton transfer would increase for ions containing coordinating alcohol ligands. Our hypothesis was the a the composite influence of increased acidity and electron donation by the alkoxides would manifest itself in an increased tendency to eliminate HCl, HBr, HI or HClO<sub>4</sub> at early CID stages (MS/MS and MS<sup>3</sup>) particularly when compared to CID of the complexes containing H<sub>2</sub>O ligands. After MS CID of these complexes, the general trend for the elimination of neutral acid relative to alcohol increased as H<sub>2</sub>O < CH<sub>3</sub>OH < CH<sub>3</sub>CH<sub>2</sub>OH. This observation supports

the hypothesis that the strength of the coordinating ligand as a proton donor may, in part, drives the tendency to eliminate the coordinating halide as part of a neutral acid molecule. It is also likely that the free energy change for the reaction is guided by the  $\text{UO}_2^-$  anion and  $\text{UO}_2^-$ alkoxide bond energies.

Figure 1: Generation of  $[\text{UO}_2\text{A}(\text{H}_2\text{O})_3]^+$  Complexes



#### 4. Conclusions

The original goal was to use ESI to generate gas-phase  $[\text{UO}_2\text{A}(\text{H}_2\text{O})_3]^+$  complexes with center atom A being  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ , and  $\text{Br}^-$  in figure one for subsequent ligand-addition studies, by way of the CID of precursor complexes with the general formula. Multiple stage CID of the complexes showed that the preferred dissociation pathways were the elimination of neutral  $\text{H}_2\text{O}$  ligands and the elimination of HA. During the experiment we found that  $[\text{UO}_2\text{A}]^+$  was formed only from the bromide and perchlorate versions of the hydrated complexes. CID of the chloride and iodide versions instead led ultimately to formation of  $[\text{UO}_2\text{OH}]^+$  and  $\text{UO}_2^+$ . The formation of  $[\text{UO}_2\text{OH}]^+$  was also observed to a lesser extent following CID of the bromide and perchlorate complexes. In general, the tendency to generate  $[\text{UO}_2\text{OH}]^+$  via the elimination of HA complex does not correlate with calculations of  $\text{UO}_2\text{A}$  bond distances or coordination energies within bis-complexes but instead follows the trend in calculated proton affinities for  $\text{UO}_2\text{Cl}_2$ ,  $\text{UO}_2\text{Br}_2$  and  $\text{UO}_2\text{I}_2$  complexes, respectively.

The loss of acid became more pronounced when coordinating  $\text{H}_2\text{O}$  was replaced by  $\text{CH}_3\text{OH}$  or  $\text{CH}_3\text{CH}_2\text{OH}$ , consistent with a hypothesis that the reaction is influenced by a combination of the relative acidities of the ligands and the strength of uranyl-ligand bonds. The relative trends match those expected based on experimental values for the gas-phase acidity of  $\text{H}_2\text{O}$  and the alcohols, and calculated bond lengths and energies for bis-uranyl complexes. However, to the best of our knowledge experimental values for intrinsic  $\text{UO}_2\text{-O}$  bond energies for complexes including  $\text{H}_2\text{O}$  or alcohol ligands are yet to be reported. Use of deuterated solvent allowed the preparation of complexes in which the alcohol ligands containing  $-\text{OD}$  groups. CID of these species showed the preferred elimination of DA rather than HA, which supports the hypothesis for intra-complex proton transfer during the reaction to eliminate the neutral acid.

#### 5. References

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