

Gas-phase H₂O and O₂ Addition to UO₂⁺ Complexes Containing Single Nitrile, Ketone or Amide Ligands

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Introduction:

The speciation and reactivity of uranium is a topic of sustained interest [1] and ongoing researches are pursued to understand its intrinsic reactivity with our environment today. In order to better understand intrinsic interactions between uranyl complexes and solvent, we have turned to gas-phase studies using ion-trap mass spectrometry to eliminate the complexity of solvating effects. Uranyl complexes can be generated freely from solution into gas phase by electrospray ionization (ESI). For example, we have generated ESI solution of uranyl nitrate by mixing the uranyl nitrate, H₂O, and acetone to produce a doubly-charged species in which the ion is coordinated with 4 or 5 acetone ligands [2]. For the purpose of this experiment bare and U(V) complexes will also be generated and studied. The abbreviation of U(V) and U(VI) species stands for the number of coordination sites of the uranium complexes.

Recent studies suggested that bare and UO₂⁺, which are U(V) species, will add molecular oxygen in gas phase, but UO₂²⁺ complexes do not. In order to behave in such manner, bare and UO₂⁺ a formal U(V) species behaves as Lewis acid-like complexes and accept electron density from donating ligands, as the result of the embracing presence of molecular O₂. [2] In the previous molecular O₂ binding studies, our group observed uranyl-acetone complexes can accept O₂ when a single, di, and tri acetone ligands are attached. These discoveries enable us to pursue the goal to investigate the influence of ligands on the tendency for H₂O and O₂ addition to UO₂⁺ complexes containing a single nitrile, ketone, or amide, using species with similar mass and degrees of freedom but different basicity. In this study the differences between U(V) and U(VI) and a U(VI)-like species will also be incorporated into the discussion. The use of ESI and ion trap mass spectrometry enabled us to demonstrate basicity as a factor that can be influential on the enhancement of the initial addition of O₂ over H₂O in various classes of ligand.

Experimental

An LCQ-DecaTM ion trap mass spectrometer was used to generate ESI mass spectra, from samples which consisted of uranyl nitrate combined with mixtures of water and nitrile, acetone, and amide ligands. The ratio of ligands/water used in this experiment was 10%. The solutions were injected into the trap using a syringe pump at a flow rate of 3-5 μL/min. The preparation of solutions, mass spectrum analysis methods, and other procedures have been detailed in references 4-6. During this intrinsic basicity and O₂ addition investigation study, precursor ion containing uranyl with one nitrile, acetone, and amide, respectively, were selected one by one. Each individual uranyl species mixture was infused into the trap in order from lowest gas phase basicity to the highest. These were isolated and stored in the ion trap for periods ranging from 1 to 1000 ms to react with adventitious water and molecular oxygen present in the vacuum and 0.1 ppm of Oxygen and He mixed collision gas for quantitative analysis and comparisons between different selected ions. When the individual uranyl complex was isolated in the trap it produced the formula of UO₂(A)(H₂O)_n(O₂), depending on the ligated species A, the influence of basicity of propionitrile, acetone, to n-methylformamide, and O₂ addition rate, as well as the basicity of the ligands.

Results & Discussion

Single ligated propionitrile, acetone, acetamide, and n-methylformamide uranyl complexes, and [UO₂]⁺ bare ion are both U(V) species. (Figure 1 shows the formation of U(V) species.) Because the distinctive UO₂ center possessed Lewis acid-like behavior, the electron rich center drew molecular O₂ toward itself to form strong O₂-containing complexes [3]. In this study, complex ions can be generated in form of [UO₂(pn)]⁺, [UO₂(act)]⁺, and [UO₂(nmf)]⁺ through ESI in the ion trap. As a result, we saw a strong increase in the direct addition of O₂ rate as

ligand basicity increased. However in the case of U(VI) species such as $[\text{UO}_2\text{OH}]^+$ for example, since there are no free electrons in the valence orbitals to interact with dioxygen, therefore no O_2 containing products were found.

Conclusion

The unique properties of U(V) center allow it to act as a strong Lewis acid that accepts electron density from its ligated donor. As a result, it attracts molecular oxygen toward the center in place of H_2O . Therefore, to further study the distinctive properties and intrinsic reactivity of U(V) center restrictions have been placed upon ligand selectivity. Propionitrile, acetone, and n-methylformamide were the ligands chosen for their similarities in degree of freedom and mass, but differences in molecular class and gas phase basicity. (ligands properties provide in T-1 Below)

Compound Name	Chem Structure	Short Hand	Mass	Degrees of freedom	Gas Phase Basicity
Propionitrile	$\text{C}_3\text{H}_5\text{N}$	pn	55.08	27	763
Acetone	$\text{C}_3\text{H}_6\text{O}$	act	58	30	782.1
N-methylformamide	$\text{C}_2\text{H}_5\text{NO}$	nmf	59.07	27	820.3

Reference

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