An FTMS Investigation of the Competition between Uranium Oxidation and Ligation Reactions

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An unexpected formation of oxidation products in the gas-phase reaction of U⁺ ions with pyrene and 9-azaphenanthrene in a Fourier transform mass spectrometer is reported. The products and reactions are described, but structures and mechanisms are not discussed.

INTRODUCTION

We have recently shown¹ that the ligation of M⁺ metal ions with aromatic hydrocarbons and/or their heterocyclic analogs can be investigated in the gas phase by laser desorption Fourier transform mass spectrometry (LDI FTMS). Positive ions such as Al⁺, V⁺, Cr⁺, Fe⁺, Ni⁺, Cu⁺, Zr⁺, Mo⁺, Ta⁺, Pt⁺, Au⁺ and U⁺ are readily formed by a single laser shot to the appropriate metal foil placed in the ionization chamber of the spectrometer. The neutral organic ligands, L, are provided in a steady state dosage by evaporation of small solid samples placed in the UHV compartment close to the metal foil. Much like Yin and coworkers,² we have observed the products of pseudo-first order consecutive reactions:

* Dedicated to Marko Branica on the occasion of his 65th birthday.
$M^+ \xrightarrow{+L} (ML-X)^+ \xrightarrow{+L} (ML_2-X)^+ \xrightarrow{+L} (ML_3-X)^+ \xrightarrow{+L} \text{etc.}$

where $X = \text{nil, } H_2, \text{ or an L fragment}$, as a function of the delay time after the laser pulse. It has been shown that (i) $M^+$ generally binds two aromatic hydrocarbon molecules and as many as four aza-analogs thereof ($U^+$ being exceptional in that it binds three and five molecules, respectively) and (ii), simultaneous use of two metals and/or two different ligands can provide measures of relative reaction rates and product stabilities. The investigations involving uranium were the only ones in which competitive reactions occurred with reactants nonintentionally, but unavoidably present in the spectrometer (water, oxygen). This is hardly surprising since heated uranium metal effectively binds everything in air except the rare gases. This property is actually used for analytical determination of rare gases in air.

In this contribution, we report some observed reactions and products. However, we do not at this time intend to discuss either the reaction mechanisms or product structures.

**EXPERIMENTAL**

Single shots of a pulsed Nd:YAG Quanta Ray DCR-11 laser operating at 1064 nm fundamental were used for producing $U^+$ ion from a small piece of pure metal. The organic substrate, pyrene (Py) or 9-aza-phenanthrene (Ap), was administered by evaporating an alcoholic solution in the vicinity to the metal sample before introducing it into the spectrometer.

All experiments were performed on the Finnigan FT/MS 2001-DD Fourier transform mass spectrometer with a 3 T superconducting magnet and a Nicolet 1280 data station. Following ion formation, the gas phase reaction of $U^+$ with Py and Ap was investigated at delay times of $10^{-4}$ to 5 s.

**RESULTS AND DISCUSSION**

Various oxidation products of $U^+$ were observed during the reaction of $U^+$ ions with pyrene (Py) and 9-aza-phenanthrene (Ap) in the mass spectrometer. These products were derived from reactions with traces of water and/or oxygen, which are very difficult to eliminate from the mass spectrometer environment. These products were neither wanted nor expected in such an abundance. However, the residual gases competed so effectively with the intended ligands, Py and Ap, that they could not be avoided. A laser shot to a clean U surface produces much $U^+$ as well as some more highly charged U-ions as it is evident in the spectra at $t = 100 \mu s$. Also $UO^+$ and
the gas phase reaction products of \( U^+ \) and \( UO^+ \) with Py and Ap can be observed at these times (Figures 1a and 1b). It can be assumed that \( UO^+ \) is a product of the gas phase reaction because, after a 30 ms delay, most of the \( U^+ \) has disappeared and its reaction products with one and/or two Py molecules (the latter being the base peak) are the most abundant constituents. However, significant amounts of \( UO^+ \) (40%), \( UOPy^+ \) (30%) and \( UOPy_2^+ \) (5%), all relative to the base peak \( UPy_2^+ \), can also be observed which indicates that these are formed from corresponding uranium species \( U^+ \), \( UPy^+ \) and \( UPy_2^+ \) (Table I). Many other reactions also occur: \( UO^+ \) is oxidized to \( UO_2^+ \), whence \( U(OH)_2^+ \) forms; after 300 ms all of the single Py-complex is transformed to \( UPy(OH)_2^+ \), the main Py_2-complexes present being \( UPy_2^+ \) (base peak), \( UOPy_2^+ \) (90%), \( UO_2Py_2^+ \) (65%), while the Py_3-complex is \( UPy_3^+ \) (90%). All of these peaks, P, are accompanied by abundant \( (P-H_2)^+ \) ions which we suppose to be precursor ions to the P's. Thus, the dehydrogenation products are always observed earlier and often at higher abundance than the P's which gain intensity at a later time. Indeed, after delay times of 5 s or greater, the only remaining species are \( UO_2Py_2^+ \) and \( UPy_3^+ \).

### Table I

<table>
<thead>
<tr>
<th>Products observed and the proposed reaction paths in the reaction of ( U^+ ) with ( L = 9 )-azaphenanthrene (Ap)</th>
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<tr>
<td>( U^+ )</td>
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<tr>
<td>( (UL-X)^+ )</td>
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<tr>
<td>( (UL_2-X)^+ )</td>
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<tr>
<td>( (UL_3-X)^+ )</td>
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<td>( (UL_4-X)^+ )</td>
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<td>( (UL_5-X)^+ )</td>
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\( L = 9 \)-azaphenanthrene (Ap)
\( X = nil, H_2, HCN \)
The reaction products and their formation by exposure of U⁺ to Ap and to the impurities (O₂ and/or H₂O) are summarized in Table I. Time and intensity dependence of U⁺ and the main products (UApₙ⁻ - 2)⁺ is shown in Figure 2. In this figure, the sum of all positive ion abundances present at each
time was normalized to 100. It is interesting to note that the oxygen is always added as a single atom, but never as a molecule; that numerous hydrogenation reactions occur, although no hydrogen was ever added; and that some oxidation products might be peroxide-complexes (Table I). Uranyl-peroxo complexes have been found to be important in aqueous media, the works of Branica et al. \(^3\)–\(^6\) being particularly persuasive. Thus, recent spectroscopic evidence indicates the existence of a \((\text{UO}_2\text{HO}_2)^+\) species in solution for which a formation constant was evaluated. \(^7\) Evidently, some connection to the species observed here in the gas phase may exist. We cannot say at this time whether the observed oxidation reactions are carried out mainly by water molecules, or they involve both \(\text{O}_2\) and \(\text{H}_2\text{O}\). However, we do expect to answer some of these questions using isotope labelling technique.

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REFERENCES


SAŽETAK

Ispitivanje usporedbnih reakcija oksidacije i ligacije uranija s pomoću FTMS

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Fourier-transformacijskom spektrometrijom masa praćeno je neočekivano nastajanje oksidacijskih produkata reakcije iona U⁺ s pirenom i 9-azafenantrenom. Opisani su produkti i reakcije, dok se strukture i mehanizmi ne objašnjavaju.