Gas-Phase Reactions of U$^+$ and U$^{2+}$ with O$_2$ and H$_2$O in a Quadrupole Ion Trap

Glen P. Jackson,$^1$‡ Fred L. King,$^1$ Douglas E. Goeringer,$^1$ and Douglas C. Duckworth*,$^1$$^4$

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506-6045, and Chemical Sciences Division, P.O. Box 2008, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6375

Received: April 15, 2002; In Final Form: June 20, 2002

Reaction pathways and rate constants of gas-phase uranium and uranium oxide ions with O$_2$ and H$_2$O have been investigated using a quadrupole ion trap mass spectrometer (QIT-MS). A new reaction pathway is identified for the reaction between U$^{3+}$ and H$_2$O, which leads to the formation of UO$^+$ via the intermediate UOH$^{2+}$. Reaction rate constants are determined for several reactions by measuring the reaction rate at different partial pressures of the reagent gas and are found to be in reasonable agreement with the literature. These rate constants include the first known measurement for the reaction of U$^{2+}$ with H$_2$O ($\sim$0.4 k$_{ADO}$). New limits on thermochemical values are also provided for certain species. These include $\Delta H_f$(UO$^{2+}$) $\leq$ 1742 kJ mol$^{-1}$ and 1614 $\leq$ $\Delta H_f$(UOH$^{2+}$) $\leq$ 1818 kJ mol$^{-1}$ and are based on the assumption that only exothermic or thermoneutral reactions are possible under the conditions used. This assumption is supported by simulations of the root-mean-square (RMS) ion kinetic energy of stored uranium ions in the QIT. Only a slight increase in the RMS ion kinetic energies, from 0.1 to 0.2 eV, is predicted over the range of trapping conditions studied (0.05 $\leq$ q, $\leq$ 0.75) corresponding to a theoretical reaction temperature of $\sim$384 K. The simulations also compare helium and neon as bath gases and show that the RMS kinetic energies are found to be very similar at long trapping times ($\geq$ 20 ms), although neon establishes steady state conditions in approximately half the time.

1. Introduction

Quadrupole ion traps (QITs) serve as one of the most versatile mass spectrometers available to physicists, chemists, and biochemists. It is possible to store ions of either charge, or both charges simultaneously, up to several kilodaltons in mass.$^1$ Trapped ions can be dissociated by a variety of methods in order to obtain thermodynamic or structural information.$^2$ It is also possible to study ion molecule reactions by substituting part or all of the bath gas with a reagent gas of interest.$^3$ Furthermore, by introducing a known quantity of reagent, and allowing a reaction to occur for a known time period, it is possible to determine the rate constant for an ion–molecule reaction.$^3$ Bonner et al. were the first to demonstrate the possibility of measuring rate constants in the QIT by studying the charge and proton-transfer reactions between small organic molecules.$^4$ Such determinations are often dependent on temperature.$^5$ To obtain meaningful quantitative data it is important to ascertain the temperature or kinetic energy of the colliding partners.$^6$ In ion beam experiments, the acceleration voltage leading to the reaction chamber determines the kinetic energy. In ion traps, however, quantification of the kinetic energy of the ions is somewhat more complicated, especially when a bath gas is introduced into the trapping region to dampen the kinetic energy of the ions.

Numerous investigators have reported reaction rate constants of gas-phase ion–molecule reactions and the mean kinetic energies associated with trapped ions.$^5$–$^7$–$^{17}$ These reactions were conducted almost exclusively in helium. The general conclusions are that the kinetic energy of trapped ions increases as a function of increasing trapping potential and decreasing bath gas pressure. An increase in kinetic energy can either increase or decrease the rate of a reaction depending on the thermodynamics involved. Rates of exothermic reactions often decrease with increasing kinetic energy, whereas the rates of endothermic reactions tend to increase with increasing kinetic energy.

The presence of a bath gas to buffer the ion kinetic energy is useful for reducing the influence of the trapping potential. Helium is the most commonly used bath gas, at pressures of $\sim$(0.1–1) $\times$ 10$^{-3}$ Torr. At this time, no direct comparisons of different bath gases have been published to determine how the gases might affect the kinetic energy or internal energy of the ions in the QIT. It has been shown, however, that increasing the partial pressure of N$_2$ in a constant trap pressure of 1.7 mTorr He/N$_2$ can increase the internal energy of a molecular ion.$^{18}$ It is not known to what extent this observation is related to the collision induced dissociation (CID) of strongly bound metal oxides (D$_0$ $>$ 800 kJ mol$^{-1}$) in QITs.$^{18}$–$^{20}$ To dissociate these strongly bound oxides, experiments were performed with neon (in place of helium) in order to achieve the high internal temperatures required. The metal oxides studied were formed via metal ion reactions with O$_2$ in the trap. Because very few studies have considered the effect of a heavier bath gas on reaction rates, it was questioned how well the oxidation rates could be measured in the QIT using neon as the bath gas. The reaction rates of uranium ions with O$_2$ are measured here and compared with literature values to assess the accuracy of this method. The approach is also used to probe other reaction rates.
Ion isolation and double resonance ejection experiments are also used to probe reaction pathways and thermodynamics of uranium ions with oxygen and water. The ability to detect and eject ions, selectively, at 0.5 meV resolution reveals a previously unknown gas-phase oxidation pathway for the doubly charged uranium ion with water.

2. Experimental Apparatus and Method of Measurement

The pulsed glow discharge ion trap mass spectrometer used in this study has been described in detail elsewhere.21 A uranium pin of natural isotopic abundance served as the sample cathode and was positioned on a direct insertion probe.22 Neon was used as the glow discharge support gas at a pressure of 0.8 Torr and as the ion trap bath gas at 0.5 mTorr. A leak valve (Series 203, Granville-Phillips, Boulder, CO) introduced compressed oxygen (Air Liquide) or water (vapor) at pressures between 9 × 10⁻⁷ and 7 × 10⁻⁶ Torr. Isotopically enriched H₂¹⁸O (66 atom % ^1⁸O, Isotec Inc., Miamisburg, OH) was used to verify the source of oxygen in the reactions involving water. An ion gauge (Vacuum Instrument Corporation, Ronkonkoma, NY) measured the pressure of oxygen (or water) before the addition of the neon bath gas and after each experiment when the neon had been evacuated.

The reaction time for the isolated ion of interest and the reagent molecule is defined as the time between the last isolation event in the scan function and the initiation of the mass spectrum. In reality, ions will continue to react during the scan function until such time as they are ejected and detected. But because the reagent ions are always the lightest (in these experiments) and the first to be ejected in the scan function (after <2 ms), no correction is necessary in these experiments to account for the reactions occurring during the acquisition period. An automated “experiment editor” varied the reaction period so that in a typical experiment, 16 mass spectra were averaged to obtain intensity measurements at 2 ms intervals from 0 to 50 ms reaction time. Plots of the reactant ion signal intensity versus time were thereby generated. The rates were verified to be pseudo-first order so that the temporal plots could be converted to a phenomenological rate, \( nk \), according to the expression

\[
-\ln \left( \frac{[M^+]_t}{[M^+]_0} \right) = nkt
\]

where \( n \) is the number density of the reagent gas, \([M^+]_0\) is the initial ion signal of reagent ion, and \([M^+]_t\) is the reagent ion signal at time \( t \). This equation also assumes a linear relationship between ion signal, as measured by the ion detector, and the number of ions (a valid assumption over small ranges).

By repeating the experiment at various values of \( n \) (different reagent gas pressures) the pseudo-first-order rate constant \( k \) can be obtained from the slope of the plot \( nk \) versus \( n \). If the rate constant for a given reaction is known, the measured rates could be used to calibrate the ion gauge.7 The fitted slopes of \( nk \) versus \( n \) are not forced through zero because reactions are observed to occur when no reagent gases are added (i.e., \( n \) is actually a sum of \( n_{\text{residual}} \) and \( n_{\text{added}} \), where \( n_{\text{residual}} \) is the residual number density of \( O_2 \) arising from contaminants in the vacuum system). Quantification of the initial reagent concentration, \( n_{\text{residual}} \), is possible, by determining the \( x \)-intercept of the slopes in Figures 4 and 5. In this study, a complication in the determination of \( n_{\text{residual}} \) for \( O_2 \) is that trace levels of \( H_2O \) are also present (in larger abundance) and contribute to the oxidation reactions of uranium ions. In these experiments, we assume that the residual pressures of \( O_2 \) and \( H_2O \) remain constant throughout, and therefore do not affect the determination of the rate constants from the slopes. This assumption is supported by the correlation of the least squares curve fitting.

3. Results and Discussion

3.1. Kinetic Energy Considerations. According to previous reports, the mean kinetic energy of an ion in the ion trap will be approximately 0.1–2 eV following 15 collisions in \(~1\times10^{-3}\) Torr He.12–14 When a bath gas is present, the kinetic energy of the ions increases only slightly with increasing trapping potential until a stability boundary is approached. Because most experiments are performed in helium, very little is reported about the effects of using a heavier bath gas such as neon. To obtain a better understanding of the kinetics of ions trapped in a neon bath gas at different trapping potentials, calculations were performed using ITSIM software.23 For comparison, calculations were performed with both helium and neon as bath gases. The simulation modeled 500 ²⁹⁹U ions at a pressure of 1 mTorr bath gas at 300 K. In Figure 1, the root-mean-square (RMS) kinetic energy of uranium ions as a function of Mathieu parameter \( q \) (1 mTorr Ne).

![Figure 1. Simulated root-mean-square (RMS) ion kinetic energy of uranium ions as a function of Mathieu parameter \( q \) (1 mTorr Ne).](image)

The total kinetic energy, KE_{total}, of ions moving through a buffer gas under the influence of an electric field is comprised of terms related to motion in the direction of the field and stochastic motion due to ion-buffer gas collisions. The relative (center-of-mass) kinetic energy between the ions and buffer gas is \( KE_{\text{stochastic}} = 3/2 k_B T_{\text{eff}} \), where

\[
T_{\text{eff}}^k = T_{\text{buf}} + \frac{m_{\text{buf}}}{3k_B} v_{\text{directed}}^2
\]

and \( T_{\text{eff}}^k \) is the ion effective translational temperature associated with \( KE_{\text{stochastic}} \). \( T_{\text{buf}} \) is the buffer gas temperature, \( v_{\text{directed}} \) is the ion velocity in the direction of the field, \( m_{\text{buf}} \) is the mass of the buffer gas, and \( k_B \) is the Boltzmann constant. Furthermore, the relative (center-of-mass) kinetic energy between the ions and neutral reactants, KE_{\text{stochastic,rxn}} = 3/2 k_B T_{\text{eff,rxn}} \), is given by

\[
T_{\text{eff,rxn}}^m = T_{\text{buf}} + \frac{m_{\text{ion}} + m_{\text{buf}}}{3k_B} \frac{m_{\text{ion}} + m_{\text{buf}}}{v_{\text{directed}}}^2\left(\frac{m_{\text{ion}} + m_{\text{buf}}}{m_{\text{ion}} + m_{\text{buf}}}ight)
\]
where $T_{\text{ex}}^{\text{rxn}}$ is the effective translational temperature for the reaction rate coefficients, and $m_{\text{ion}}$ and $m_{\text{rxn}}$ are the ion and reactant masses, respectively. A good estimate of $v_{\text{directed}}$ can be obtained from the Wannier equation\textsuperscript{25} for the total laboratory kinetic energy, $KE_{\text{lab}}$.

$$KE_{\text{lab}} = 3/2k_BT_{\text{buf}} + 1/2m_{\text{ion}}v_{\text{directed}}^2 + 1/2m_{\text{buf}}v_{\text{directed}}^2$$  (4)

The first term on the right-hand side is due to the thermal energy of the buffer gas, the second term results from the velocity of the ion packet, and the last term is due to conversion of ion drift motion to random motion via collisions with the buffer gas.

Because ions generally were stored at low trapping potentials for at least 20–25 ms before the reaction period, they are assumed to be kinetically cooled to approximately the calculated RMS kinetic energy. For the reaction, $U^+$ + O$_2$, making the approximation $KE_{\text{total}} \approx 0.13$ eV, solving eq 4 for $v_{\text{directed}}$, and substituting into eq 3 yields $T_{\text{ex}}^{\text{rxn}} \approx 384$ K; the corresponding relative kinetic energy of the reactants $KE_{\text{stochastic}}^{\text{rxn}} \approx 0.050$ eV (4.8 kJ mol$^{-1}$). The maximum internal energy of the neutral reactant is equal to $KE_{\text{stochastic}}^{\text{rxn}}$ (only electronic excitations are possible for atomic ions), thus implying that the observed reactions are unlikely to be endothermic by more than ~5 kJ mol$^{-1}$, which is well within the error of most reported enthalpies. For the case of diatomic ions under similar reaction conditions, the maximum internal energy (now partitioned between ions and neutral reactants) is also $KE_{\text{stochastic}}^{\text{rxn}}$ and therefore does not contribute significantly to the energy available for activation/reaction. In all the reactions considered here, two moles of reagents react to form two moles of products, so entropy effects are negligibly small (at near-room-temperature conditions) and are therefore ignored.

### 3.2. Reactions with O$_2$

Figure 2 summarizes the reaction pathways examined in this study that involve molecular oxygen. Shown next to each arrow is the measured rate constant ($\times 10^{-10}$ cm$^3$ s$^{-1}$). The rate constants for reactions of singly charged uranium ions with oxygen have been known for some time,\textsuperscript{26} but reaction rate constants for the doubly charged species have been measured only recently.\textsuperscript{27} Tables 1–3 provide thermodynamic and kinetic data both from literature and from results derived in this work. Enthalpies of formation in Table 1 (with the exception of UO$^{2+}$ and UOH$^{2+}$) were used to calculate the enthalpies of reactions in Tables 2 and 3. For UO$^{2+}$ and UOH$^{2+}$, limits for the enthalpies of formation were determined from the exothermic reactions observed and reported in Tables 2 and 3. Other values necessary for the calculations (e.g., $\Delta H_i(O)$, $\Delta H_i(H_2O)$) are taken from reference 28, with the exception of the gas-phase proton affinity of water that is taken from reference 29.

### Table 1: Thermochemical Data of Species of Interest

<table>
<thead>
<tr>
<th>species (M)</th>
<th>$\Delta H_f(M,O)$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U$^{2+}$</td>
<td>2277 ± 50$^{15}$</td>
</tr>
<tr>
<td>UO$^{2+}$</td>
<td>$^{&lt;}2047^{33}$</td>
</tr>
<tr>
<td>UOH$^{2+}$</td>
<td>$^{1410}^{\pm}1818^{8}$</td>
</tr>
<tr>
<td>UO$_2$$^{2+}$</td>
<td>1553 ± 250$^{33}$</td>
</tr>
<tr>
<td>U$^+$</td>
<td>1129 ± 4$^{28,35}$</td>
</tr>
<tr>
<td>UO$^+$</td>
<td>582$^{35}$</td>
</tr>
<tr>
<td>UOH$^+$</td>
<td>516 ± 35$^{4}$</td>
</tr>
<tr>
<td>UO$_2$$^+$</td>
<td>54 ± 50$^{38}$</td>
</tr>
<tr>
<td>O$^*$</td>
<td>5$^{738,35}$</td>
</tr>
<tr>
<td>N$_2$</td>
<td>88 ± 20$^{4}$</td>
</tr>
<tr>
<td>O</td>
<td>249 ± 0.1$^{28}$</td>
</tr>
</tbody>
</table>

$^*$ This work.

### Table 2: Reactions of Singly Charged Uranium Species with Molecular Oxygen and Water

<table>
<thead>
<tr>
<th>reactants</th>
<th>products</th>
<th>$\Delta H_f$ (kJ mol$^{-1}$)</th>
<th>rate constant ($\times 10^{-10}$ cm$^3$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U$^+$ + H$_2$O</td>
<td>UO$^+$ + H$_2$</td>
<td>$^-&lt;10^*$</td>
<td>10$^d$</td>
</tr>
<tr>
<td>U$^+$ + H$_2$O</td>
<td>UOH$^+$ + H</td>
<td>$\leq 0^d$</td>
<td>see text</td>
</tr>
<tr>
<td>U$^+$ + O$_2$</td>
<td>UO$^+$ + O</td>
<td>$\leq 0^{27,33,4}$</td>
<td>1$^d$</td>
</tr>
<tr>
<td>UO$^+$ + H$_2$O</td>
<td>UO$_2$$^+$ + H$_2$</td>
<td>not observed</td>
<td>$&lt;0.1^d$</td>
</tr>
<tr>
<td>UO$^+$ + H$_2$O</td>
<td>UO$_2$$^+$ + H$_2$O$^*$</td>
<td>not observed</td>
<td>$&lt;0.1^d$</td>
</tr>
<tr>
<td>UO$^+$ + O$_2$</td>
<td>UO$_3$$^+$ + O$^*$</td>
<td>$\leq 0^{27,33,4}$</td>
<td>0.44$^d$</td>
</tr>
<tr>
<td>UO$_2$$^+$ + O$_2$</td>
<td>UO$_3$$^+$ + O$_2$</td>
<td>$\geq 0^{27,33}$</td>
<td>$&lt;0.37$</td>
</tr>
</tbody>
</table>

$^*$ Calculated from decay constants in ref 27 assuming 20% partial pressure of O$_2$ in air at 4 × 10$^{-5}$ Torr air pressure. $^d$ This work.

### Table 3: Reactions of Doubly Charged Uranium Species with Molecular Oxygen and Water

<table>
<thead>
<tr>
<th>reactants</th>
<th>products</th>
<th>$\Delta H_f$ (kJ mol$^{-1}$)</th>
<th>rate constant ($\times 10^{-10}$ cm$^3$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U$^{2+}$ + H$_2$O</td>
<td>UO$^{2+}$ + H$_2$</td>
<td>$\leq 4$</td>
<td>10$^d$</td>
</tr>
<tr>
<td>U$^{2+}$ + H$_2$O</td>
<td>UOH$^{2+}$ + H</td>
<td>$\leq 0^d$</td>
<td>see text</td>
</tr>
<tr>
<td>U$^{2+}$ + O$_2$</td>
<td>UO$^{2+}$ + O$_2$</td>
<td>$\leq 0^{27,33}$</td>
<td>0.4$^d$</td>
</tr>
<tr>
<td>UO$^{2+}$ + H$_2$O</td>
<td>UO$_2$$^{2+}$ + H$_2$O$^*$</td>
<td>not observed</td>
<td>$&lt;0.37$</td>
</tr>
<tr>
<td>UO$^{2+}$ + H$_2$O</td>
<td>UO$_2$$^{2+}$ + H$_2$O$^*$</td>
<td>not observed</td>
<td>$&lt;0.37$</td>
</tr>
</tbody>
</table>

$^*$ Calculated from decay constants in ref 27 assuming 20% partial pressure of O$_2$ in air at 4 × 10$^{-5}$ Torr air pressure. $^d$ Calculated from decay constants in ref 27 assuming 20% partial pressure of O$_2$ in air at 4 × 10$^{-5}$ Torr air pressure.

$^*$ This work.

### 3.2.1. U$^+$ Reaction with O$_2$

The thermodynamic and kinetic aspects of reaction A are well known, and this reaction provides a suitable probe system for the ion trap.

$$U^+ + O_2 \rightarrow UO^+ + O$$  (A)

Experiments were first conducted to ensure that charge conservation is maintained and that the reaction from U$^+$ to UO$^+$
Figure 3. Ion signal intensities versus time for the reaction of U⁺ with O₂ (1.3 × 10⁻⁶ Torr O₂). Bath gas is neon at 0.5 mTorr, qₑ = 0.6.

Figure 4. Measured reaction rates of U⁺ (filled diamonds) and UO⁺ (open diamonds) with O₂ versus relative number density of added O₂. Values shown are the average of four different qₑ values on three separate days with ±1 s.d.

Figure 5. Measured reaction rates versus relative number density of added O₂ to determine the rate constants for the reactions of U²⁺ (filled diamonds) and UO²⁺ (open diamonds) with O₂. Values shown are the average of four different qₑ values on three separate days with ±1 s.d.

does in fact proceed through the intermediate UO⁺, Figure 3 is a plot of the ion signal intensities of each species as a function of time for the reaction U⁺ + O₂ at a nominal oxygen number density of 4 × 10¹⁰ cm⁻³ (~1.3 × 10⁻⁶ Torr). The constant total ion signal demonstrates that charge conservation is maintained. The temporal profiles shown in Figure 3 are indicative of a two-step reaction sequence in which the reaction proceeds through the intermediate UO⁺. Resonance ejection of the intermediate UO⁺ confirmed that all the U⁺ losses were accounted for in the UO⁺ channel. Therefore, the measured decrease in ion signal of U⁺ over time can be used to calculate the rate of reaction A according to eq 1.

Reaction rates for reaction A were measured at four different trapping potentials between 0.2 ≤ qₑ ≤ 0.8 at four different pressures of O₂. The trapping potential had no statistically significant affect on the measured reaction rates for this reaction, based on the external precision of the measurements. This observation is consistent with the simulations presented earlier, whereby the RMS kinetic energy of uranium ions did not significantly increase over this range of trapping potentials. Although this specific reaction is not highly sensitive to kinetic energy effects, the reaction rates have been shown to decrease (~10%) as the kinetic energy of the U⁺ increases (from 0 to 5 eV in lab frame). A reaction that is more sensitive to kinetic effects would be required to examine further the effects of rf heating at different values of qₑ.

The reaction rates for U⁺ at several trapping potentials were averaged for each partial pressure of oxygen, measured on three separate days, and are shown in Figure 4 (top curve). A linear regression line reveals a rate constant for reaction A of k = 9.2 ± 0.5 × 10⁻¹⁰ cm³ s⁻¹ (95% CL). This is in good agreement with the two previous reported values of this reaction of 8.5 ± 1 × 10⁻¹⁰ cm³ s⁻¹ by Johnsen and Biondi and 8 × 10⁻¹⁰ cm³ s⁻¹ by Gieray et al. Corneth et al. measured this reaction rate as 1.17kADO ± 40%, and we interpret this to be k = 6.5 ± 2.6 × 10⁻¹⁰ cm³ s⁻¹, in reasonable agreement with the other values (to calculate kADO the polarizability of O₂ was taken from reference 28).

3.2.2. UO⁺ Reaction Rate with O₂. To observe reaction B, UO⁺ ions were selectively isolated by applying a two-frequency resonance ejection on U⁺ and UO⁺+, before allowing the reaction with admitted O₂ to proceed.

\[ \text{UO}^+ + \text{O}_2 \rightarrow \text{UO}_2^+ + \text{O}^+ \]  \hspace{1cm} \text{(B)}

Measurements were again made at trapping potentials ranging from 0.2 ≤ qₑ ≤ 0.8, and no effect was found on the reaction rates. Figure 4 (lower curve) shows the averages of the rates measured at each O₂ pressure for four different trapping potentials. Data collected on three separate days are also included in the error bars (2σ, n ~ 12) in this plot to demonstrate the day-to-day repeatability of these experiments. The difference in the intercepts for the two lines shown in this figure is due to differences in the reactivity of U⁺ and UO⁺+. It was found that U⁺ readily reacts with residual water, while UO⁺ reacts so slowly with water that the product is not observed prior to O₂ introduction.

The rate constant for reaction B is found to be k = 9.0 ± 0.6 × 10⁻¹⁰ cm³ s⁻¹ (95% CL), the same as that of the bare uranium ion. Gieray et al. report a rate that corresponds to approximately 1 × 10⁻⁹ cm³ s⁻¹, slightly faster than the reported rates for U⁺. Their experiments were conducted in air, however, and this value assumes a 20% composition of O₂ in air and that no other species interfere with the measurement. Corneth et al. report a rate of 0.95kADO ± 40%, and from this we calculate a k of 5.3 ± 2 × 10⁻¹⁰ cm³ s⁻¹. No other rate constants for this reaction were found in the extant literature.

3.2.3. U²⁺ Reaction with O₂. The pulsed glow discharge ion source generates sufficient quantities of doubly charged ions that their reaction pathways and rates can also be examined. At these low pressures of oxygen it is possible to measure the very fast reaction C.

\[ \text{U}^2+ + \text{O}_2 \rightarrow \text{UO}_2^+ + \text{O}^+ \]  \hspace{1cm} \text{(C)}

Figure 5 (top curve) is a plot of the reaction rates of U²⁺ versus the relative added number density of oxygen. Analysis of the slope gives a rate constant of 1.8 ± 0.4 × 10⁻⁹ cm³ s⁻¹ (95% CL). Geiray et al. provide the only other known measurement of this rate as 1.3 × 10⁻⁹ cm³ s⁻¹, again in reasonable agreement. It is interesting to note that although the predicted rate (kADO = 1.1 × 10⁻⁹ cm³ s⁻¹) underestimates the measured rate constant for reaction C, the predicted rate for the doubly...
charged uranium is twice the predicted rate of the singly charged uranium ion. The measured values for $U^+$ and $U^{2+}$ (9.2 and 18 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, respectively) are at least consistent with predicted rates, viz., if both the reactions proceed at the collision rate then the rate for the doubly charged species should be twice that of the singly charged species.\textsuperscript{32}

Because this reaction is exothermic, an upper limit of $\Delta H_f$ ($\text{UO}_2^{2+}$) $\leq 2028$ kJ mol$^{-1}$ can be obtained from reaction C, using values from Table 1. This limit is consistent with the value obtained by Cornehl et al. of $\Delta H_f$ (UO$^{2+}$) $\leq 2047$ kJ mol$^{-1}$, obtained by the reaction of U$^{2+}$ with CO$_2$.\textsuperscript{33}

3.2.4. UO$^{2+}$ Reaction with O$_2$. Reaction D is found to proceed with a pseudo-first-order rate constant of $3.7 \pm 1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (95% CL).

$$\text{UO}_2^{2+} + \text{O}_2 \rightarrow \text{UO}_2^{2+} + \text{O}^+ \quad (D)$$

At any given pressure, reaction D is approximately 50 times slower than the bare uranium doubly charged ion and becomes rate limiting for the formation of $\text{UO}_2^{2+}$ from $U^{2+}$. Cornelh et al. note that the rate of formation D is more than 1 order of magnitude slower than reaction C, occurring at approximately 4% of the collision rate.\textsuperscript{31,33} If we assume reaction C to occur at the collision rate, then reaction D occurs at approximately 2% of the collision frequency, in reasonable agreement with the previous reports.

3.2.5. UO$^{2+}$ Reaction with O$_2$. Decreasing the low-mass cutoff value from 110 m/z to 25 m/z during the reaction period facilitated the observation of $\text{O}_2^+$, the charge exchange product of reaction E.

$$\text{UO}_2^{2+} + \text{O}_2 \rightarrow \text{UO}_2^{2+} + \text{O}_2^+ \quad (E)$$

However, the reaction rate could not be measured satisfactorily because the reagent $\text{UO}_2^{2+}$ could not be obtained in sufficient quantity. This is because reaction E proceeds at a rate faster than reaction D ($>3.7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$) and prevents the accumulation of $\text{UO}_2^{2+}$. Resonant ejection of $\text{UO}_2^{2+}$ during the reaction period of $\text{UO}_2^{2+}$ with $\text{O}_2$ prevents the formation of both $\text{UO}_2^{2+}$ and $\text{O}_2^+$, indicating that the alternative charge exchange reaction (not shown in Figure 1) in equation F is not an energetically feasible pathway.

$$\text{UO}_2^{2+} + \text{O}_2 \nrightarrow \text{UO}_2^{2+} + \text{O}_2^+ \quad (F)$$

This indicates that the ionization potential of $\text{UO}_2^+$ is less than that of $\text{O}_2$ (12.06 eV). Also, given that $\Delta H_f$ ($\text{O}_2^+$) = 1165 kJ mol$^{-1}$ and $\Delta H_f$ ($\text{UO}_2^+$) = 582 $\pm$ 13 kJ mol$^{-1}$, the enthalpy of formation of $\text{UO}_2^+$ must be less than or equal to 1747 kJ mol$^{-1}$. This value is considerably smaller than the previous upper limits of 2028 kJ mol$^{-1}$ obtained in section 3.2.3, and 2047 kJ mol$^{-1}$ determined by Cornelh et al.\textsuperscript{33}

3.3. Reactions with H$_2$O. The reactions that occur between uranium-containing ions and water are summarized in Figure 6. Isotopically enriched H$_2^{18}$O was used in order to distinguish between the reactions with added H$_2^{18}$O and those with residual H$_2$O$_{16}$O and H$_2^{16}$O.

3.3.1. $U^+$ Reaction with H$_2$O. There seems to be some disagreement in the literature regarding the relative rates for reactions G and H.

$$U^+ + \text{H}_2 \rightarrow \text{UO}^+ + \text{H}_2 \quad (G)$$

$$U^+ + \text{H}_2 \rightarrow \text{UOH}^+ + \text{H} \quad (H)$$

In low-energy ion beam experiments, both reactions were shown to be exothermic with a branching ratio of approximately 10:1 in favor of reaction G.\textsuperscript{34} In ICR experiments, reaction H was not observed when the bare uranium ions were sufficiently cooled prior to the reaction.\textsuperscript{31} The minor product UOH$^+$ was observed in the QIT with a branching ratio close to 10:1, in agreement with the ion beam experiments. From ion beam experiments, Armentrout and Beauchamp\textsuperscript{34} propose a reaction mechanism in which the products of reactions G and H are formed from a similar reactive intermediate, HU$^-$OH$^+$. They show that although both products are formed at the lowest kinetic energies explored, the formation of UOH$^+$ is thermodynamically favored product at low kinetic energies and that the UOH$^+$ product channel competes more at higher kinetic energies. The product ratio of $\sim 10:1$ observed in the QIT agrees with the lowest energy observations made by in the ion beam experiments by Armentrout and Beauchamp,\textsuperscript{34} again indicating that the uranium ions are close to room temperature.

The total rate of loss of $U^+$ due to reaction with H$_2$O is $1.0 \pm 1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, slightly faster than the reaction with $O_2$ (reaction A). Armentrout and Beauchamp\textsuperscript{34} also found the cross section for this reaction to be larger than the cross section for the reaction with $O_2$. Cornelh et al.\textsuperscript{31} found the reaction rate constant with water to be 0.47$k_{ADD}$ $\pm$ 40%, which equates to $k = 8.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, also faster than the reaction rate with $O_2$ (This calculation was based on the polarizability and dipole values from ref 28 and a “locking factor” of 0.25 obtained from Su and Bowers.\textsuperscript{32}) Sufficient quantities of UOH$^+$ could not be isolated in order to study the reactions between UOH$^+$ and H$_2$O.

3.3.2. UO$^+$ Reaction with H$_2$O. Reactions I and J have been shown to be exothermic processes.

$$\text{UO}_2^+ + \text{H}_2 \rightarrow \text{UO}_2^{2+} + \text{H}_2 \quad (I)$$

$$\text{UO}_2^+ + \text{H}_2 \rightarrow \text{UO}_2^{2+} + \text{H} \quad (J)$$

In the present work, the reaction between UO$^+$ and water was found to proceed at a rate of $1.5 \pm 1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and showed a branching ratio of approximately 1:1, in agreement with Armentrout and Beauchamp.\textsuperscript{34} Cornelh and co-workers\textsuperscript{31} state that the formation of UO$^+_2$H$^+$ was not observed in their studies. Experiments by Armentrout and Beauchamp and those presented here were conducted at much higher partial pressures (and total pressures) than the work of Cornelh et al. Higher

\begin{center}
\includegraphics[width=\textwidth]{figure6.png}
\end{center}
pressures would encourage three-body reactions, or subsequent cooling collisions by a third body, which would not be likely at lower pressures. In the absence of a third body it is possible that an initial exothermic step could provide the driving force to eliminate a molecule of \( \text{H}_2 \) from a reaction with water, i.e., reactions G and I. If a third body is present at a time frame shorter than that available for dehydrogenation, the third body could take away the excess energy and allow a lower energy channel (i.e., the loss of H) to be competitive, reactions H and J. In Armentrout and Beauchamp’s experiments,\(^3^4\) the third body would have to be another reagent molecule (because the collision cell pressure consists only of the reagent gas), but in these experiments the third body is more likely to be a neon bath gas atom.

3.3.3. \( \text{U}^{2+} \) Reaction with \( \text{H}_2\text{O} \). Two possible reactions between \( \text{U}^{2+} \) and \( \text{H}_2\text{O} \) are given below

\[
\text{U}^{2+} + \text{H}_2\text{O} \rightarrow \text{UO}^{2+} + \text{H}_2 \quad (K)
\]

\[
\text{U}^{2+} + \text{H}_2\text{O} \rightarrow \text{UOH}^{2+} + \text{H} \quad (L)
\]

Although the charged products of reactions K and L differ in \( m/2 \) by only 0.5, these ions can be selectively ejected from the QIT to determine the secondary reaction products of each ion. When \( \text{UO}^{2+} \) is resonantly ejected, the product mass spectra include the ions \( \text{UOH}^{2+}, \text{H}_2\text{O}^{+}, \) and \( \text{UO}^{+} \) (as well as the starting reagent \( \text{U}^{2+} \)). No \( \text{UOH}^{+} \) or \( \text{H}_2\text{O}^{+} \) is observed, indicating that charge transfer between \( \text{UOH}^{2+} \) and \( \text{H}_2\text{O} \) (reaction M) does not occur.

\[
\text{UOH}^{2+} + \text{H}_2\text{O} \rightarrow \text{UOH}^{+} + \text{H}_2\text{O}^{+} \quad (M)
\]

Detection of the products \( \text{UO}^{+} \) and \( \text{H}_2\text{O}^{+} \) indicate that the reaction proceeds via the protonation of a water molecule in the reaction

\[
\text{UOH}^{2+} + \text{H}_2\text{O} \rightarrow \text{UO}^{+} + \text{H}_2\text{O}^{+} \quad (N)
\]

Thus, while it is not possible to form \( \text{UO}^{+} \) from a reaction between \( \text{U}^{2+} \) and \( \text{O}_2 \), it is possible to form \( \text{UO}^{+} \) from \( \text{U}^{2+} \) via the reaction with water, as demonstrated in the reaction sequence L and N. Because reaction L is exothermic, \( \Delta H_{f} (\text{H}) = 218 \text{ kJ mol}^{-1} \), and \( \Delta H_{r} (\text{H}_2\text{O}) = -241 \text{ kJ mol}^{-1} \), an upper limit of 1818 \( \pm 50 \) kJ mol\(^{-1}\) is obtained for \( \Delta H_{r} (\text{UOH}^{2+}) \). Likewise, given \( \Delta H_{r} (\text{H}_2\text{O}^{+}) = 592 \text{ kJ mol}^{-1} \) and that reaction N is also exothermic, a limit is also obtained for \( \Delta H_{r} (\text{UOH}^{2+}) \geq 1410 \pm 13 \text{ kJ mol}^{-1} \). This bracketing gives limits for the enthalpy of formation of \( \text{UOH}^{2+} \) of 1410 \( \leq \Delta H_{f} (\text{UOH}^{2+}) \leq 1818 \text{ kJ mol}^{-1} \).

Reliable reaction rate constants could not be determined for the doubly charged uranium ions because significant ion losses were observed during the course of the reactions. These losses could be due to an unidentified reaction loss path but are more likely due to scattering of the lighter ions that are formed during the reactions (i.e., \( \text{H}_3\text{O}^{+} \)). If all the \( \text{U}^{2+} \) losses do indeed pass quantitatively through \( \text{UO}^{2+} \) or \( \text{UOH}^{2+} \), the reaction rate constant for the combined reactions K and L would be \( 1.0 \times 10^{-9} \text{ cm}^{3} \text{ s}^{-1} \). This equates to approximately 0.44 \( \text{ADO}^{-} \). Because \( \text{H}_3\text{O}^{+} \) was observed at low trapping potentials and the loss rate of \( \text{UOH}^{2+} \) was faster than the loss rate of \( \text{UO}^{2+} \), the loss of charge is probably due to the fast protonation of water in the form of \( \text{H}_3\text{O}^{+} \).

3.3.4. \( \text{UO}^{2+} \) Reaction with \( \text{H}_2\text{O} \). Under the conditions of these experiments, reactions O and P were not observed.

\[
\text{UO}^{2+} + \text{H}_2\text{O} \rightarrow \text{UO}_2^{2+} + \text{H}_2 \quad (O)
\]

\[
\text{UO}^{2+} + \text{H}_2\text{O} \rightarrow \text{U}^{+} + \text{H}_2\text{O}^{+} \quad (P)
\]

It is not established if these reactions are endothermic or just too slow to be measured. Because the slowest measurable rate on this system is approximately \( 1 \times 10^{-11} \text{ cm}^{3} \text{ s}^{-1} \), we provide this value as an upper limit for reactions O and P.

4. Conclusions

This work describes a methodology for measuring reaction rate constants in a quadrupole ion trap using neon as the bath gas. Kinetic energy effects are considered to be very small (converting less than 5 kJ mol\(^{-1}\) to endothermic reactions) based on ion trap simulations and theoretical considerations. In the simulations, neon brings the kinetic energy of the ions to a steady state value more quickly than does helium, and this reduces the necessary cooling period before making a rate measurement. The reaction rates and products observed between uranium ions and \( \text{H}_2\text{O} \) agree with work conducted in low energy ion beam experiments, but disagree, in select cases, with similar reactions observed in an ICR. These differences are likely to be the result of third body collisions in the QIT and ion beam experiments that help take away excess energy from the reaction intermediates.

The use of a neon bath gas is proving to be extremely useful for advanced applications of ion traps, including dissociating strongly bound oxide ions\(^{19,20} \) and for measuring the thermodynamics and kinetics of reactions. It is hoped that these techniques will afford a promising approach to studying transuranic ions and compounds, where the QIT lends itself particularly well to radiation containment controls. Benefits would include size (for glovebox applications), cost, and the ability to measure reaction rates, thermochemistry, and bond dissociation energies (from CID rates) in a single instrument.

Acknowledgment. The authors thank John K. Gibson, of Oak Ridge National Lab, for many useful comments and suggestions during the preparation of this manuscript. We are also grateful to Graham Cooks for use of the ITSIM software. Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

References and Notes