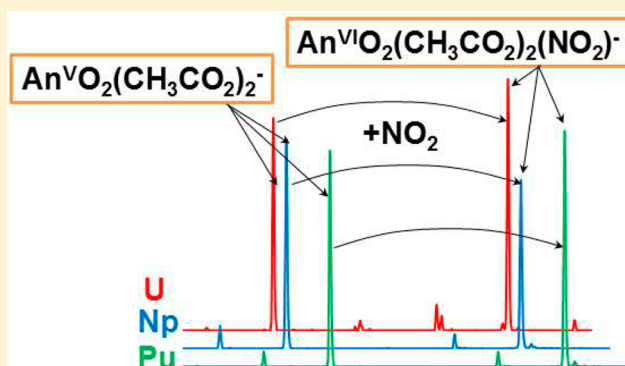


Oxidation of Actinyl(V) Complexes by the Addition of Nitrogen Dioxide Is Revealed via the Replacement of Acetate by Nitrite

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Supporting Information

ABSTRACT: The gas-phase complexes $\text{AnO}_2(\text{CH}_3\text{CO}_2)_2^-$ are actinyl(V) cores, $\text{An}^{\text{V}}\text{O}_2^+$ (An = U, Np, Pu), coordinated by two acetate anion ligands. Whereas the addition of O_2 to $\text{U}^{\text{V}}\text{O}_2(\text{CH}_3\text{CO}_2)_2^-$ exothermically produces the superoxide complex $\text{U}^{\text{VI}}\text{O}_2(\text{O}_2)(\text{CH}_3\text{CO}_2)_2^-$, this oxidation does not occur for $\text{Np}^{\text{V}}\text{O}_2(\text{CH}_3\text{CO}_2)_2^-$ or $\text{Pu}^{\text{V}}\text{O}_2(\text{CH}_3\text{CO}_2)_2^-$ because of the higher reduction potentials for Np^{V} and Pu^{V} . It is demonstrated that NO_2 is a more effective electron-withdrawing oxidant than O_2 , with the result that all three $\text{An}^{\text{V}}\text{O}_2(\text{CH}_3\text{CO}_2)_2^-$ exothermically react with NO_2 to form nitrite complexes, $\text{An}^{\text{VI}}\text{O}_2(\text{CH}_3\text{CO}_2)_2(\text{NO}_2)^-$. The assignment of the NO_2^- anion ligand in these complexes, resulting in oxidation from An^{V} to An^{VI} , is substantiated by the replacement of the acetate ligands in $\text{AnO}_2(\text{CH}_3\text{CO}_2)_2(\text{NO}_2)^-$ and $\text{AnO}_2(\text{CH}_3\text{CO}_2)_3^-$ by nitrites, to produce the tris(nitrite) complexes $\text{AnO}_2(\text{NO}_2)_3^-$. The key chemistry of oxidation of An^{V} to An^{VI} by the addition of neutral NO_2 is established by the substitution of acetate by nitrite. The replacement of acetate ligands by NO_2^- is attributed to a metathesis reaction with nitrous acid to produce acetic acid and nitrite.



INTRODUCTION

Knowledge of the structures, bonding, and reactivities of elementary molecular actinide species reveals the fundamental aspects of 5f-element chemistry and provides a foundation for understanding and predicting the behavior of actinides in complex systems.^{1,2} The linear mono- and dipositive actinyl ions, $[\text{O}=\text{An}=\text{O}]^{+/2+}$, are important species in the chemistry of uranium, neptunium, and plutonium.^{3,4} For $\text{U}^{\text{V}}\text{O}_2^+$, the frontier molecular orbitals (σ_w , σ_g , π_g , and π_u) are fully occupied, resulting in strong An–O bonds.^{4–12} The single electron localized in U 5f₇ orbitals is available to form equatorial bonds and can be abstracted by a Lewis base ligand, forming complexes comprising oxidized $\text{U}^{\text{VI}}\text{O}_2^{2+}$.^{7,13} Condensed-phase complexes of $\text{U}^{\text{VI}}\text{O}_2(\eta^2\text{-peroxo } \text{O}_2)$ have been synthesized,^{14,15} and there are several cases of $\text{U}^{\text{VI}}\text{O}_2^{2+}$ units bridged by peroxide in a μ -dioxo mode.^{16–21} The gas-phase addition of O_2 to $\text{U}^{\text{V}}\text{O}_2^+$ complexes^{22,23} results in $\text{U}^{\text{VI}}\text{O}_2(\eta^2\text{-superoxo } \text{O}_2)^+$.¹³ In the latter complex, the side-on-bound O_2 ligand forms a two-electron, three-center bond with U^{V} , oxidizing U^{V} to U^{VI} .

Whereas gas-phase hydrated U^{V} , $\text{U}^{\text{V}}\text{O}_2(\text{H}_2\text{O})_{2,3}^+$, is oxidized to U^{VI} by the addition of O_2 , this phenomenon is not observed for the corresponding neptunyl(V) and plutonyl(V) hydrates.²⁴ Density functional theory calculations indicate that, unlike the superoxide structure of the uranium complexes, in the lowest-energy structure of hypothetical $\text{NpO}_2(\text{O}_2)(\text{H}_2\text{O})_n^+$, the O_2 ligand is very weakly bound to neptunium in an end-on (η^1) mode, with the Np^{V} oxidation state retained.²⁴ The observation

of $\text{An}^{\text{VI}}\text{O}_2(\text{O}_2)(\text{H}_2\text{O})_n^+$ for An = U, but not Np and Pu, is attributed to the much lower VI/V reduction potential for uranium (0.09 V) compared to neptunium (1.16 V) and plutonium (0.94 V).²⁵ In essence, O_2 can abstract an electron from UO_2^+ but not from NpO_2^+ or PuO_2^+ .

Discrete oxidation of a metal center by the addition of a neutral gas is unusual, with O_2 addition to uranyl(V) being a rare example. Metal carbonyls can be synthesized by reaction with CO, but the bonding and oxidation states in the resulting species are complex, with the oxidation state of the metal center not necessarily directly correlated with the number of CO ligands.²⁶ The ability of a neutral gas to affect distinct oxidation by adduct formation might be related to the electron affinity (EA) of the added ligand, which is an indication of its propensity to undergo reduction by withdrawal of the electron charge. The EA of NO_2 , 2.3 eV,²⁷ is almost 2 eV higher than that of O_2 (EA = 0.4 eV²⁸). Also, in contrast to O_2 (and CO), NO_2 is reactive with water to form HNO_2 , a weak acid that dissociates to H^+ and NO_2^- .^{29–31} Accordingly, NO_2 was identified as a candidate electron-withdrawing oxidant that might surmount the higher VI/V reduction potentials of Np^{V} and Pu^{V} and oxidize them to their hexavalent states. It should be noted that oxidation by adduct formation contrasts with oxidation by donation of an oxidizing atom. That N_2O oxidizes

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$\text{An}^{\text{IV}}\text{O}^{2+}$ to $\text{An}^{\text{VI}}\text{O}_2^{2+}$ ($\text{An} = \text{U}, \text{Np}, \text{Pu}$)³² is unrelated to the electron-donating capacity of N_2O but rather to facile donation of an O atom.

It has recently been demonstrated that the uranyl(V) carboxylate anion complex, $\text{U}^{\text{V}}\text{O}_2(\text{CH}_3\text{CO}_2)_2^-$, which is produced by electrospray ionization (ESI), adds O_2 to produce the uranyl(VI) superoxide complex, $\text{U}^{\text{VI}}\text{O}_2(\text{O}_2)(\text{CH}_3\text{CO}_2)_2^-$ (Figure 1a).³³ In view of the inability of O_2 to similarly oxidize

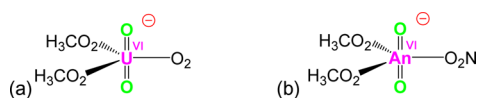


Figure 1. Schematic structures of (a) $\text{U}^{\text{VI}}\text{O}_2(\text{O}_2)(\text{CH}_3\text{CO}_2)_2^-$ and (b) $\text{An}^{\text{VI}}\text{O}_2(\text{CH}_3\text{CO}_2)_2(\text{NO}_2)^-$.

Np^{V} and Pu^{V} ,²⁴ we have explored NO_2 as a potentially more effective electron-acceptor oxidant than O_2 . Association reactions of $\text{An}^{\text{V}}\text{O}_2(\text{CH}_3\text{CO}_2)_2^-$ ($\text{An} = \text{U}, \text{Np}, \text{Pu}$) with NO_2 indicate oxidation of An^{V} to An^{VI} . It was demonstrated that NO_2 replaces carboxylate ligands to produce nitrite complexes, $\text{AnO}_2(\text{NO}_2)_2$,³³ confirming the nature of the NO_2 ligand as a nitrite; this displacement is attributed to a metathesis reaction with HNO_2 .

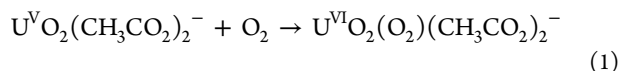
EXPERIMENTAL METHODS

The general experimental approach has been described previously.³⁴ Anionic actinyl acetate complexes, $\text{AnO}_2(\text{CH}_3\text{CO}_2)_2^-$ and $\text{AnO}_2(\text{CH}_3\text{CO}_2)_3^-$ for $\text{An} = \text{U}, \text{Np},$ and Pu , were produced by ESI of ethanol solutions containing 200 μM AnO_2^{2+} and various concentrations of acetate. The actinyl stock solutions were 10 mM $\text{UO}_2(\text{ClO}_4)_2$ at pH = 4, 28 mM $\text{NpO}_2(\text{ClO}_4)_2$ at pH = 1, and 8 mM $\text{PuO}_2(\text{ClO}_4)_2$ at pH = 1. The isotopes U-238, Np-237, and Pu-242 are all radioactive and must be handled with proper controls.³⁵ A 240 mM aqueous solution of $\text{CH}_3\text{CO}_2\text{H}$ and NH_4OH at pH = 7 was added to the ESI solutions to give actinyl/ligand ratios of ca. 1:4 for uranium, 1:8 for neptunium, and 1:16 for plutonium, which provided optimum yields of the complex ions. Actinyl diacetate nitrite complexes, $\text{AnO}_2(\text{CH}_3\text{CO}_2)_2(\text{NO}_2)^-$, were produced by ESI using the actinyl acetate solutions with NaNO_2 added to give $\text{NO}_2^-/\text{CH}_3\text{CO}_2^-$ ratios of 1:3.

The experiments were performed using an Agilent 6340 quadrupole ion trap mass spectrometer with MS^n collision-induced dissociation (CID) capability; the CID energy is an instrumental parameter that provides an indication of relative ion excitation. Ions in the trap can undergo ion–molecule reactions at $\sim 300\text{ K}$ ³⁶ by applying a reaction time of up to 10 s. Anion mass spectra were acquired using the following parameters: solution flow rate, 60 $\mu\text{L}/\text{h}$; nebulizer gas pressure, 15 psi; capillary voltage offset and current, -3800 V and 15.9 nA; end plate voltage offset and current, -500 V and 125 nA; dry gas flow rate, 4 L/min; dry gas temperature, 325 $^\circ\text{C}$; capillary exit, -50.0 V ; skimmer, -36.3 V ; octopole 1 and 2 direct current (dc), -10.9 and -3.0 V ; octopole radio-frequency (RF) amplitude, 190 V_{pp} ; lens 1 and 2, 10.0 and 91.0 V; trap drive, 80. N_2 gas for nebulization and drying was supplied from the boil-off of a liquid-nitrogen Dewar. The background water pressure in the ion trap is estimated as $\sim 10^{-6}$ Torr;³⁷ reproducibility of the hydration rates of $\text{UO}_2(\text{OH})^+$ ²⁴ established that the water pressure was constant to within <10%. The helium buffer gas pressure in the trap is constant at $\sim 10^{-4}$ Torr. The ion trap has been modified to allow for the introduction of reagent gases through a leak valve;³⁵ NO_2 gas (stated purity of $\geq 99.5\%$, Sigma-Aldrich; actual purity may be lower) was introduced into the ion trap to maintain a constant (unknown) pressure. Reactions with O_2 result from background O_2 gas in the ion trap.

RESULTS AND DISCUSSION

Addition of O_2 and NO_2 to $\text{An}^{\text{V}}\text{O}_2(\text{CH}_3\text{CO}_2)_2^-$. As reported previously, among $\text{An}^{\text{V}}\text{O}_2(\text{CH}_3\text{CO}_2)_2^-$, the complex with $\text{An} = \text{U}$ distinctively reacted with background O_2 in the ion trap to produce the superoxide $\text{U}^{\text{VI}}\text{O}_2(\text{O}_2)(\text{CH}_3\text{CO}_2)_2^-$; see reaction 1 (Figure S1, Supporting Information).³³



This discrepancy between the three actinyl(V) complexes is consistent with previous results for hydrates of AnO_2^+ , for which O_2 addition was observed for $\text{U}^{\text{V}}\text{O}_2^+$ but not for $\text{Np}^{\text{V}}\text{O}_2^+$ and $\text{Pu}^{\text{V}}\text{O}_2^+$.²⁴ The ability of O_2 to oxidize U^{V} but not Np^{V} or Pu^{V} has been attributed to the $\text{U}^{\text{VI/V}}$ reduction potential, which is lower than the others by ca. 1 eV.²⁵ The EA of O_2 , 0.4 eV,³⁸ is sufficient to oxidize U^{V} , for which the $\text{U}^{\text{VI/V}}$ reduction potential is +0.09 V, but is not adequate to oxidize An^{V} with reduction potentials of ca. 1 eV higher.

The results upon the introduction of NO_2 into the ion trap and reaction with the three $\text{An}^{\text{V}}\text{O}_2(\text{CH}_3\text{CO}_2)_2^-$ are shown in Figure 2. For all three of the complexes, reaction 2 is dominant.

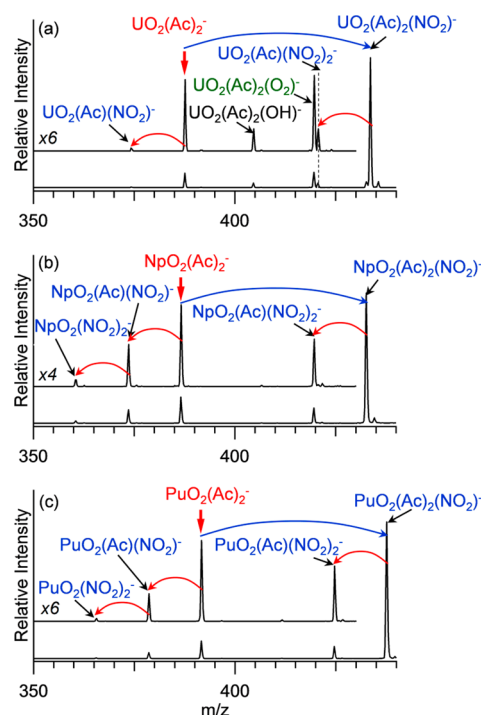
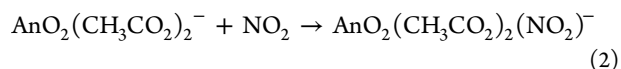


Figure 2. Mass spectra after exposure of $\text{An}^{\text{V}}\text{O}_2(\text{Ac})_2^-$ ($\text{Ac} = \text{CH}_3\text{CO}_2$) to the same NO_2 pressure for 100 ms: (a) $\text{An} = \text{U}$; (b) $\text{An} = \text{Np}$; (c) $\text{An} = \text{Pu}$. In each case, the dominant reaction is the addition of NO_2 to produce $\text{An}^{\text{VI}}(\text{CH}_3\text{CO}_2)_2(\text{NO}_2)^-$ (blue arrows). Replacement of CH_3CO_2 by NO_2 is also apparent (red arrows). For $\text{An} = \text{U}$, additional minor products result from O_2 addition and hydrolysis.

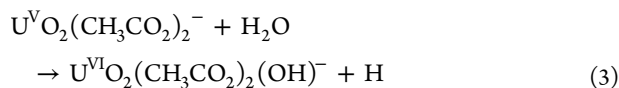
The efficiency of reaction 2 is similar for $\text{An} = \text{U}, \text{Np},$ and Pu , as expected for addition reactions that do not exhibit substantial transition-state barriers.



The concentration of NO_2 (and other reactant gases) in the trap is many orders of magnitude greater than that of reactant ions, which is minuscule, such that the gas pressure can be

considered to be constant, with reaction 2 exhibiting pseudo-first-order kinetics. The similarities of the reaction rates, as inferred from Figure 2, suggest that the differing sizes of the actinides, due to actinide contraction, do not have a significant effect on the addition efficiencies. In a previous computational study, it was shown that the propensity for $U^V O_2^+$ to add oxygen to yield $U^{VI} O_2(O_2)^+$, whereas $Np^V O_2^+$ does not, is due to electronic factors, not a steric hindrance for the latter.²⁴ Given that the ionic radius of Np^{5+} , 0.75 Å, is only 0.01 Å smaller than that of U^{5+} , 0.76 Å,³⁹ it is unsurprising that steric effects should not substantially affect this chemistry. The proposed schematic structure for the product of reaction 2 is shown in Figure 1b. Neutral NO_2 has a gas basicity (GB) of only 560 kJ/mol, significantly lower than that of H_2O (GB = 660 kJ/mol).⁴⁰ Given that hydrates are not observed under these experimental conditions, it is improbable that the NO_2 moiety in $AnO_2(CH_3CO_2)_2(NO_2)^-$ is a weakly bound neutral ligand. Instead, we propose that it can be represented as a nitrite, NO_2^- , such that oxidation from An^V to An^{VI} has occurred. This interpretation is substantiated by the replacement of $CH_3CO_2^-$ by NO_2^- . The products of these replacement reactions, $AnO_2(CH_3CO_2)(NO_2)_2^-$ and $AnO_2(NO_3)_2^-$, are apparent in Figure 2; this substitution phenomenon is validated below.

As is apparent in Figure 2a, for $UO_2(CH_3CO_2)_2^-$, the hydrolysis reaction (3) with background water in the ion trap is observed, along with reactions (1) and (2).



Reaction (3) is another manifestation of the higher stability of U^{VI} compared with Np^{VI} and Pu^{VI} . The absence of hydrates in the presence of hydrolysis, which requires association of a water molecule to the metal center, suggests that the electrostatic interaction between water and the metal center is too weak to induce binding under these experimental conditions. This is consistent with the interpretation that the NO_2 ligand in $An^{VI} O_2(CH_3CO_2)_2(NO_2)^-$ is not an electrostatically bound neutral but rather an anion.

Replacement of $CH_3CO_2^-$ by NO_2^- . In Figure 3, it is seen that isolation of $AnO_2(CH_3CO_2)_2(NO_2)^-$ in the presence of NO_2 results in the sequential replacement of both of the $CH_3CO_2^-$ ligands to yield $AnO_2(NO_3)_3^-$. In Figure 4, it is apparent that this replacement similarly occurs for $AnO_2(CH_3CO_2)_3^-$. The results in Figure 5 demonstrate that NO_2^- replaces both O_2^- and $CH_3CO_2^-$ in $UO_2(CH_3CO_2)_2(O_2)^-$. The replacement of anionic $CH_3CO_2^-$ and O_2^- ligands by NO_2^- provides convincing evidence that the NO_2 ligands in these complexes are also anionic, i.e., NO_2^- , and that the addition of NO_2 to $An^V O_2(CH_3CO_2)_2^-$ results in oxidation to produce $An^{VI}(CH_3CO_2)_2(NO_2)^-$.

It is apparent from Figures 3 and 4 that the replacement of $CH_3CO_2^-$ by NO_2^- is more facile for $NpO_2(CH_3CO_2)_3^-$ and $PuO_2(CH_3CO_2)_3^-$ than for $UO_2(CH_3CO_2)_3^-$. This conclusion is evident from the relative yields of the replacement products relative to the remaining reactant ion: compared with the corresponding neptunium and plutonium complexes, both $UO_2(Ac)_2(NO_2)^-$ (Figure 3) and $UO_2(Ac)_3^-$ (Figure 4) are less depleted relative to the exchange products under the same conditions. Temporal evolution of the reactants and products (Supporting Information, Figures S2 and S3) also shows the

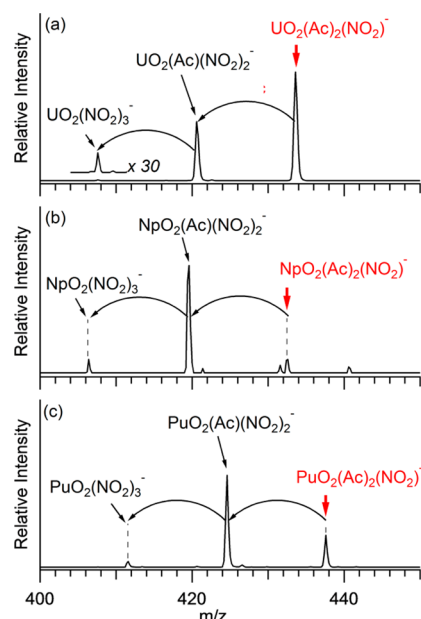


Figure 3. Mass spectra after exposure of $AnO_2(Ac)_2(NO_2)^-$ ($Ac = CH_3CO_2$) to the same NO_2 pressure for 6 s: (a) $An = U$; (b) $An = Np$; (c) $An = Pu$. Replacement of Ac by NO_2 produced $AnO_2(Ac)(NO_2)_2^-$ and $AnO_2(NO_3)_3^-$. Acetate replacement by NO_2 is attributed to a metathesis reaction with HNO_2 (see the text).

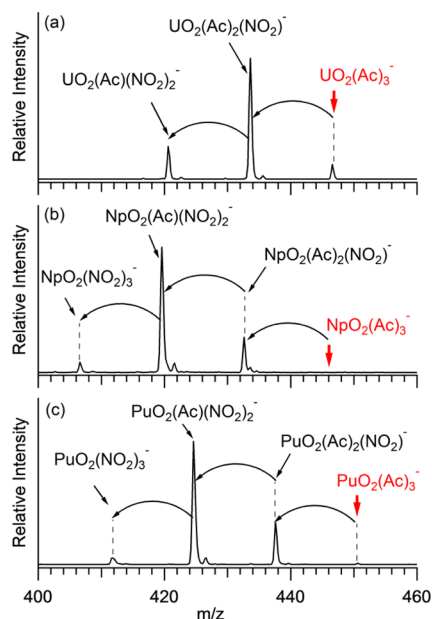


Figure 4. Mass spectra after exposure of $An^{VI} O_2(Ac)_3^-$ ($Ac = CH_3CO_2$) to the same NO_2 pressure for 10 s: (a) $An = U$; (b) $An = Np$; (c) $An = Pu$. Replacement of CH_3CO_2 by NO_2 produced $AnO_2(CH_3CO_2)_2(NO_2)^-$, $AnO_2(CH_3CO_2)(NO_2)_2^-$, and $AnO_2(NO_3)_3^-$ for $An = Np$ and Pu . Acetate replacement by NO_2 is attributed to a reaction with HNO_2 (see the text).

more rapid exchange for the neptunium and plutonium complexes. This greater resistance toward displacement may be related to the higher redox stability of uranyl(VI), which could result in a higher-energy intermediate state during replacement of CH_3CO_2 by NO_2 . In particular, a manifestation of the substantially lower reduction potential of $U^V O_2^+$ versus $Np^V O_2^+/PuO_2^+$ would be less charge transfer from an electron-donating ligand, such as an acetate anion, to uranyl(VI),

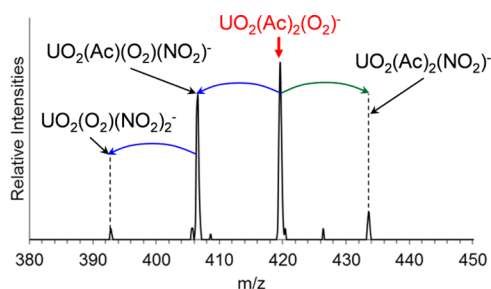
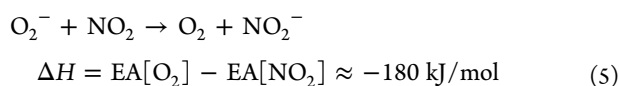
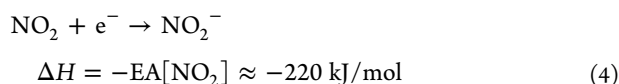


Figure 5. Mass spectra after exposure of $\text{UO}_2(\text{Ac})_2(\text{O}_2)^-$ ($\text{Ac} = \text{CH}_3\text{CO}_2$) to NO_2 for 5 s. Replacement of CH_3CO_2 (blue arrows) was dominant; replacement of O_2 by NO_2 was less prominent (green arrow). The predominance of the replacement of CH_3CO_2 by NO_2 provides evidence for the proposed acid metathesis reaction.

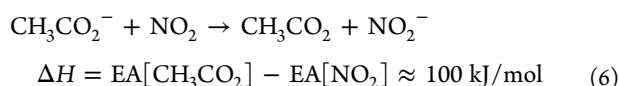
resulting in more ionic (less covalent) bonding compared with the corresponding neptunyl(VI) and plutonyl(VI) complexes. The less efficient exchange reactions for uranyl(VI) suggest that the more ionic uranyl(VI)–ligand bond is more resistant to cleavage. As remarked above, the ability of NO_2 to oxidize Np^{V} and Pu^{V} , whereas O_2 does not, may be related to the greater EA of NO_2 , 2.3 eV,²⁷ versus that of O_2 , 0.4 eV;²⁸ a neutral with a greater EA should act as a more effective electron-withdrawing oxidant. The VI/V reduction potentials of neptunium and plutonium are 1.16 and 0.94 eV,²⁵ respectively, whereas the EA of NO_2 is greater than that of O_2 by 1.9 eV; on the basis of these relationships, oxidation of Np^{V} and Pu^{V} by NO_2 but not O_2 is reasonable. It is also reasonable that NO_2 should exothermically displace O_2 in $\text{UO}_2(\text{CH}_3\text{CO}_2)_2(\text{O}_2)^-$.

The concept of oxidation occurring by electron transfer from a metal center to a ligand is represented by reaction (4) and that by ligand displacement by reaction (5).



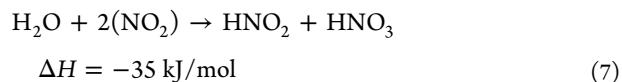
In a superoxide, there is bonding between the O atoms and the metal such that the O_2 ligand is not strictly represented as O_2^- ,¹³ although this is fundamentally its nature.⁴¹ Similarly, the interaction between NO_2 and a metal atom is not purely ionic, and the ligand is not precisely described as bare NO_2^- . Nonetheless, the EA of a neutral, and its propensity to become anionic such as by the formation of an acid by reaction with water, provides an indication of its capacity to oxidize by electron withdrawal.

Less explicable than the replacement of O_2 by NO_2 is the replacement of CH_3CO_2 ($\text{EA} = 3.3 \text{ eV}^{42}$) by NO_2 , which has a significantly lower EA (2.3 eV). Considering these ligands as anionic, the direct replacement reaction would formally correspond to reaction (6).

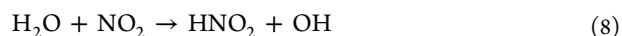


That CH_3CO_2 , with a higher EA, should be more strongly bound to the actinyl(VI) moieties than NO_2 is borne out by the CID spectra for $\text{NpO}_2(\text{CH}_3\text{CO}_2)_2(\text{NO}_2)^-$ and $\text{PuO}_2(\text{CH}_3\text{CO}_2)_2(\text{NO}_2)^-$ (Figures S4 and S5): the dominant pathway is loss of NO_2 .

As has been discussed by others,^{29–31} because of the presence of residual water in vacuum systems, it is impractical to prevent partial hydrolysis of NO_2 gas to produce HNO_2 and HNO_3 according to reaction (7).

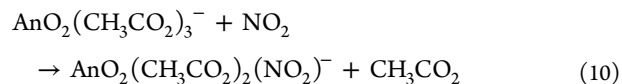
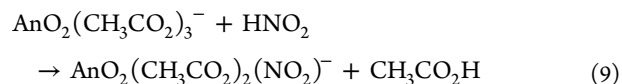


Evidence for the presence of HNO_2 in the ion trap is provided by the addition of HNO_2 to $\text{PuO}(\text{NO}_3)_3^-$ under essentially the same experimental conditions as those employed in the present work (Figure S6). At the low pressures in the ion trap, termolecular reaction (7) is unlikely; instead, this reaction would more likely to occur between NO_2 and water adsorbed on the interior of the ion trap. This is substantiated by the persistence of HNO_2 for extended periods (weeks) in the ion trap after volatile NO_2 has been removed; this persistence is monitored, for example, by the $\text{PuO}(\text{NO}_3)_3^-$ addition reaction noted above (Figure S6). Notably, there was no evidence for HNO_3 in the gas phase, which could result in the replacement of CH_3COO^- by NO_3^- . An explanation for this is that the very strong acid HNO_3 reacts with the surfaces of the ion trap and is not present at an appreciable concentration in the gas phase; HNO_2 is a much weaker acid ($\text{p}K_{\text{a}} = 3.37^{43}$) such that it can remain intact and desorb from the trap surfaces. An alternative to reaction (7) is reaction (8) on the metallic surfaces of the ion trap.

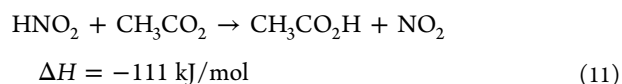


Although reaction (8) is endothermic by 168 kJ/mol in the gas phase,³⁸ the energy of adsorption or reaction of the hydroxyl product with a metallic surface could render it exothermic. Such a surface reaction would also account for the persistence of adsorbed HNO_2 for extended periods.

The presence of HNO_2 in the ion trap allows reaction (9) to occur, rather than the direct replacement of CH_3CO_2 by NO_2 [reaction (10)].

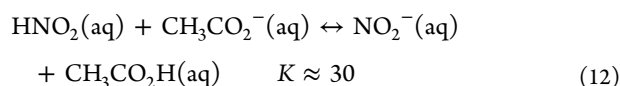


Whereas reaction (10) should be endothermic because of the greater EA of CH_3COO^- versus NO_2 [reaction (6)], reaction (9) could be enabled by the exothermicity of metathesis reaction (11). The exothermicity of reaction (11) is slightly greater than the endothermicity of reaction (6) such that reaction (10) should be endothermic, while reaction (9) should be exothermic, by ca. 10 kJ/mol, so that it can occur spontaneously.³⁸



In the case of $\text{UO}_2(\text{CH}_3\text{CO}_2)_2(\text{O}_2)^-$ (Figure 5), the more facile replacement of CH_3CO_2^- than O_2^- is consistent with reaction (9); the O_2^- ligand should be more susceptible to replacement by NO_2 than CH_3CO_2^- by NO_2 if it were a direct substitution such as in eq 10. If reaction (9) is responsible for the observed exchange, then the exchange kinetics would allow an evaluation

of the pressure of HNO₂ in the trap if the rate constant for reaction (9) were known or could be estimated as efficient. However, the different kinetics for the uranium, neptunium, and plutonium complexes (Figure 4 and Figure S3) indicate that the reactions are not necessarily efficient and that a rate constant cannot be assumed. It would be desirable to probe the reversibility of reaction (9) and other proposed reactions, but it is not practical to introduce gaseous acetic acid into the ion trap in a controlled manner to perform these experiments; it is the production of HNO₂ by the reaction of NO₂ with H₂O in the trap that enables reaction (9). The aqueous solution properties of HNO₂ (pK_a = 3.37) and CH₃CO₂H (pK_a = 4.75)⁴³ are in correspondence with the gas-phase behavior. Given that HNO₂ is a stronger acid than CH₃CO₂H, the equilibrium constant for reaction (12) (K ≈ 30) indicates that the formation of NO₂⁻(aq) is more favorable than the formation of CH₃CO₂⁻(aq).⁴³



A key point is that, regardless of the reaction that results in the substitution of CH₃CO₂⁻ by NO₂⁻, the formation of AnO₂(NO₂)₃⁻ from AnO₂(CH₃CO₂)₂(NO₂)⁻ and AnO₂(CH₃CO₂)₃⁻ provides evidence that NO₂ in these complexes is an anionic ligand that is comparable to the anionic CH₃CO₂ ligands that coordinate to the actinyl cores. This characterization as a nitrite anion, NO₂⁻, establishes that the addition of neutral NO₂ to An^VO₂(CH₃CO₂)₂⁻ corresponds to oxidation to An^{VI}O₂(CH₃CO₂)₂(NO₂)⁻. The acetate replacement results demonstrate that the NO₂ ligands are nitrite, NO₂⁻, in all of the complexes and that the addition of NO₂ to the actinyl(V) complexes results in the reduction to NO₂⁻ concomitant with oxidation to actinyl(VI). The results effectively exclude the alternative possibility that the NO₂ addition products are merely electrostatically bound adducts with no change in the oxidation state of the actinides. Further evidence for the exclusion of adduct formation is that, despite relatively abundant water in the ion trap, there was never any evidence for hydrates or any other adducts. As remarked above, such adducts are too weakly bound to be observed under these experimental conditions. The CID results below provide additional evidence that these are not weakly bound NO₂ adducts.

CID of AnO₂(CH₃CO₂)₂(NO₂)⁻. CID was performed for AnO₂(CH₃CO₂)₂(NO₂)⁻ produced by the gas-phase addition of NO₂ to AnO₂(CH₃CO₂)₂⁻ and by ESI of a solution containing CH₃CO₂⁻ and NO₂⁻. The CID spectra for the gas-phase addition products are shown in Figure S4 and that for the ESI product in Figure S5. The AnO₂(CH₃CO₂)₂(NO₂)⁻ complexes produced by ESI of solutions containing acetate and nitrite anions are irrefutably actinyl(VI) coordinated by two CH₃CO₂⁻ ligands and one NO₂⁻ ligand. If the complex produced by the gas-phase addition of NO₂ also contains NO₂⁻, then the CID behavior should be similar. Indeed, their CID results both show that the dominant fragmentation pathway is elimination of NO₂ for An = Np and Pu (the CID spectra for the uranyl species are more complex). This result reveals that NO₂⁻ is more weakly bound to actinyls than CH₃CO₂⁻, which is in accord with the comparative EAs. A complication in directly comparing the CID spectra of AnO₂(CH₃CO₂)₂(NO₂)⁻ produced by ESI of NO₂⁻ solutions with those for AnO₂(CH₃CO₂)₂(NO₂)⁻ produced by gas-phase

NO₂ addition is the presence of NO₂ in the ion trap during the latter CID process. A discussion of these results can be found in the Supporting Information. The key result of the CID experiments is that there is no striking difference between the CID spectra for the AnO₂(CH₃CO₂)₂(NO₂)⁻ complexes produced by gas-phase addition and by nitrite ESI, which supports the assignment of nitrite ligands in both.

CONCLUSIONS

Whereas U^V is oxidized to U^{VI} by the addition of O₂ to produce superoxides, the analogous oxidation is not observed for Np^V or Pu^V. This disparity is attributed to the substantially higher VI/V reduction potentials for neptunium and plutonium, which renders oxidation by O₂ addition thermodynamically unfavorable. It was surmised that NO₂ might be a better electron-withdrawing oxidant than O₂ based on its greater EA and its propensity to hydrolyze and produce a NO₂⁻ anion in nitrous acid. It was found that NO₂ associates with uranyl(V), neptunyl(V), and plutonyl(V) carboxylate complexes to yield An^{VI}O₂(CH₃CO₂)₂(NO₂)⁻ (An = U, Np, Pu) in which oxidation of An^V to An^{VI} is achieved by the reduction of NO₂ to NO₂⁻. The nature of the nitrite ligand as an anion was substantiated by the replacement of CH₃CO₂⁻ by NO₂⁻; this remarkable ligand displacement phenomenon is attributed to a metathesis reaction with HNO₂ to produce CH₃CO₂H. The oxidation of Np^V and Pu^V establishes that NO₂ is a more effective electron-withdrawing oxidant than O₂.

The present results demonstrate an unusual gas-phase addition reaction that results in conversion of a neutral molecule to a formally anionic ligand concomitant with oxidation of the coordinated metal center. Although the experimental results are conclusive, it would certainly be desirable to computationally characterize the nature of the NO₂ addition products, a challenging undertaking that is beyond the scope of this purely experimental study. This distinctive behavior of NO₂ reflects the important and complex oxidation/reduction chemistry of nitrogen oxides with varying compositions and charge states. This work suggests that other gases with high EAs may be capable of acting as electron-withdrawing metal oxidants.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01385.

Mass spectra for reactions of AnO₂(CH₃CO₂)₂⁻ with background gases in the ion trap, CID mass spectra of AnO₂(CH₃CO₂)₂(NO₂)⁻ produced by the gas-phase addition of NO₂ to AnO₂(CH₃CO₂)₂⁻ and by ESI (An = U, Np, Pu), a discussion of the CID results, plots showing the temporal evolution for reactions with HNO₂, and a mass spectrum showing the addition of HNO₂ to PuO(NO₃)₃⁻ (PDF) (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Morse, J. W.; Choppin, G. R. *Rev. Aquat. Sci.* **1991**, *4*, 1.
- (2) Silva, R. J.; Nitsche, H. *Radiochim. Acta* **1995**, *70–71*, 377.
- (3) Denning, R. G. *Struct. Bonding (Berlin)* **1992**, *79*, 215.
- (4) Denning, R. G. *J. Phys. Chem. A* **2007**, *111*, 4125.
- (5) McGlynn, S. P.; Smith, J. K. *J. Mol. Spectrosc.* **1961**, *6*, 188.
- (6) McGlynn, S. P.; Smith, J. K. *J. Mol. Spectrosc.* **1961**, *6*, 164.
- (7) Pepper, M.; Bursten, B. E. *Chem. Rev.* **1991**, *91*, 719.
- (8) Straka, M.; Dyall, K. G.; Pyykkö, P. *Theor. Chem. Acc.* **2001**, *106*, 393.
- (9) Su, J.; Zhang, K.; Schwarz, W. H. E.; Li, J. *Inorg. Chem.* **2011**, *50*, 2082.
- (10) Dau, P. D.; Su, J.; Liu, H. T.; Huang, D. L.; Li, J.; Wang, L. S. *J. Chem. Phys.* **2012**, *137*, 064315.
- (11) Dau, P. D.; Su, J.; Liu, H. T.; Liu, J. B.; Huang, D. L.; Li, J.; Wang, L. S. *Chemical Science* **2012**, *3*, 1137.
- (12) Su, J.; Dau, P. D.; Qiu, Y. H.; Liu, H. T.; Xu, C. F.; Huang, D. L.; Wang, L. S.; Li, J. *Inorg. Chem.* **2013**, *52*, 6617.
- (13) Bryantsev, V. S.; de Jong, W. A.; Cossel, K. C.; Diallo, M. S.; Goddard, W. A.; Groenewold, G. S.; Chien, W.; Van Stipdonk, M. J. *J. Phys. Chem. A* **2008**, *112*, 5777.
- (14) Alcock, N. W. *J. Chem. Soc. A* **1968**, 1588.
- (15) Kubatko, K. A. H.; Helean, K. B.; Navrotsky, A.; Burns, P. C. *Science* **2003**, *302*, 1191.
- (16) Westland, A. D.; Tarafder, M. T. H. *Inorg. Chem.* **1981**, *20*, 3992.
- (17) Charpin, P. P.; Lance, M.; Soulie, E.; Vigner, D. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *41*, 884.
- (18) Bhattacharjee, M.; Chaudhuri, M. K.; Purkayastha, R. N. D. *Inorg. Chem.* **1986**, *25*, 2354.
- (19) Rose, D.; Chang, Y. D.; Chen, Q.; Zubieta, J. *Inorg. Chem.* **1994**, *33*, 5167.
- (20) Thuéry, P.; Nierlich, M.; Baldwin, B. W.; Komatsuzaki, N.; Hirose, T. *J. Chem. Soc., Dalton Trans.* **1999**, 1047.
- (21) Thuéry, P.; Masci, B. *Supramol. Chem.* **2003**, *15*, 95.
- (22) Groenewold, G. S.; Cossel, K. C.; Gresham, G. L.; Gianotto, A. K.; Appelhans, A. D.; Olson, J. E.; Van Stipdonk, M. J.; Chien, W. J. *Am. Chem. Soc.* **2006**, *128*, 3075.
- (23) Leavitt, C. M.; Bryantsev, V. S.; de Jong, W. A.; Diallo, M. S.; Goddard, W. A., III; Groenewold, G. S.; Van Stipdonk, M. J. *J. Phys. Chem. A* **2009**, *113*, 2350.
- (24) Rios, D.; Michelini, M. C.; Lucena, A. F.; Marçalo, J.; Bray, T. H.; Gibson, J. K. *Inorg. Chem.* **2012**, *51*, 6603.
- (25) Konings, R. J. M.; Morss, L. R.; Fuger, J. *The Chemistry of the Actinide and Transactinide Elements*, 3rd ed.; Springer: Dordrecht, The Netherlands, 2006; Vol. 4.
- (26) Ricks, A. M.; Gagliardi, L.; Duncan, M. A. *J. Am. Chem. Soc.* **2010**, *132*, 15905.
- (27) Ervin, K. M.; Ho, J.; Lineberger, W. C. *J. Phys. Chem.* **1988**, *92*, 5405.
- (28) Ervin, K. M.; Anusiewicz, W.; Skurski, P.; Simons, J.; Lineberger, W. C. *J. Phys. Chem. A* **2003**, *107*, 8521.
- (29) Heinemann, C.; Cornehl, H. H.; Schröder, D.; Dolg, M.; Schwarz, H. *Inorg. Chem.* **1996**, *35*, 2463.
- (30) Kim, S. K.; Kang, H. *J. Phys. Chem. Lett.* **2010**, *1*, 3085.
- (31) Jarvis, M. J. Y.; Blagojevic, V.; Koyanagi, G. K.; Bohme, D. K. *J. Phys. Chem. Chem. Phys.* **2010**, *12*, 4852.
- (32) Gibson, J. K.; Haire, R. G.; Santos, M.; Marçalo, J.; Pires de Matos, A. *J. Phys. Chem. A* **2005**, *109*, 2768.
- (33) Lucena, A. F.; Carretas, J. M.; Marçalo, J.; Michelini, M. C.; Gong, Y.; Gibson, J. K. *J. Phys. Chem. A* **2015**, *119*, 3628.
- (34) Gong, Y.; Gibson, J. K. *J. Phys. Chem. A* **2013**, *117*, 783.
- (35) Rios, D.; Rutkowski, P. X.; Shuh, D. K.; Bray, T. H.; Gibson, J. K.; Van Stipdonk, M. J. *J. Mass Spectrom.* **2011**, *46*, 1247.
- (36) Gronert, S. *J. Am. Soc. Mass Spectrom.* **1998**, *9*, 845.
- (37) Rutkowski, P. X.; Michelini, M. C.; Bray, T. H.; Russo, N.; Marçalo, J.; Gibson, J. K. *Theor. Chem. Acc.* **2011**, *129*, 575.
- (38) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1.
- (39) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.* **1976**, *32*, 751.
- (40) Linstrom, P. J.; Mallard, W. G. *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; National Institute of Standards and Technology: Gaithersburg, MD, 2015.
- (41) Huang, W.; Xu, W. H.; Su, J.; Schwarz, W. H. E.; Li, J. *Inorg. Chem.* **2013**, *52*, 14237.
- (42) Wang, X. B.; Woo, H. K.; Wang, L. S.; Minofar, B.; Jungwirth, P. *J. Phys. Chem. A* **2006**, *110*, 5047.
- (43) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 71st ed.; CRC Press: Boca Raton, FL, 1991.