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Oxidation Studies of Dipositive Actinide Ions, An^{2+} (An = Th, U, Np, Pu, Am) in the Gas Phase: Synthesis and Characterization of the Isolated Uranyl, Neptunyl, and Plutonyl Ions $UO_2^{2+}(g)$, $NpO_2^{2+}(g)$, and $PuO_2^{2+}(g)$

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Reactions of atomic and ligated dipositive actinide ions, An^{2+}, AnO^{2+}, $AnOH^{2+}$, and AnO_2^{2+} (An = Th, U, Np, Pu, Am) were systematically studied by Fourier transform ion cyclotron resonance mass spectrometry. Kinetics were measured for reactions with the oxidants, N_2O, C_2H_4O (ethylene oxide), H_2O, O_2, CO_2, NO, and CH_2O. Each of the five An^{2+} ions reacted with one or more of these oxidants to produce AnO^{2+}, and reacted with H_2O to produce $AnOH^{2+}$. The measured pseudo-first-order reaction rate constants, k, revealed disparate reaction efficiencies, k/k_{COL}: Th^{2+} was generally the most reactive and Am^{2+} the least. Whereas each oxidant reacted with Th^{2+} to give ThO^{2+}, only C_2H_4O oxidized Am^{2+} to AmO^{2+}. The other An^{2+} exhibited intermediate reactivities. Based on the oxidation reactions, bond energies and formation enthalpies were derived for the AnO^{2+}, as were second ionization energies for the monoxides, IE[AnO^+]. The bare dipositive actinyl ions, UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+}, were produced from the oxidation of the corresponding AnO^{2+} by N_2O, and by O_2 in the cases of UO^{2+} and NpO^{2+}. Thermodynamic properties were derived for these three actinyls, including enthalpies of formation and electron affinities. It is concluded that bare UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+} are thermodynamically stable toward Coulomb dissociation to $\{AnO^+ + O^+\}$ or $\{An^+ + O_2^+\}$. It is predicted that bare AmO_2^{2+} is thermodynamically stable. In accord with the expected instability of Th(VI), ThO^{2+} was not oxidized to ThO_2^{2+} by any of the seven oxidants. The gas-phase results are compared with the aqueous thermochemistry. Hydration enthalpies were derived here for uranyl and plutonyl; our $\Delta H_{hyd}[UO_2^{2+}]$ is substantially more negative than the previously reported value, but is essentially the same as our $\Delta H_{hyd}[PuO_2^{2+}]$.

Introduction

Former detailed studies of the gas-phase chemistry of actinide ions have largely focused on naturally occurring Th and U, with the particular emphasis being on the latter.[1−10] The ability to examine highly radioactive actinides has enabled the extension of such studies to higher members of the series.[11] Recently, detailed quantitative investigations of gas-phase actinide ion chemistry have been performed by Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS). These first transuranic studies were performed with Np^+,[12] Pu^+,[12] and Am^+,[13] with an emphasis placed on oxidation and electron-transfer reactions. The FTICR-MS experiments have provided fundamental and essential thermodynamic quantities, such as bond energies and ionization energies for elementary actinide oxide molecules, specifically AnO and AnO_2 (An = Th, U, Np, Pu, Am). Substantial corrections to key properties have resulted from these new studies. The initial transuranic FTICR-MS studies[12,13] demonstrated the value of this technique for determining fundamental aspects of actinide chemistry and accurately established critical properties of elementary actinide molecules.

In aqueous chemistry, the only monopositive actinide ions normally encountered are the dioxo ions, UO_2^+(aq), NpO_2^+(aq), PuO_2^+(aq), and AmO_2^+(aq),[14] and all four of these have also been prepared as bare gas-phase ions.[3,12,13] Although the AnO_2^+ can be found in aqueous solutions, the dipositive actinyl ions, AnO_2^{2+}, are particularly important in the chemistry of U, Np, Pu, and Am.[14−19] Uranyl, neptunyl, plutonyl, and americyl are hexavalent actinide species of varying stability that are found in solution, and many properties of these actinyls have been studied extensively.[14−19] To fully understand the nature of such species, it is imperative to have information for the bare species unperturbed by coordination. The first synthesis of the bare uranyl dipositive ion, UO_2^{2+}, was carried out previously under FTICR-MS conditions similar to those employed in the present study.[6] The stability of bare UO_2^{2+} and the second ionization energy of the dioxide, IE[UO_2^+] (i.e., the electron affinity of UO_2^{2+}), were estimated based on the exothermicity of oxidation and electron-transfer reactions.[6]

A central goal of the present studies was to investigate dipositive ions of Np, Pu, and Am. Among the fundamental issues are the intrinsic stabilities of gas-phase actinyl dipositive ions free from stabilization afforded by bonding interactions with solvent or coordinating molecules and/or counterions, such as occur in the condensed phase. For example, the reported enthalpy of hydration of UO_2^{2+} is −1345 kJ mol^{-1}, which is comparable to the hydration enthalpy of U^{2+}.[20] Given the substantial coordination energies acquired in condensed-phase environments, it is not a priori evident that actinyls stable in liquids or solids will exist as isolated gaseous species. Specif-

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ically, a bare dipositive AnO_2^{2+} may be intrinsically unstable with regard to Coulombic dissociation to two monopositive ions, $\{AnO^+ + O^+\}$ or $\{An^+ + O_2^+\}$.[6,21] The aqueous actinyl ions become progressively less stable upon proceeding across the grouping: $UO_2^{2+}(aq) > NpO_2^{2+}(aq) \approx PuO_2^{2+}(aq) > AmO_2^{2+}(aq)$.[14,19] This trend is a manifestation of the decreasing stability of the hexavalent oxidation state upon proceeding from U to Am, as well as the particular stability of Np(V). A similar trend in stability is exhibited in the solid state. For example, the four uranyl halides, $UO_2X_2(s)$ (X = F, Cl, Br, I), have been reported[15] whereas only $AmO_2F_2(s)$ is known to exist.[18] Accordingly, the demonstrated stability of bare UO_2^{2+} [6] does not necessarily imply that the bare transuranic NpO_2^{2+}, PuO_2^{2+}, and/or AmO_2^{2+} ions are thermodynamically stable species.

In the work reported here, reactions of Th^{2+}, U^{2+}, Np^{2+}, Pu^{2+}, and Am^{2+}, with several oxidants (N_2O, C_2H_4O (ethylene oxide), H_2O, O_2, CO_2, NO, and CH_2O) were studied by FTICR-MS. The kinetics of formation of the primary AnO^{2+} and, in some cases, secondary AnO_2^{2+} ions were measured and are evaluated in the context of bond energies, ionization energies, and formation enthalpies. Reactions of the An^{2+} with H_2O additionally produced dipositive hydroxide ions. Except for a few reactions of bare and ligated U^{2+},[6,9] these gas-phase oxidation reactions have not been studied previously. The ionization energies of the monopositive dioxides, $IE[AnO_2^+]$ (An = U, Np, Pu), were determined via electron-transfer reactions from selected neutral reagents to AnO_2^{2+}. The intrinsic stabilities of the three bare AnO_2^{2+} against dissociation into two singly charged ions are also evaluated. Comparisons are made with the previous data for gas-phase U^{2+} chemistry, with theoretical results for uranium species, and with aqueous actinide ion chemistries. New thermodynamic properties are reported for several key actinide species, including hydration enthalpies for UO_2^{2+} and PuO_2^{2+}. Due to the paucity of accurate gas-phase thermodynamic data for actinide species, we try to acquire as much information as possible from the experimental results that, in some cases and to some extent, may correspond to making somewhat rudimentary assumptions in the thermochemical evaluations.

Experimental Section

The experiments were performed in a Finnigan FT/MS 2001-DT FTICR mass spectrometer, equipped with a 3 T superconducting magnet, and controlled by a Finnigan Venus Odyssey data system. The instrument incorporates a Spectra-Physics Quanta-Ray GCR-11 Nd:YAG laser operated at the fundamental wavelength (1064 nm) for direct laser desorption/ionization (LDI) of solid samples into the ICR cell.

The actinide samples were binary alloys of the actinide (An) metal in a Pt matrix. These alloys were prepared by arc melting the An metal and Pt in water-cooled copper crucibles under Ti-gettered high-purity argon. The amounts of the An used ranged from ~2 mg of Am, to ~6 mg of Np and Pu, to >20 mg of Th and U. The resulting alloy compositions (mol percent) were ~2% Am, ~5% Np and Pu, and ~20% Th and U. Employing dilute alloys in a robust Pt matrix enabled use of relatively large samples while reducing the quantities of the An, the potential for oxidation of the actinides, and the transfer of An material during handling and in the FTICR-MS instrument. The isotopes employed and their alpha-decay half-lives ($t_{1/2}$) were: natural Th-232, $t_{1/2} = 1.4 \times 10^{10}$ y; depleted U, 99.8% U-238, $t_{1/2} = 4.5 \times 10^9$ y (0.2% U-235, $t_{1/2} = 7.0 \times 10^8$ y); Np-237, $t_{1/2} = 2.1 \times 10^6$ y; Pu-242, $t_{1/2} = 3.8 \times 10^5$ y; and Am-243, $t_{1/2} = 7.4 \times 10^3$ y. The comparative half-lives indicate the need to minimize quantities of the shorter-lived higher transuranics.

The metal samples employed for the electron-transfer calibration experiments were unalloyed pieces of high-purity Mn, Ge, Sn, Pb, and Bi. The reagent gases, N_2O, O_2, CO_2, and NO, were commercial products (>99% purity) and were used as supplied. The C_2H_4O was also a commercial product (>99% purity) and was degassed prior to use. The H_2O was thoroughly deoxygenated by bubbling it with high-purity N_2, and then degassing by freeze-evacuation-thaw cycles. Dry, gaseous CH_2O was prepared from a commercial aqueous solution according to a literature procedure.[22]

The reagents were introduced into the spectrometer through a leak valve to pressures in the range of 3×10^{-8} to 2×10^{-7} Torr, and their purities were confirmed by electron ionization mass spectra. The neutral reagent pressures measured with a Bayard−Alpert type ionization gauge were calibrated using standard reactions of methane[23] and acetone[24] ions. The gauge readings were corrected for the relative sensitivities of the different reagents according to the approach of Bartmess and Georgiadis[25] using experimental molecular polarizabilities.[26]

Actinide metal ions were produced in the FTICR-MS by LDI of the alloy samples mounted on the solids probe and inserted into the instrument such that the desorbed ions directly entered the ICR source cell. All reactions, ion manipulations, and analyses were performed in the source cell of the dual-cell FTICR-MS. The same procedure was employed for the pure metals used in the electron-transfer calibration measurements. By increasing the laser irradiance it was possible to produce substantial amounts of doubly ionized metal ions. The facile production of An^{2+} is largely attributed to the relatively small sum of the first two ionization energies, $\{IE[An] + IE[An^+]\}$, which are ~18 eV (1 eV = 96.4853 kJ mol^{-1}) for the five An.[19] Although the $\{IE[M] + IE[M^+]\}$ for the calibration metals range from 22.0 eV (Sn) to 24.0 eV (Bi),[26] it was possible to generate sufficient M^{2+} by LDI to measure electron-transfer rates. Isolation of the An^{2+} and the calibration M^{2+} ions was achieved using single-frequency, frequency-sweep, or SWIFT excitation.[27] The actinide oxide and hydroxide ions, AnO^{2+}, AnO_2^{2+} or $AnOH^{2+}$, when formed in sufficient amounts with a particular reagent, were also isolated using single-frequency, frequency-sweep, or SWIFT excitation. In some cases, the actinide oxide ions were produced by reaction of the An^{2+} with N_2O introduced into the spectrometer through pulsed valves, to study their subsequent reactions with other reagents. In a few cases, due to their low yields, the actinide oxide or hydroxide ions could not be isolated and double-resonance experiments were conducted to uncover the reaction sequences.

The reactant ions were thermalized by collisions with argon, which was introduced into the spectrometer through pulsed valves to pressures of ~10^{-5} Torr, or through a leak valve to a constant pressure in the range of $(1-5) \times 10^{-6}$ Torr. The reproducibility of the reaction kinetics, as well as the linearity of semilog plots of normalized reactant ion intensities versus time, indicated thermalization of the reactant ions. When there was more than one product ion, consistent product distributions for different collisional cooling periods or collision gas pressures also indicated that effective thermalization had been achieved. Another indication of the effectiveness of the thermalization procedure was the absence of the electron-transfer channel in the reactions of An^{2+} ions in which it was not expected to occur.

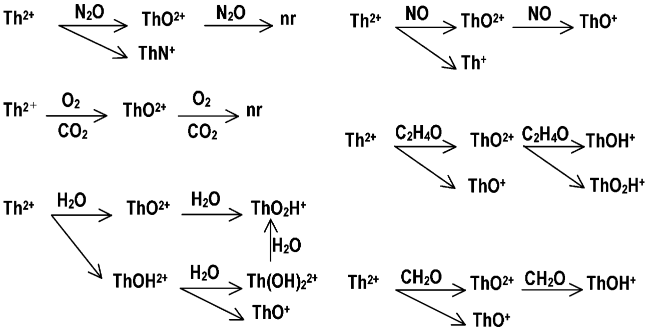
It is well-known that laser-ablated metal ions are produced with excess kinetic energies and can also be formed in electronically excited states.[28] In the actinides, relativistic effects play an important role and the occurrence of strong spin−orbit coupling makes electronic relaxation less demanding than in d-transition metals;[11] therefore, collisional cooling of electronic excited states eventually formed in the LDI process is deemed to be a more straightforward process. Collisional cooling as performed in the present study is also usually sufficient to remove any excess translational energy on the ions formed by LDI. Several previous studies under the conditions employed in this work indicated that for singly charged actinide metal ions thermal ground-state chemistry was dominant.[7,8,12,13] In the two previous studies of the reactivity of An^{2+} ions that were performed under similar experimental conditions,[6,8] no evidence was found for the involvement of excited states in the observed chemistry. In what concerns the nonactinide metals used in the present study, Mn, Ge, Sn, Pb, and Bi, the corresponding M^{2+} ions all have excited electronic states that are rather high in energy (the ground states are $3d^5$ for Mn^{2+}, ns^2 for Ge^{2+}, Sn^{2+}, and Pb^{2+}, and $6s^26p^1$ for Bi^{2+}, and the first excited states lie at ca. 2.5 eV for Bi^{2+}, 3.3 eV for Mn^{2+}, and 6−7 eV for Ge^{2+}, Sn^{2+}, and Pb^{2+} [29]), which are not expected to be formed in the LDI procedure; collisional cooling as performed in this work is likely to remove any excess kinetic energy.

Because the steady-state concentration of the neutral reagent was much larger than that of the reactant ions, pseudo-first-order kinetics were exhibited, whereby the ion A^{2+} reacting with the molecule B was depleted according to the rate law: $d[A^{2+}]/dt = -k[A^{2+}][B]$. Rate constants (values of k) were determined from the pseudo-first-order decay of the relative signals of the reactant ions as a function of time at constant neutral pressures, [B]. Each decay was followed until the relative intensity of the reacting dipositive ion had reached less than 10% of its initial intensity. Along with the absolute rate constants, reaction efficiencies are reported as k/k_{COL}, where the k_{COL} is the collisional rate constant derived from the modified variational transition-state/classical trajectory theory developed by Su and Chesnavich;[30] the k/k_{COL} values are particularly useful for comparative purposes. Collisional rate constants were calculated using experimental molecular polarizabilities and dipole moments of the neutral reagents.[26] Due to uncertainties in the pressure measurements, we estimate errors up to ±50% in the measured absolute rate constants; however, relative errors in the rate constants and efficiencies (k/k_{COL}) are estimated to be only ±20%.

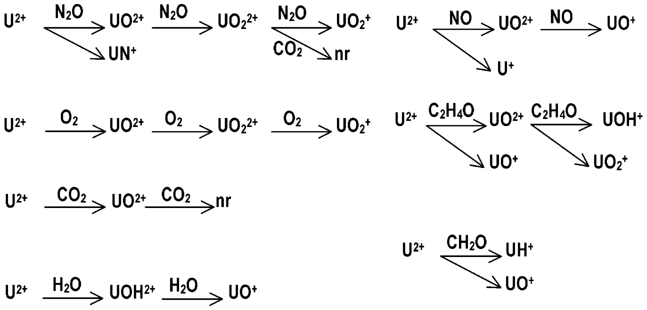
In the reactions in which two singly charged products were generated, the product distributions were determined using the relative abundances of the metal-containing ions. The low-mass ions formed in these charge-separation reactions showed rather low and variable intensities, most probably due to the high kinetic energies that they acquire,[31] which results in their loss from the ICR cell. The high-mass metal-containing ions formed will have low kinetic energies[31] and, therefore, their intensities are expected to be reproducible (as it was in fact observed) and the product distributions obtained thereby are not expected to be significantly affected by experimental parameters.

Care was taken to minimize the interference of reactions with residual hydrocarbons, water, and/or oxygen in the spectrometer. This was accomplished by using long pumping periods after the solids probe was inserted into the high-vacuum chamber but before introducing the oxidizing reagents. Base pressures in the turbomolecular-pumped mass spectrometer were typically $\sim 10^{-8}$ Torr. The oxidation and electron-transfer measurements were verified by comparisons with reactions that occurred under background conditions. When the reactions with residual gases were significant, the measured reaction rates and product distributions were adjusted for reactions with these before and after the rate measurements.

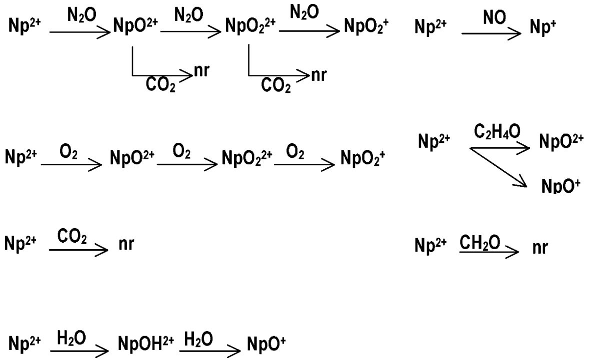
SCHEME 1. Reaction Sequences of Th^{2+} with Oxidants



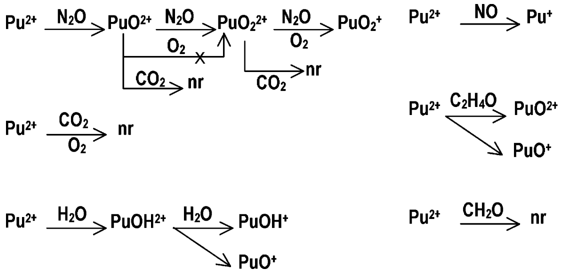
SCHEME 2. Reaction Sequences of U^{2+} with Oxidants



SCHEME 3. Reaction Sequences of Np^{2+} with Oxidants



SCHEME 4. Reaction Sequences of Pu^{2+} with Oxidants



Results and Discussion

The reactions studied in this work are summarized in Schemes 1−5, where a "no reaction" designation (nr) indicates that $k/k_{COL} < \sim 0.001$, the typical detection limit. The results are discussed in detail below for reactions of the atomic metal ions, An^{2+}, the monoxide ions, AnO^{2+}, the hydroxide ions, $AnOH^{2+}$, and for electron transfers to the dipositive actinyls, AnO_2^{2+}. The reaction products were either a dipositive product and a neutral, or two monopositive ions. In contrast to the former type of

SCHEME 5. Reaction Sequences of Am^{2+} with Oxidants

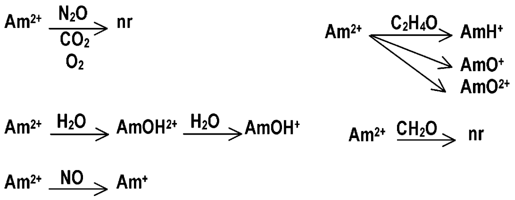


TABLE 1: Bond Energies and Ionization Energies for the Neutral Reagent Molecules, RO[a]

RO	N_2O	C_2H_4O	H_2O	O_2	CO_2	NO	CH_2O
BDE[R−O] (kJ mol^{-1})	167	354	491	498	532	632	751
IE[RO] (eV)	12.89	10.56	12.62	12.07	13.78	9.26	10.88

[a] All values are from ref 47. The bond energies (BDE[R−O]) are accurate to ±1 kJ mol^{-1} or better; the ionization energies (IE[RO]) are accurate to ±0.01 eV or better.

reaction, the latter involves electron transfer and requires an exothermicity sufficient to overcome the repulsive interactions, as described by an energy surface derived from a Landau−Zener type of model.[31−46] Thus, whereas reactions that result in a charged and a neutral product can be presumed to be thermoneutral or exothermic under the present low-energy experimental conditions (i.e., $\Delta H_{rxn} \leq 0$), reactions that result in two positively charged species must be substantially exothermic (i.e., $-\Delta H_{rxn} > 1-2$ eV[31]). The thermochemistry associated with reactions of a dipositive reactant ion and a neutral to give two monopositive product ions is too uncertain to be assessed in detail—it can only be inferred that these reactions must be substantially exothermic. In the particular case of electron transfers from neutrals to dipositive ions, sufficient information on thermodynamic thresholds and kinetics[31−46] exists to make some reasonable estimates and comparisons of the ionization energies of UO_2^+, NpO_2^+, and PuO_2^+ based on the observed electron-transfer kinetics for the AnO_2^{2+} and M^{2+} (M = Sn, Pb, Mn, Ge, and Bi). The nonactinide metal ions were studied to provide a calibration for the actinide results. Bond dissociation energies (BDE[RO]) and ionization energies (IE[RO]) for the neutral reagents are given in Table 1. For the reactions studied here, two particles reacted to give two product particles, so that entropy changes can be presumed to be negligible, making it valid to interpret the observations in terms of reaction enthalpies (i.e., $\Delta H_{rxn} \leq 0$) rather than free energies (i.e., $\Delta G_{rxn} \leq 0$).[48]

An^{2+} + RO Reactions. *Formation of AnO^{2+}*. The rate constants and k/k_{COL} ratios for the reactions of the An^{2+} with the oxidants are given in Table 2. When a reaction was not observed, the upper limit for k is $\sim 1 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, resulting in a limit for k/k_{COL} of approximately ≤ 0.001; the k_{COL} values are in the range of $(1-5) \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1}. Some of the uranium ion reactions studied in the present work have been examined previously by others. The measured rate constant for the U^{2+}/O_2 oxidation reaction, $k = 5.9 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, compares with $k = 1.1 \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} measured previously using FTICR-MS,[6] and $k = 1.8 \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} measured by Jackson et al. using quadrupole ion trap mass spectrometry (QIT-MS).[9] The value of k obtained for the U^{2+}/H_2O reaction was 4.9×10^{-10} cm^3 $molecule^{-1}$ s^{-1} from this work and $\sim 1 \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} from Jackson et al.[9] While the higher values of k obtained with QIT-MS can be due to the different experimental conditions in terms of neutral pressures, the difference encountered for the U^{2+}/O_2 reaction relative to the previous FTICR-MS study[6] is probably caused by changes in the pressure calibrations and/or thermalization procedures. The values from the previous FTICR-MS work and the present work are still within the reported uncertainties: 30% and 50%, respectively. No uncertainties have been indicated for the k values obtained in the QIT-MS work.[9]

With each of the studied An^{2+}, AnO^{2+} was a product for at least one oxidant. Since the observed reactions are presumed to be thermoneutral or exothermic, lower limits for the bond dissociation energies, BDE[An^{2+}-O] in Table 3, are obtained directly. The results can alternatively be stated as formation enthalpies but are presented here as bond energies to facilitate comparisons. For example, BDE[U^{2+}-O] ≥ 632 kJ mol^{-1} based on oxidation of An^{2+} by NO is equivalent to $\Delta H_f[UO^{2+}] \leq 1894 \pm 50$ kJ mol^{-1}. An advantage of citing bond energies rather than enthalpies of formation is that the large uncertainty associated with $\Delta H_f[An^{2+}]$ (notably $\Delta H_f[U^{2+}] = 2277 \pm 50$ kJ mol^{-1} [49]) is not introduced into the comparative values. Based on the oxidation of Am^{2+} by C_2H_4O, facile oxidation by N_2O would be anticipated based on thermodynamic considerations alone. Although Pu^{2+} and Am^{2+} react with C_2H_4O at the same efficiency, the product distributions are quite disparate (see Table 2). Since Am^{2+} is oxidized by C_2H_4O, the inert nature of Am^{2+} toward N_2O must reflect a significant kinetic barrier, perhaps related to the higher energy necessary to excite a 5f electron of Am^{2+} to an outer valence orbital compared with earlier An^{2+}.[50] This lack of reactivity of Am^{2+} with N_2O can also be due to spin restrictions, associated with the spin-forbidden nature of the decomposition of singlet N_2O to singlet N_2 and triplet O, as investigated in detail recently by Bohme and co-workers for first-, second-, and third-row atomic monocations.[51] Due to such kinetic effects on reactivity, the nonoccurrence of a reaction cannot be taken to imply that it is thermodynamically unfavorable. Given this important caveat, some estimates of BDEs can nonetheless be made based on relative reaction rates.

The U^{2+} ion reacts with CH_2O almost as efficiently as does Th^{2+}, indicating favorable overall kinetics for both of these An^{2+} reactant ions. ThO^{2+} is the dominant product for the Th^{2+}/CH_2O reaction (the other product is ThO^+), whereas UO^{2+} is not observed from the U^{2+}/CH_2O reaction (instead, the products are UH^+ and UO^+). From the available thermodynamic data,[47,49,53] it is possible to estimate that the formation of ThO^+ in the CH_2O reaction is exothermic by 280 kJ mol^{-1}, while the formation of UO^+ is exothermic by 200 kJ mol^{-1} and that of UH^+ is also exothermic by 273 kJ mol^{-1}. The fact that these reaction channels have similar exothermicities, AnO^{2+} is only formed for Th and both An^{2+} reactant ions have favorable overall kinetics, suggests that the oxidation of U^{2+} to UO^{2+} by CH_2O is thermodynamically unfavorable. It is therefore reasonable to assign 751 kJ mol^{-1} as an upper limit to BDE[U^{2+}-O]. The high oxidation efficiencies of Th^{2+} and U^{2+} with CO_2 indicate that a minimal kinetic barrier exists for this reagent, so that the lack of reaction between Np^{2+} and CO_2 suggests 532 kJ mol^{-1} as an approximate upper limit for BDE[Np^{2+}-O]. Similarly, the efficient oxidation of Th^{2+}, U^{2+}, and Np^{2+} by O_2 indicates favorable kinetics, so that the inert nature of Pu^{2+} and Am^{2+} with O_2 leads us to assign 498 kJ mol^{-1} as an upper limit for both BDE[Pu^{2+}-O] and BDE[Am^{2+}-O]. Given these considerations, we initially estimate BDE[Pu^{2+}-O] and BDE[Am^{2+}-O] as 430 ± 80 kJ mol^{-1}. In view of the constraints of our interpretation of the oxidation results, i.e., BDE[Pu^{2+}-O] and BDE[Am^{2+}-O] are both in the approximate range of 354−498 kJ mol^{-1}, we arrive at the estimates for BDE[Pu^{2+}-O] and

TABLE 2: Rate Constants and Product Distributions of the Reactions of An^{2+} with Oxidants[a]

An^{2+}	Th^{2+}	U^{2+}	Np^{2+}	Pu^{2+}	Am^{2+}
N_2O					
k	0.57	0.56	0.36	0.24	<0.001
k/k_{COL}	0.41	0.40	0.25	0.17	<0.001
product(s)	ThO^{2+}/45% ThN^+/55%	UO^{2+}/55% UN^+/45%	NpO^{2+}/100%	PuO^{2+}/100%	none
C_2H_4O					
k	0.96	1.02	0.87	0.73	0.72
k/k_{COL}	0.28	0.30	0.25	0.21	0.21
products	ThO^{2+}/20% ThO^+/80%	UO^{2+}/20% UO^+/80%	NpO^{2+}/10% NpO^+/90%	PuO^{2+}/5% PuO^+/95%	AmO^{2+}/5% AmO^+/15% AmH^+/80%
H_2O					
k	0.67	0.49	0.20	0.006	0.003
k/k_{COL}	0.15	0.11	0.05	0.001	0.001
product(s)	ThO^{2+}/10% $ThOH^{2+}$/90%	UOH^{2+}/100%	$NpOH^{2+}$/100%	$PuOH^{2+}$/100%	$AmOH^{2+}$/100%
O_2					
k	0.62	0.59	0.53	<0.001	<0.001
k/k_{COL}	0.56	0.53	0.48	<0.001	<0.001
product	ThO^{2+}/100%	UO^{2+}/100%	NpO^{2+}/100%	None	None
CO_2					
k	0.72	0.50	<0.001	<0.001	<0.001
k/k_{COL}	0.55	0.38	<0.001	<0.001	<0.001
product	ThO^{2+}/100%	UO^{2+}/100%	None	None	None
NO					
k	0.53	0.36	0.25	0.29	0.28
k/k_{COL}	0.42	0.29	0.20	0.23	0.22
product(s)	ThO^{2+}/20% Th^+/80%	UO^{2+}/15% U^+/85%	Np^+/100%	Pu^+/100%	Am^+/100%
CH_2O					
k	0.79	0.43	<0.001	<0.001	<0.001
k/k_{COL}	0.18	0.10	<0.001	<0.001	<0.001
product(s)	ThO^{2+}/90% ThO^+/10%	UO^+/20% UH^+/80%	None	None	None

[a] The pseudo-first-order reaction rate constants, k, are in units of 10^{-9} cm^3 molecule^{-1} s^{-1} ($k < 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} is the typical detection limit); the estimated errors are ±50% absolute and ±20% relative. The product distributions have uncertainties of ±10%.

TABLE 3: Bond Dissociation Energies for An^{2+}-O[a]

An^{2+}-O	Th^{2+}-O	U^{2+}-O	Np^{2+}-O	Pu^{2+}-O	Am^{2+}-O
BDE[An^{2+}-O]	≥ 751	≥ 632 (690 ± 60)	≥ 498 (530 ± 30)	≥ 354 (460 ± 50)	≥ 354 (400 ± 50)

[a] The BDE[An^{2+}-O] are in kJ mol^{-1}. The definitive lower limits were derived from observed oxidation reactions. The estimates in parentheses were obtained as discussed in the text.

BDE[Am^{2+}-O] that are given with the BDE[U^{2+}-O] and BDE[Np^{2+}-O] estimates included in Table 3.

Formation of AnOH^{2+}. Each of the five studied An^{2+} reacted with H_2O to produce the hydroxide, $AnOH^{2+}$ (+ H), which indicates that BDE[An^{2+}-OH] $\geq$ 499 kJ mol^{-1}.[47] The results show that U^{2+} reacts with H_2O to produce only UOH^{2+}. This contrasts with the observation of both UOH^{2+} and UO^{2+} from the U^{2+}/H_2O reaction studied by QIT-MS,[9] and may be related to the different pressures encountered in the two techniques and a greater degree of collisional cooling of nascent products in the higher-pressure QIT experiments.[52] It is notable that the same lower limit found for BDE[Pu^{2+}-OH] and BDE[Am^{2+}-OH], 499 kJ mol^{-1}, is greater than the estimated BDE[Pu^{2+}-O] and BDE[Am^{2+}-O] given in Table 3. It may be unexpected that what are presumed to be formally double covalent M^{2+}-O bonds should be weaker than the single covalent M^{2+}-OH bonds. However, a similar counterintuitive phenomenon appears elsewhere in the periodic table. For example, in the case of Sr^+, where only one electron is available outside of the closed Kr electron core, BDE[Sr^+-OH] $\approx$ 443 kJ mol^{-1} is significantly larger than BDE[Sr^+-O] $\approx$ 299 kJ mol^{-1}.[53] In the case of Eu^+ there are several quasi-valence 4f electrons but BDE[Eu^+-OH] $\geq$ 464 kJ mol^{-1} is also larger than BDE[Eu^+-O] = 398 kJ mol^{-1}.[54] Armentrout[55] has considered this general effect for transition metals and rationalized very strong M^+-OH bonding for metals with vacant valence d-orbitals (which would include the actinides) based on a particularly significant contribution from π-donation from the hydroxyl ligand to the metal, which results in strong dative bonding. In the particular case of doubly charged MOH^{2+}, stabilization relative to MO^{2+} might also result from “the presence of the hydrogen atom, which facilitates the distribution of the positive charge”, as suggested by Schröder and Schwarz.[21] Because the 5f electrons of the transneptunium actinides are ineffective at covalent bonding,[11] if the energy needed to promote the localized 5f electrons from the ground-state An^{2+} ion is not compensated by the additional bonding, it can be expected that a single rather than a double covalent bond would exist in AnO^{2+}, as must be the case for SrO^+. The energies needed to excite the An^{2+} from their ground states to the lowest lying state having two non-5f valence electrons, [Rn]$5f^{n-2}6d^2$ (where n is the total number of electrons outside of the Rn core), are as follows (in eV): 0.01 for Th^{2+}; 2.41 for U^{2+}; 4.2 ± 0.7 for Np^{2+}; 6.2 ± 0.7 for Pu^{2+}; and 8.7 ± 0.6 for Am^{2+}.[50] The increasingly large promotion energies across the series would be expected to result in weaker M^{2+}-O bonds, possibly to the extent that these bonds should be considered as single, rather than double, covalent bonds for AmO^{2+} and possibly even for PuO^{2+}. This single bond character might also apply to EuO^+ because for Eu^+ the energy to promote a

TABLE 4: Thermochemisty of Actinide Monoxides

An	IE[AnO] (eV)	$\Delta H_f[AnO^+]$ (kJ mol^{-1})	$\Delta H_f[AnO^{2+}]$[f](kJ mol^{-1})	IE[AnO^+][g](eV)	$\Delta H_f[AnO^{2+}]$[h](kJ mol^{-1})	IE[AnO^+][i](eV)
Th	6.60[a]	617 ± 17[d]	≤ 1847	≤ 12.8	N/A	N/A
U	6.03[b]	614 ± 25[d]	≤ 1944	≤ 13.8	1836 ± 78	12.7 ± 0.8
Np	6.1 ± 0.2[c]	585 ± 46[e]	≤ 1979	≤ 14.7	1918 ± 42	13.8 ± 0.6
Pu	6.1 ± 0.2[c]	527 ± 55[d]	≤ 1975	≤15.4	1848 ± 54	13.7 ± 0.8
Am	6.2 ± 0.2[c]	551 ± 30[c]	≤ 1936	≤14.5	1869 ± 54	13.7 ± 0.6

[a] From Goncharov et al.[61] [b] From Han et al.[59,60] The precise value is 6.0313 ± 0.0006 eV. [c] From Santos et al.,[13] adjusted for the revised IE[AnO]. $\Delta H_f[AmO^+]$ is an estimate.[13] [d] From Hildenbrand et al.,[49] adjusted for the revised IE[AnO]. [e] From Lias et al.,[53] adjusted for the revised IE[AnO]. [f] These upper limits were derived from the observed oxidation reactions. [g] These upper limits to IE[AnO^+] result from the tabulated upper limits to $\Delta H_f[AnO^{2+}]$. [h] These $\Delta H_f[AnO^{2+}]$ are derived from the estimated BDE[An^{2+}-O] given in Table 3, using the procedure described in the text. [i] These IE[AnO^+] are derived from the $\Delta H_f[AnO^{2+}]$ in the adjacent column.

localized 4f electron to an outer bonding orbital is 3.75 eV, which is the largest for any monopositive lanthanide ion, Ln^+.[56]

Thermodynamic Considerations. The present results indicate that AnO^{2+} and $AnOH^{2+}$ (An = Th, U, Np, Pu, Am) are stable dications. As outlined by Schröder and Schwarz,[21] an AB^{2+} dication is thermochemically stable if IE[A^+] < IE[B], because the {A^{2+}−B} complex is then stable toward Coulombic dissociation into {A^++B^+} even if the binding energy in AB^{2+} is minimal; if IE[A^+] slightly exceeds IE[B], the AB^{2+} dication may still be thermochemically stable, provided the binding energy BDE[A^{2+}−B] compensates for the difference of the IEs. As the IE[An^+] lie in the range of 11.7−12.0 eV,[19] and both IE[O] = 13.6 eV and IE[OH] = 13.0 eV are significantly greater than 12 eV,[53] AnO^{2+} and $AnOH^{2+}$ should be thermochemically stable relative to dissociation into {An^++O^+} and {An^++OH^+} for all five studied An, in accord with our observations. In the case of $AnOH^{2+}$, the dissociation into {AnO^++H^+} should also be considered. There are no values of IE[AnO^+] in the literature, but below we estimate these quantities and summarize them in Table 4. The IE[AnO^+] obtained lie in the approximate range of 12.5−14 eV and therefore, taking into account that IE[H] = 13.6 eV,[53] we may infer that all the $AnOH^{2+}$ ions are also thermochemically stable relative to {AnO^++H^+}, as observed experimentally, with the binding energy between AnO^{2+} and H evidently compensating for the small difference in the IEs for some of the An. Notably, the unusually low third ionization energies for the early actinides[19] render AnX^{3+} as candidate diatomic tripositive ions and Schröder et al.[57] have accordingly prepared UF^{3+}.

The AnO^{2+} and $AnOH^{2+}$ ions were the only dipositive products of the An^{2+} + RO reactions. Some of the reactions resulted in two monopositive ions, such as {ThN^++NO^+} and {UH^++CHO^+}. As discussed above, there is an indeterminate thermodynamic threshold for such reactions due to the repulsive Coulombic interaction between the product ions. Derived lower limits for bond energies based on the requirement for net exothermicity are generally not particularly useful, as they underestimate these lower limits to an unknown degree (e.g., ≥ 100 kJ mol^{-1}). For example, the reaction of U^{2+} with CH_2O to give UO^+ and CH_2^+ requires that BDE[U^+-O] ≥ 597 ± 50 kJ mol^{-1}, which is consistent with a threshold of ≥ 100 kJ mol^{-1}, and with the reported BDE[U^+-O] = 796 ± 56 kJ mol^{-1}.[49] The thermodynamic implications for reactions that yield two monopositive ions appear consistent with an exothermic threshold of 100 kJ mol^{-1} or greater, but do not provide additional insights into bonding in the actinide product ions. The important exception to this is electron-transfer reactions, and these are discussed in detail below.

With the NO reagent, electron transfer to give An^+ and NO^+ was the dominant reaction channel for Th^{2+} and U^{2+} reactants ions, and the sole channel for Np^{2+}, Pu^{2+} and Am^{2+}. The IE[An^+] are in the range of 11.7−12.0 eV for the five studied An,[19] and IE[NO] = 9.3 eV (Table 1), so that electron transfer from NO to An^{2+} is exothermic by at least 2.4 eV in each case, this being well in excess of the expected threshold barrier according to Landau−Zener type considerations.[31−46] The neutral reagent with the next lowest ionization energy was C_2H_4O (IE = 10.6 eV). The exothermicity for electron transfer from C_2H_4O to the An^{2+} is ≤ 1.4 eV, and in no case was simple electron transfer from C_2H_4O to an An^{2+} observed. These findings are consistent with the electron-transfer results presented below.

Kinetic Considerations. The oxidation kinetics for the dipositive An^{2+} can be compared with the corresponding kinetics for the monopositive An^+[12,13] and Ln^+.[58] The reactions with N_2O are of particular interest because all of the pertinent metal ion−oxygen bond energies exceed BDE[N_2-O], so that all of the oxidation reactions are exothermic and the results can be assessed in the context of kinetics. As indicated in a previous section, Bohme and co-workers have recently made a comprehensive study of the reactivity of first-, second-, and third-row atomic monocations with N_2O, in which the issue of spin conservation was specifically addressed, in view of the spin-forbidden nature of the decomposition of singlet N_2O to singlet N_2 and triplet O.[51] The reactivity of actinide and lanthanide cations with N_2O can also be affected by spin restrictions, but the lack of data on the electronic structures of the lanthanide and actinide oxide cations, as well as the insuficient data on the electronic structures of the actinide cations, makes this effect extremely difficult to evaluate.

Koyanagi and Bohme[58] found a clear correlation between the reaction efficiencies for oxidation of the Ln^+ by N_2O and the energies for promotion from the ground-state Ln^+ electronic configuration to a configuration with two nonbonding 4f electrons, [Xe]$4f^{n-2}5d6s$, where *n* represents the total number of electrons outside of the closed xenon core of the Ln^+. This is consistent with the necessity for two non-4f valence electrons to form a Ln^+=O double bond, and a reaction mechanism that proceeds by abstraction of the oxygen atom from N_2O by direct formation of the Ln^+=O bond. In this scenario the reaction intermediate can be represented as $Ln^+\cdots O\cdots N-N$.

The results for oxidation of An^+ by N_2O (An = Th, U, Np, Pu, Am) indicated a comparable relationship between kinetics and promotion energies.[12,13] The k/k_{COL} for the An^+/N_2O oxidation reactions were 0.68/Th^+, 0.47/U^+, 0.48/Np^+, 0.02/Pu^+ and 0.004/Am^+.[12,13] The promotion energies from the An^+ ground states to the [Rn]$5f^{n-1}6d7s$ configurations are as follows: 0/Th^+ ([Rn]$6d^27s$ ground state), 0.04 eV/U^+, 0/Np^+, 1.08 eV/Pu^+, and 2.5 ± 0.1 eV/Am^+.[50] It is seen that the oxidation efficiencies for Th^+, U^+, and Np^+, each of which has a promotion energy at or very close to zero, are comparably high (k/k_{COL} = 0.5−0.7). The oxidation efficiency then decreases drastically for Pu^+ (k/k_{COL} = 0.02), which has a promotion energy of 1.08 eV; the efficiency decreases even further for

Am^+ ($k/k_{COL} = 0.004$), which has a promotion energy of ~2.5 eV. The inverse correspondence between the oxidation rates and the promotion energies suggests a similar interpretation to that for the Ln^+,[58] as has been suggested previously.[12,13] Specifically, it would seem that the kinetics of oxidation of the An^+ by N_2O are determined by the energy needed to attain a configuration at the metal center with two non-5f electrons available to form the An^+-O bond. The reduced reactivities of Pu^+ and Am^+ indicate that promotion is necessary and that the 5f electrons cannot effectively participate in the An^+-O bond. Because the promotion energies are zero or minimal for Th^+, U^+, and Np^+, this relationship does not reveal whether the 5f electrons for these lighter actinide ions may be involved in bonding.

For Th^{2+} and U^{2+} both AnO^{2+} and AnN^+ were products of the reactions with N_2O; the oxidation efficiencies for these two cases are obtained by multiplying the overall k/k_{COL} by the fraction of AnO^{2+} product, 0.45 for Th^{2+} and 0.55 for U^{2+}. The efficiencies, k/k_{COL}, for the An^{2+}/N_2O oxidation reactions are as follows: $0.18/Th^{2+}$, $0.22/U^{2+}$, $0.25/Np^{2+}$, $0.17/Pu^{2+}$, and $<0.001/Am^{2+}$. For the An^{2+}, the lowest-lying excited states with two non-5f valence electrons are $[Rn]5f^{n-2}6d^2$ (the lowest $[Rn]5f^{n-2}6d7s$ configurations are each significantly higher in energy) and the promotion energies from the ground states are[50] 0.01 eV/Th^{2+}, 2.41 eV/U^{2+}, 4.2 ± 0.7 eV/Np^{2+}, 6.2 ± 0.7 eV/Pu^{2+}, and 8.7 ± 0.6 eV/Am^{2+}. Because the oxidation efficiencies are essentially the same ($k/k_{COL} \approx 0.2$) for Th^{2+}, U^{2+}, Np^{2+}, and Pu^{2+}, while the promotion energies monotonically increase from 0.01 eV for Th^{2+} to ~6.2 eV for Pu^{2+}, it is apparent that the model used for the An^+/N_2O oxidation reactions is not applicable. One possibility is that the 5f electrons can participate in An^{2+}-O bonding for U^{2+}, Np^{2+}, and Pu^{2+} but not for Am^{2+}, which is not oxidized by N_2O. That the An^{2+}-O bond strengths evidently decrease across the series would then reflect a decreasing effectiveness of the 5f electrons in metal−oxygen bonding. Alternatively, as with hydrocarbon activation,[32] oxygen-abstraction from N_2O by dipositive ions may proceed by an entirely different mechanism than for the monopositive ions, that does not necessarily require participation of the 5f electrons. In this case, the inert nature of Am^{2+} toward N_2O could reflect a lesser exothermicity and/or a significant barrier for that particular oxidation reaction.

AnO^{2+} + RO Reactions. *Thermochemistry of AnO^{2+}*. It was possible to examine only a limited suite of reactions of AnO^{2+} ions due to the need to produce adequate quantities of AnO^{2+} in primary reactions. The AnO^{2+} ions did not react with CO_2 (the AmO^{2+}/CO_2 reaction could not be studied). Both ThO^{2+} and UO^{2+} underwent electron transfer with NO. The rate constant measured for ThO^{2+} was $k = 4.9 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, which corresponds to $k/k_{COL} = 0.40$; the rate was not determined for the UO^{2+}/NO reaction and the AnO^{2+}/NO reactions could not be studied for NpO^{2+}, PuO^{2+}, and AmO^{2+}. The only product of the reaction of ThO^{2+} with H_2O, ThO_2H^+, presumably the oxide hydroxide of tetravalent Th ($[O{=}Th{-}OH]^+$), was formed inefficiently ($k/k_{COL} = 0.001$). ThO^{2+} reacted with CH_2O to produce $ThOH^+$ (+ CHO^+) with a rate constant of $k = 5.9 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, which corresponds to $k/k_{COL} = 0.13$. This reaction was not studied for the other AnO^{2+} since they are not produced from the reaction of the other An^{2+} with CH_2O. With C_2H_4O, ThO^{2+} formed $ThOH^+$ (40%) and ThO_2H^+ (60%), while UO^{2+} produced UOH^+ (40%) and UO_2^+ (60%). The measured rate constants were $k = 7.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for ThO^{2+} and $k = 7.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for UO^{2+}, which correspond to $k/k_{COL} = 0.22$ and $k/k_{COL} = 0.21$, respectively. The remaining AnO^{2+}/C_2H_4O reactions could not be studied.

The $\Delta H_f[AnO^+]$ values are generally derived from $\Delta H_f[AnO]$ and IE[AnO].[49] Heaven and co-workers have recently determined very accurate IE[UO][59,60] and IE[ThO][61] values by a sophisticated spectroscopic technique. Their new values, included in Table 4 for ThO and UO, represent substantial corrections, of +0.5 eV and +0.3 eV respectively, to previous experimental values.[49] Santos et al.[13] obtained ionization energies for PuO and AmO using an approach that was based on IE[UO] as a calibration value. In view of the new value for IE[UO],[59,60] we have revised IE[PuO] and IE[AmO] to the values given in Table 4. The IE[NpO] included in Table 4 also represent our upward revision to the literature value[49] based on the new values for IE[UO] and IE[ThO] determined by Heaven and co-workers[59−61] and the results from Santos et al.[13] As both NpO^+ and PuO^+ did not react with 1,3-butadiene and were found to have essentially identical reactivities (both the product distributions and k/k_{COL}) with isoprene,[13] it is concluded that IE[NpO] ≈ IE[PuO] and a value of 6.1 ± 0.2 eV is now assigned to both, in accord with the previously described approach.[13] These upward revisions to both IE[NpO] (previously 5.7 eV[49]) and IE[PuO] (previously 5.8 eV[49]) are in accord with the experimentally substantiated[59−61] conclusion that AnO ionization energies determined by electron ionization appearance threshold measurements on high-temperature actinide oxide vapors are likely to be significantly lower than the actual values due to the presence of excited-state oxide molecules.[59,60,62] The $\Delta H_f[AnO^+]$ values in Table 4 are from the indicated sources after adjustments for the revised IE[AnO]; the value for $\Delta H_f[AmO^+]$ is derived from the estimated $BDE[Am^+{-}O] = 560 \pm 30$ kJ mol^{-1} that was reported previously.[13]

The oxidation reactions of the An^{2+} ions establish upper limits to the dipositive monoxide ion formation enthalpies through the following relationship: $\Delta H_f[AnO^{2+}] \leq \{\Delta H_f[An^{2+}] - BDE[RO] + \Delta H_f[O]\}$, where BDE[RO] corresponds to the largest bond energy for which oxidation of An^{2+} was observed, and the resulting values are included in Table 4. The corresponding upper limits to the second ionization energies of the actinide monoxides, $IE[AnO^+] = \{\Delta H_f[AnO^{2+}] - \Delta H_f[AnO^+]\}$, are also given in Table 4. To obtain estimates of the $IE[AnO^+]$, we can use the $BDE[AnO^{2+}]$ values in Table 3 and arrive at $\Delta H_f[AnO^{2+}]$ through the following relationship: $\Delta H_f[AnO^{2+}] = \{\Delta H_f[An^{2+}] + \Delta H_f[O] - BDE[AnO^{2+}]\}$. Using the $\Delta H_f[An^{2+}]$ from Hildenbrand et al.[49] and $\Delta H_f[O] = 249$ kJ mol^{-1} from Lias et al.,[53] the resulting values obtained are included in the penultimate column of Table 4. The $IE[AnO^+]$ derived from these estimates are given in the final column of Table 4. The results suggest that $IE[UO^+]$ is ~1 eV lower than $IE[AnO^+] \approx 13.7$ eV for the three transuranic AnO^+. The $IE[AnO^+]$, and in particular those of the transuranic AnO^+ for which there is an increasing tendency for the stabilization of the +3 oxidation state, can be compared with $IE[LaO^+] = 15.2 \pm 0.4$ eV.[63] As both of the metal-centered electrons in $\{La{=}O\}^+$ are expected to be involved in covalent bonding, it is not surprising that the ionization energy of LaO^+ is apparently significantly greater than ionization energies of AnO^+ for which there are nonbonding valence electrons. Whereas the ionization energies of AnO^+ (An = U, Np, Pu, Am) are only ~1−2 eV higher than those of the bare An^+,[26,49] the ionization energy of LaO^+ is ~4 eV higher than that of La^+.[26,63]

The Bare Actinyl Ions: UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+}. Of special interest are oxidation reactions of AnO^{2+} that produce AnO_2^{2+}, the bare actinyl dipositive ions. Because AmO^{2+} was

TABLE 5: Rate Constants for $AnO^{2+} + RO \rightarrow AnO_2^{2+} + R$[a]

RO	N_2O	O_2
ThO^{2+}		
k	<0.001	<0.001
k/k_{COL}	<0.001	<0.001
UO^{2+}		
k	0.44	0.037
k/k_{COL}	0.31	0.03
NpO^{2+}		
k	0.39	0.012
k/k_{COL}	0.28	0.01
PuO^{2+}		
k	0.26	<0.001
k/k_{COL}	0.19	<0.001

[a] The pseudo-first-order reaction rate constants, k, are in units of 10^{-9} cm^3 molecule^{-1} s^{-1}; the estimated errors are ±50% absolute and ±20% relative. The only products were AnO_2^{2+}. It was not practical to study these reactions with AmO^{2+}.

formed only from the reaction of Am^{2+} with C_2H_4O and in minute amounts, the potential generation of AmO_2^{2+} could not be probed in detail. Although ThO^{2+} was produced in reactions with all seven of the oxidants, ThO_2^{2+} did not form in any of the ThO^{2+}/RO reactions. Thorium would formally be in an unstable hexavalent state in the hypothetical linear thoranyl species, $[O{=}Th{=}O]^{2+}$ (though a cyclic peroxide structure could feasibly incorporate Th(IV)); the aqueous thoranyl ion has not been identified.[14,64] The two reactions that yielded the bare actinyls, AnO_2^{2+}, are given by eqs 1 and 2:

$$AnO^{2+}(g) + N_2O(g) \rightarrow AnO_2^{2+}(g) + N_2(g) \quad [An = U, Np, Pu] \quad (1)$$

$$AnO^{2+}(g) + O_2(g) \rightarrow AnO_2^{2+}(g) + O(g) \quad [An = U, Np] \quad (2)$$

The measured rate constants (cm^3 molecule^{-1} s^{-1}) and corresponding reaction efficiencies (k/k_{COL}) for these reactions are given in Table 5. For reaction (2) with UO^{2+}, a rate constant $k = 4.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} was obtained from the previous FTICR-MS study,[6] and Jackson et al.[9] obtained $k = 3.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}; both of these earlier values are in good agreement with our value of 3.7×10^{-11} cm^3 molecule^{-1} s^{-1}. Reaction (1) for UO^{2+} was also studied previously by FTICR-MS,[6] and a rate constant of $k = 1.4 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} was obtained. In this case, our value of 4.4×10^{-10} cm^3 molecule^{-1} s^{-1} is significantly smaller and, as discussed previously for the case of the U^{2+}/O_2 reaction, the differences probably result from changes in the pressure calibration and/or thermalization procedures. The accordance of the k values for reaction (2) may reflect the fact that the rates are substantially smaller than those for reaction (1). In any event, if we compare the k values for the consecutive reactions in the U^{2+}/N_2O and U^{2+}/O_2 systems between the two FTICR-MS measurements, we see that in the prior work[6] the ratios 1:1 and 1:0.04 were obtained with N_2O and O_2, respectively, while in the present work similar ratios were obtained: 1:0.8 for N_2O and 1:0.06 for O_2. Again, we emphasize relative values of the rate constants rather than absolute values.

Studies had not previously been carried out for Np or Pu, and our results represent the first preparation and identification of the bare gas-phase neptunyl and plutonyl ions, $NpO_2^{2+}(g)$ and $PuO_2^{2+}(g)$. Though not as stable or prevalent as uranyl, both neptunyl and plutonyl are important species in aqueous and solid-state chemistry.[14−17]

Limits for the enthalpies of formation of the AnO_2^{2+} ions can be derived from the observed reactions of AnO^{2+} and AnO_2^{2+} ions. The occurrence of electron transfer from N_2O to UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+} establishes lower limits through the following relationship: $\Delta H_f[AnO_2^{2+}] \geq \{\Delta H_f[AnO_2^{+}] + IE[N_2O]\}$. The $\Delta H_f[UO_2^{+}]$ and $\Delta H_f[PuO_2^{+}]$ values given by Hildenbrand et al.[49] were evidently obtained from the neutral thermochemistry through the relationship $\Delta H_f[AnO_2^{+}] = \{\Delta H_f[AnO_2] + IE[AnO_2]\}$; a value for $\Delta H_f[NpO_2^{+}]$ was not reported. The revised values for $IE[UO_2] = 6.128 \pm 0.003$ eV[59,60] (previously reported as 5.5 ± 0.5 eV[49]) and $IE[PuO_2] = 7.03 \pm 0.12$[12] (previously reported as 9.4 ± 0.5 eV[49]) are used to adjust the literature $\Delta H_f[AnO_2^{+}]$[49] to the following: $\Delta H_f[UO_2^{+}] = 115 \pm 50$ kJ mol^{-1} (previously reported as 54 ± 50 kJ mol^{-1} [49]) and $\Delta H_f[PuO_2^{+}] = 270 \pm 54$ kJ mol^{-1} (previously reported as 498 ± 54 kJ mol^{-1} [49]). The particularly substantial revision to the latter value is in accord with the recent upward revision by Santos et al.[12] of $BDE[OPu^{+}\text{-}O]$ from ∼260 kJ mol^{-1} to ∼520 kJ mol^{-1}. The lower limits that result from these new values are: $\Delta H_f[UO_2^{2+}] \geq 1359 \pm 50$ kJ mol^{-1} and $\Delta H_f[PuO_2^{2+}] \geq 1514 \pm 54$ kJ mol^{-1}. Upper limits can be derived from the oxidation of UO^{2+} and NpO^{2+} by O_2, and of PuO^{2+} by N_2O through the relationship $\Delta H_f[AnO_2^{2+}] \leq \{\Delta H_f[AnO^{2+}] - BDE[RO] + \Delta H_f[O]\}$. Using the $\Delta H_f[AnO^{2+}]$ values from Table 4, the following limits are derived: $\Delta H_f[UO_2^{2+}] \leq 1587 \pm 78$ kJ mol^{-1}, $\Delta H_f[NpO_2^{2+}] \leq 1669 \pm 42$ kJ mol^{-1}, and $\Delta H_f[PuO_2^{2+}] \leq 1930 \pm 54$ kJ mol^{-1}.

The following ranges are then obtained for UO_2^{2+} and PuO_2^{2+}: $\Delta H_f[UO_2^{2+}] = 1473 \pm 192$ kJ mol^{-1} and $\Delta H_f[PuO_2^{2+}] = 1722 \pm 262$ kJ mol^{-1}. Using the relationship $IE[AnO_2^{+}] = \{\Delta H_f[AnO_2^{2+}] - \Delta H_f[AnO_2^{+}]\}$ gives $IE[UO_2^{+}] = 14.1 \pm 2.1$ eV and $IE[PuO_2^{+}] = 15.0 \pm 2.8$ eV. Based on the observation of electron transfer from N_2O to both UO_2^{2+} and PuO_2^{2+}, the lower limit for both of these ionization energies is established as 12.89 eV and the ranges are reduced to the following: $IE[UO_2^{+}] = 14.6 \pm 1.7$ eV and $IE[PuO_2^{+}] = 15.4 \pm 2.5$ eV. If we further make the conservative estimate that electron transfer from N_2O to AnO_2^{2+} must be exothermic by at least 1 eV to proceed,[31] we conclude that $IE[AnO_2^{+}] \geq 13.9$ eV (An = U, Np, Pu) and obtain $IE[UO_2^{+}] = 15.1 \pm 1.2$ eV and $IE[PuO_2^{+}] = 15.9 \pm 2.0$ eV. Although it might be doubtful that an exothermicity of 1 eV is sufficient to overcome the Coulomb barrier for electron transfer according to a Landau−Zener type of approach, as indicated by several studies,[31−46] employing this minimal value of 1 eV ensures that we keep our estimates under a reasonable uncertainty. Because only a lower limit could be assigned for $IE[NpO_2^{+}]$ and the values for $IE[UO_2^{+}]$ and $IE[PuO_2^{+}]$ have large associated uncertainties, the electron-transfer measurements described below were used to refine these second ionization energies.

Based on the exothermic occurrence of reactions (1) and (2), we conclude that $BDE[OPu^{2+}\text{-}O] \geq 167$ kJ mol^{-1}, $BDE[OU^{2+}\text{-}O] \geq 498$ kJ mol^{-1}, and $BDE[ONp^{2+}\text{-}O] \geq 498$ kJ mol^{-1}. Koyanagi and Bohme[58] have concluded that oxidation of metal ions by O_2 are kinetically favorable processes, in accord with the assumption that was employed above in arriving at the estimated BDEs for PuO^{2+} and AmO^{2+} given in Table 3. Similar kinetic considerations[58] should generally apply to oxidation of other MO^{2+} by O_2. Accordingly, considering the low rate constants measured for reaction (2), we propose that the bond energies for UO_2^{2+} and NpO_2^{2+} are close to the lower limit established from oxidation by O_2. Further, as the rate constant was somewhat greater for UO^{2+} compared with NpO^{2+}, we infer that the bond energy for UO_2^{2+} is somewhat greater than that for NpO_2^{2+}. Our estimates are then BDE[OU^{2+}-O] ≈ 560 ± 30 kJ mol^{-1} and BDE[ONp^{2+}-O] ≈ 520 ± 20 kJ mol^{-1}.

Relationship between Gaseous and Aqueous Actinyls. The four aqueous actinyl species, AnO_2^{2+}(aq), where An = U, Np, Pu, and Am, are known stable species and have been thermochemically characterized.[19] The relative enthalpies for the eq 3 indicate the comparative stabilities of the actinyl species when proceeding from UO_2^{2+}(aq) to AmO_2^{2+}(aq).

$$AnO_2^{2+}(aq) \rightarrow An^{2+}(g) + O_2(g) \qquad (3)$$

Equation 3 corresponds to removing hydrated AnO_2^{2+}(aq) from solution to the gas phase, followed by dissociation of the AnO_2^{2+}(g) into An^{2+}(g) + O_2(g). This is a reasonable indication of the comparative net bonding in the free actinyls if the enthalpy of hydration is comparable for all four AnO_2^{2+}. The hydration behaviors of UO_2^{2+} and PuO_2^{2+} are similar, with five coordinating water molecules and predicted similar hydration energies.[65] Hay et al.[66] have summarized experimental and theoretical results which indicate that $[AnO_2(H_2O)_5]^{2+}$ exhibit comparable hydration properties for An = U, Np, and Pu. Markus and Loewenschuss[67] argued that the actinyl hydration enthalpies are dominated by charge-dipole interactions, determined by the effective charge +2 on the actinide atoms, and should be similar to those of dipositive ions; this is confirmed below. The enthalpies of hydration of the An^{2+} vary by only ~60 kJ mol^{-1} between U^{2+} and Am^{2+}; these An^{2+} hydration enthalpies monotonically decrease across the series, by ~20 kJ mol^{-1} between adjacent actinides.[20] Although a relatively small correction for more exothermic hydration energies with increasing atomic number could be applied, to a first approximation it is assumed here that the hydration enthalpies are essentially the same for all four actinyls, so that the relative enthalpies for reaction (3) can be taken as an indication of the comparative net metal–oxygen bonding in the free actinyls.

Using the $\Delta H_f[AnO_2^{2+}(aq)]$ from Morss[19] and the $\Delta H_f[An^{2+}(g)]$ from Hildenbrand et al.,[49] the following enthalpies for reaction (3) are obtained (in kJ mol^{-1}): U, 3296 ± 50; Np, 3060 ± 29; Pu, 2881 ± 22; and Am, 2672 ± 21. The large uncertainty in the value for U derives from the remarkably large uncertainty in IE[U^+] of 0.5 eV.[49] The enthalpies for reaction (3) are employed to estimate differences between the enthalpies for eq 4 for the four actinyls.

$$AnO_2^{2+}(g) \rightarrow An^{2+}(g) + 2O(g) \qquad (4)$$

For U and Np, the values for reaction (3) would suggest that $\Delta H[(\mathbf{4})/U] - \Delta H[(\mathbf{4})/Np] = 236 \pm 58$ kJ mol^{-1}. Our estimates for BDE[An^{2+}-O] and BDE[OAn^{2+}-O] for U^{2+} and Np^{2+} (Table 3 and values cited above) result in $\Delta H[(\mathbf{4})/U] \approx \{690 + 560\} = 1250$ kJ mol^{-1}, $\Delta H[(\mathbf{4})/Np] \approx \{530 + 520\} = 1050$ kJ mol^{-1}, and thus $\Delta H[(\mathbf{4})/U] - \Delta H[(\mathbf{4})/Np] \approx 200$ kJ mol^{-1}. This last value is in good agreement with that derived from reaction (3). Tupitsyn[68] has suggested a lower IE[U^+] than that given by Hildenbrand et al.,[49] which would reduce $\Delta H[(\mathbf{3})/U]$, and thereby further improve the agreement. The satisfactory results of this assessment for the comparative stabilities of UO_2^{2+} and NpO_2^{2+} support the use of thermochemical values in aqueous solution (i.e., eq 3) to estimate the comparative bonding in the free actinyl dipositive ions (i.e., eq 4). It is also noted that our value for $\Delta H[(\mathbf{4})/U]$ of 1250 kJ mol^{-1} is in good agreement with a theoretical value of 1230 kJ mol^{-1} recently reported by Majumdar et al.[69] The $\Delta H[(\mathbf{3})/Np] - \Delta H[(\mathbf{3})/Pu] \approx 179 \pm 37$ kJ mol^{-1} and $\Delta H[(\mathbf{3})/Pu] - \Delta H[(\mathbf{3})/Am] \approx 209 \pm 30$ kJ mol^{-1} can be combined with $\Delta H[(\mathbf{4})/Np] \approx 1050$ kJ mol^{-1} to obtain $\Delta H[(\mathbf{4})/Pu] \approx 870$ kJ mol^{-1} and $\Delta H[(\mathbf{4})/Am] \approx 660$ kJ mol^{-1}. The substantial decrease in the intrinsic stabilities of the actinyls upon progressing from UO_2^{2+} to AmO_2^{2+} is clearly indicated by these four estimated $\Delta H[(\mathbf{4})/An]$.

Finally, our estimates for BDE[Pu^{2+}-O] ≈ 460 ± 50 kJ mol^{-1} and BDE[Am^{2+}-O] ≈ 400 ± 50 kJ mol^{-1} (Table 3) result in BDE[OPu^{2+}-O] ≈ 410 kJ mol^{-1} and BDE[OAm^{2+}-O] ≈ 260 kJ mol^{-1}; the uncertainty associated with these latter two values is estimated as approximately ±100 kJ mol^{-1}. The derived value for BDE[OPu^{2+}-O] is thermochemically consistent with the observation of the oxidation of PuO^{2+} by N_2O, and the lack of PuO^{2+} oxidation by O_2. The estimate for BDE[OAm^{2+}-O] suggests that free AmO_2^{2+} might result from the reaction of AmO^{2+} with N_2O, if there are no kinetic restrictions to this oxidation reaction; unfortunately, this particular reaction was impractical to study in the present work.

$AnOH^{2+}$ + H_2O Reactions. All five of the studied An^{2+} ions reacted with H_2O to form the primary product, $AnOH^{2+}$; the rate constants for the reactions are included in Table 2. This was the only product observed, with the exception of a 10% ThO^{2+} branch. With each of the $AnOH^{2+}$ ions, a reaction with a second H_2O molecule was observed. The reaction rate constants for $PuOH^{2+}$ and $AmOH^{2+}$ with H_2O could not be measured due to the inefficient production of the primary products (k/k_{COL} = 0.001), but the reaction pathways were established by double-resonance experiments in which the primary $AnOH^{2+}$ ions were ejected and the effect on the secondary product distributions monitored. The reaction rate constants (cm^3 molecule^{-1} s^{-1}) and efficiencies (k/k_{COL}) for the other $AnOH^{2+}$ ions with H_2O were as follows: $ThOH^{2+}$/7.1 × 10^{-10}, 0.16; UOH^{2+}/1.49 × 10^{-9}, 0.34; and $NpOH^{2+}$/1.17 × 10^{-9}, 0.27. The products of these reactions are included in Schemes 1–5. Reactions yielding two monopositive ion products were dominant, with a dipositive cation, $Th(OH)_2^{2+}$, formed only from the $ThOH^{2+}/H_2O$ reaction (35% $Th(OH)_2^{2+}$/65% ThO^+). The distinctive formation of $Th(OH)_2^{2+}$ can be taken to reflect the special stability of tetravalent Th, and its appearance indicates that BDE[$HOTh^{2+}$-OH] ≥ 499 kJ mol^{-1}.[47]

With the exception of $Th(OH)_2^{2+}$, the $AnOH^{2+}/H_2O$ reactions resulted in monopositive products: AnO^+ and/or $AnOH^+$. The monoxide ion was the sole monopositive product for Th, U, and Np, whereas both the monoxide and hydroxide were formed with Pu, and only the hydroxide was formed with Am. The formation of the AnO^+ species corresponds to proton transfer from $AnOH^{2+}$ to H_2O, indicating that the four gaseous $AnOH^{2+}$ ions (An = Th, U, Np, and Pu) are stronger Brønsted acids as compared to H_3O^+; i.e., the proton affinity of H_2O is greater than that of the AnO^+. As with all reactions that produce two cations, the extent of exothermicity (i.e., the relative acidity here) is not well established. In the case of $AmOH^{2+}$ with H_2O, only an electron-transfer reaction occurs, to give $AmOH^+$+H_2O^+, which indicates that IE[$AmOH^+$] exceeds IE[H_2O] = 12.62 eV by the threshold barrier for this reaction, presumably at least 1 eV.[31] We conclude that IE[$AnOH^+$] ≥ 13.6 eV for An = Pu and Am. This lower limit is almost 2 eV greater than IE[Pu^+] and IE[Am^+][49] and contrasts with IE[$LaOH^+$] = 10.8 ± 0.4 eV,[63] which is slightly smaller than IE[La^+] = 11.1 eV.[26] The relationship between the ionization energies of $PuOH^+$ and $AmOH^+$ and those of the bare Pu^+ and Am^+ ions suggests a similarity to transition metal hydroxide ions.[70,71] In the case of VOH^+, for example, IE[VOH^+] = 16.0 ± 0.4 eV[70,71] is ~1.3 eV greater than IE[V^+].[26] The observation that in these $AnOH^{2+}/H_2O$ reactions only proton transfer occurs for $ThOH^{2+}$, UOH^{2+}, and $NpOH^{2+}$, both proton transfer and electron transfer occur for $PuOH^{2+}$, and only electron transfer occurs for $AmOH^{2+}$, indicates a decreasing acidity of the $AnOH^{2+}$ and/or increasing ionization energy of the $AnOH^{+}$ upon proceeding across this portion of the actinide series. These results are in accord with the general trend for greater stability of lower oxidation states with increasing atomic number for the transuranium actinides.

It was also found that the secondary $Th(OH)_2^{2+}$ product reacts rather efficiently with a third H_2O molecule by proton transfer, with a reaction rate constant of $k = 9.9 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, which corresponds to $k/k_{COL} = 0.23$. The product, ThO_2H^+, is presumed to be the oxide hydroxide, $[OThOH]^+$, and Th remains tetravalent in an ion with a reduced net charge.

Electron-Transfer Reactions: Estimating the Ionization Energies of AnO_2^+. The actinyl ions, UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+}, each exhibited electron transfer with both O_2 and N_2O. Since the ionization energy of N_2O is 12.89 eV, it is concluded that $IE[AnO_2^+] \geq 12.89$ eV for An = U, Np, and Pu. As discussed below, this lower limit is an underestimate of the actual minimum exothermicity due to the nature of electron transfer from a neutral to a dipositive cation. From the same considerations, the absence of electron transfer with CO_2 cannot be used to establish an upper limit of 13.78 eV for the three $IE[AnO_2^+]$.

Marcus[72] employed a Born−Haber cycle based on the lattice energy of solid uranyl fluoride to obtain $\{IE[UO_2] + IE[UO_2^+]\} = 17.0 \pm 0.3$ eV. Using the very accurate $IE[UO_2] = 6.128 \pm 0.003$ eV determined by Han et al.,[59,60] this implies that $IE[UO_2^+] = 10.9 \pm 0.3$ eV, which contrasts with the lower limit of 12.8 eV reported previously[6] and with our lower limit of 12.9 eV (based on the observation of electron transfer to UO_2^{2+} from N_2O). We have examined electron-transfer reactions to obtain more accurate $IE[AnO_2^+]$ (An = U, Np, Pu) values given the importance of these fundamental quantities.

The ionization energies of neutral PuO_2 and AmO_2 have been determined by the electron-transfer "bracketing" technique,[12,13] using reactions of the type: $A^+ + B \rightarrow A + B^+$. In those experiments, the AnO_2^+ ions were exposed to different neutral reagents and the occurrence or nonoccurrence of electron transfer from the various neutrals established lower and upper limits for $IE[AnO_2]$. This "bracketing" approach is straightforward for monopositive cations as both the reactants and products consist of a neutral and a +1 ion, which exhibit an attractive interaction such that the kinetics are efficient and electron transfer can accordingly be interpreted in the context of thermodynamics. In contrast, the cationic products of the analogous electron-transfer experiments with dipositive cations, $A^{2+} + B \rightarrow A^+ + B^+$, exhibit a repulsive Coulombic interaction. The manifestations of this repulsive interaction have been discussed for a large number of systems.[21,31−46] Essentially, the repulsive interaction between the product ions introduces a substantial enthalpy during the electron-transfer process that must be exceeded for transfer to occur. This interaction depends on several factors, as first described by Spears et al.[36] using a simplified curve-crossing model of the Coulombic repulsion of products and the ion-induced dipole (and eventually ion−dipole) attraction of reagents. The minimum exothermicity, $\Delta E = IE[A^+] - IE[B]$, for the observation of electron transfer from B to A^{2+} has been estimated as ~1 eV[31] for the case of transition metal ions and organic neutrals, while in the case of the large C_{60}^{2+} ion, Bohme and co-workers[37−39] have estimated that electron transfer must be ~2.1 eV exothermic to occur. Although a lower barrier for electron transfer could be expected to occur for a large cation like C_{60}^{2+}, as compared with a smaller metal cation M^{2+}, due to a smaller Coulomb repulsion term, the evidence that in C_{60}^{2+} the two positive charges are located in two opposite points of the fullerene structure[37−41] may result in a smoother attractive curve as compared with one originated by a M^{2+} ion, and, therefore, in a shorter curve-crossing distance and consequent increased barrier for electron transfer.

TABLE 6: Rate Constants for Electron-Transfer from N_2O and CO_2 to Dipositive Metal Ions[a]

		N_2O			CO_2		
M^{2+}	$IE[M^+]$ (eV)	ΔE[b]	k	k/k_{COL}	ΔE[b]	k	k/k_{COL}
Sn^{2+}	14.63	1.74	0.008	0.01	0.85	(0.002)[c]	(0.001)[c]
Pb^{2+}	15.03	2.14	0.15	0.11	1.25	0.011	0.008
Mn^{2+}	15.64	2.75	0.76	0.44	1.86	0.014	0.014
Ge^{2+}	15.93	3.04	0.89	0.55	2.15	0.33	0.22
Bi^{2+}	16.69	3.80	0.56	0.40	2.91	0.45	0.34

[a] The pseudo-first-order reaction rate constants, k, are in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. The estimated errors are ±50% absolute and ±20% relative. The second ionization energies, $IE[M^+]$, are from ref 26. [b] ΔE is the difference between the ionization energies, $\{IE[M^+] - IE[N_2O]\}$ or $\{IE[M^+] - IE[CO_2]\}$, in eV. [c] The correction to k for electron-transfer to Sn^{2+} from background gases is uncertain by the measured rate constant ($k = 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}) for the Sn^{2+}/CO_2 reaction. From these results it cannot be concluded that electron-transfer from CO_2 to Sn^{2+} occurred at a measurable rate.

The early work of Spears et al.[36] indicated that, as predicted from the curve-crossing model, upon reaching a certain excess exothermicity, the efficiency of electron transfer to a dipositive ion should be high and remain nearly constant with increasing exothermicity: the threshold exothermicity, ΔE, for electron transfer to Mg^{2+} was ~1.2 eV and the transfer efficiency was essentially constant for ΔE over the range of 2.1−5.8 eV. This "plateau" phenomenon is reflected by the dominance of electron transfer over other reaction channels above $\Delta E \sim 2.5$ eV (which corresponds to a critical transfer distance of ~6 Å) as reported by Roth and Freiser.[31] Results given below for the electron transfer from N_2O to metal dipositive ions are in accord with such a leveling of reaction efficiency above a certain ΔE.

In the present study, the efficiency of electron transfer for two of the neutral reagents, N_2O and CO_2, was studied with several dipositive metal ions having a range of electron affinities. The results are given in Table 6, where from the results with CO_2 it would appear that the electron-transfer onset occurs at $\Delta E \sim 1.2$ eV. Because $k/k_{COL} = 0.001$ is considered the detection limit for this technique, the apparently measurable rate for the Sn^{2+}/CO_2 electron-exchange reaction deserves further consideration. As noted in Table 6, the correction for electron transfer from the background was comparable to the very low measured Sn^{2+}/CO_2 rate constant, and the adjustment to the measured electron-transfer rate is uncertain by approximately the detection limit. Accordingly, the results presented in Table 6 cannot necessarily be taken to indicate electron transfer from CO_2 to Sn^{2+}. This conclusion in conjunction with other considerations discussed below indicate that for the purposes of this calibration it should be considered that the extent of electron transfer from CO_2 to Sn^{2+} is negligible under fully thermal conditions. This interpretation is supported by other studied electron-transfer reactions, in particular, in the work of Spears et al.[36] that reported an electron-transfer efficiency of only 0.008 for Mg^{2+}/CO_2 ($\Delta E = 1.27$ eV), in accord with the Pb^{2+}/CO_2 results here, and reported no transfer for Mg^{2+}/CO ($\Delta E = 1.03$ eV). It would seem highly improbable that Sn^{2+}/CO_2 ($\Delta E = 0.85$ eV) should exhibit electron transfer at a measurable rate under thermal conditions.

The calibration for electron transfer with N_2O and CO_2 was performed using atomic metal dipositive ions. Somewhat different behavior might be expected for dioxo cations because factors including the polarizability of the AnO_2^+ products are pertinent.[36] However, previous results[31] suggest that such factors are relatively minor, except for extreme cases such as C_{60}^{2+}[37−39] where a very large dipositive ion is involved. The actinyl ions can be approximately represented as $O{=}An^{2+}{=}O$, with the +2 charge located on the metal, so that electron-transfer behavior should be similar to that for bare metal ions. This is in contrast to a large molecular ion such as C_{60}^{2+} where the two positive charges may be located in two opposite points of the fullerene structure.[37−41] Accordingly, it is considered valid to employ a calibration with bare M^{2+} to estimate AnO_2^+ ionization energies; the uncertainties assigned to the IE[AnO_2^+] reported below take into consideration the nature of the calibration. The results with N_2O indicate that the electron-transfer efficiency becomes essentially constant ($k/k_{COL} \sim 0.5$) for $\Delta E > \sim 2.5$ eV, in accord with the evaluation by Roth and Freiser.[31] Our results with CO_2 are also consistent with this. From the M^{2+}/N_2O and M^{2+}/CO_2 calibration results, it would appear that the barrier to electron transfer does not vary substantially among the five M^{2+} that were employed: k/k_{COL} increases with ΔE until a nearly constant value is attained for $\Delta E > 2.5$. This minor effect of the nature of the metal ion enhances confidence in the validity of this calibration for the oxo-ligated actinide metal dipositive ions.

The following electron-transfer rate constants (cm^3 molecule^{-1} s^{-1}) and efficiencies (k/k_{COL}) were measured for the actinyls with N_2O: $UO_2^{2+}/3.2 \times 10^{-11}$, 0.02; $NpO_2^{2+}/6.8 \times 10^{-10}$, 0.49; $PuO_2^{2+}/5.7 \times 10^{-10}$, 0.42. Comparing these efficiencies with those obtained for metal dications with N_2O (Table 6), we conclude that the ionization energy of UO_2^+ is similar to that of Sn^+: IE[UO_2^+] = 14.6 ± 0.4 eV. This value is consistent with the derived upper limit of 16.2 eV, the range of 14.6 ± 1.7, and the narrower range of 15.1 ± 1.2 eV, where it was assumed that $\Delta E \geq 1$ eV. It is also within the range of 15.4 ± 2.6 eV that was previously reported based on experimental results.[6] In that report,[6] calculated values for IE[UO_2^+] of 14.63 and 15.05 eV were also given. Three calculational determinations of IE[UO_2^+] have been reported in recent years.[62,69,73] Zhou et al.[73] obtained 15.31 eV; Gagliardi et al.[62] obtained two values, 14.02 and 14.36 eV (and also cited values of 14.41 and 15.25 eV from earlier work); and Majumdar et al.[69] obtained values of 19.4 and 19.71 eV. With the exception of the last two values in excess of 19 eV, which are well above the thermochemically established upper limit of 16.2 eV, the other results from theory are in reasonable agreement with our experimental value of 14.6 ± 0.4 eV.

As the k/k_{COL} are essentially the same within the ±20% relative uncertainty (all are in the range of 0.40−0.55) for Mn^{2+}, Ge^{2+}, Bi^{2+}, NpO_2^{2+}, and PuO_2^{2+}, we conclude that the ΔE for electron transfer to these two actinyls from N_2O lie near or in the "plateau" region, which occurs above IE[Pb^+] = 15.03 eV, IE[NpO_2^+] and IE[PuO_2^+] ≥ 15.0 ± 0.4 eV. It is evident from the comparative rate constants for electron transfer from N_2O, that both IE[NpO_2^+] and IE[PuO_2^+] are significantly greater than IE[UO_2^+], in accord with the thermodynamic properties in aqueous solution discussed below. None of the three AnO_2^{2+} ions exhibited electron transfer with CO_2, suggesting that all three ΔE were below the necessary threshold. Based on the calibration with dipositive metal ions (Table 6), it would appear that the electron-transfer threshold for CO_2 is between IE[Sn^+] = 14.6 eV (ΔE = 0.9 eV) and IE[Pb^+] = 15.0 eV (ΔE = 1.3 eV). Given that IE[NpO_2^+] and IE[PuO_2^+] are greater than IE[UO_2^+] from the N_2O results, and should not substantially exceed IE[Pb^+] from the CO_2 results, we assign the following values: IE[NpO_2^+] ≈ IE[PuO_2^+] = 15.1 ± 0.4 eV. Comparing the dioxide second ionization energies with the corresponding values for the monoxides (Table 4), we conclude that IE[AnO_2^+] > IE[AnO^+], as would generally be expected. These new IE[AnO_2^+] are combined with the revised ΔH_f[AnO_2^+] given above, 115 ± 50 kJ mol^{-1} for UO_2^+ and 270 ± 54 kJ mol^{-1} for PuO_2^+, to obtain ΔH_f[UO_2^{2+}] = 1524 ± 63 kJ mol^{-1} and ΔH_f[PuO_2^{2+}] = 1727 ± 66 kJ mol^{-1}. These values compare favorably with the more uncertain values estimated above, ΔH_f[UO_2^{2+}] = 1473 ± 192 kJ mol^{-1} and ΔH_f[PuO_2^{2+}] = 1722 ± 262 kJ mol^{-1}.

The following electron-transfer rates for AnO_2^{2+} ions with O_2 were measured: $UO_2^{2+}/k = 1.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, k/k_{COL} = 0.11; and $NpO_2^{2+}/k = 3.6 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, k/k_{COL} = 0.32. A M^{2+} calibration was not performed using O_2, but the actinyl results are qualitatively consistent with the smaller IE[O_2] and resulting larger ΔE, and with IE[NpO_2^+] > IE[UO_2^+].

Hydration Enthalpies of the Dipositive and Monopositive Actinyl Ions. Knowing ΔH_f[AnO_2^{2+}(g)] and ΔH_f[AnO_2^{2+}(aq)],[19] it is possible to calculate the hydration enthalpies, ΔH_{hyd}[AnO_2^{2+}], by the standard procedure applied to both bare actinide ions and UO_2^{2+}.[20] The pertinent relationship is given by eq 5:[20]

$$\Delta H^0_{hyd}[M^{z+}] = \Delta H^0_f[M^{z+}(aq)] - \Delta H^0_f[M^{z+}(g)] + z(\Delta H^0_f[H^+(g)] + \Delta H^0_{hyd}[H^+(aq)]) \quad (5)$$

In eq 5, ΔH^0_f[H^+(g)] = 1530 kJ mol^{-1}.[53] We use ΔH^0_{hyd}[H^+(aq)] = −1091 ± 10 kJ mol^{-1} from Halliwell and Nyburg.[74] An alternative value of ΔH^0_{hyd}[H^+(aq)] = −1150 ± 1 kJ mol^{-1} was recently reported by Tissandier et al.[75] The earlier value is used here to retain consistency with other assessments that have relied on this value.[20] If ΔH^0_{hyd}[H^+(aq)] = −1150 kJ mol^{-1} is confirmed as the accurate value, the hydration enthalpies derived here (and elsewhere) must be adjusted by −118 kJ mol^{-1} for dipositive ions (z = 2) and by −59 kJ mol^{-1} for monopositive ions (z = 1).

Using our ΔH_f[UO_2^{2+}(g)] = 1524 ± 63 kJ mol^{-1} and ΔH_f[UO_2^{2+}(aq)] = −1019 ± 3 kJ mol^{-1},[19] we obtain ΔH_{hyd}[UO_2^{2+}] = −1665 ± 64 kJ mol^{-1}. This hydration enthalpy is substantially more exothermic than the −1345 kJ mol^{-1} reported by Markus and Loewenschuss[67] and by Rizkalla and Choppin,[20] where both used ΔH_f[UO_2^{2+}(g)] = 1210 kJ mol^{-1} from Markus.[72] The ΔH_{hyd}[UO_2^{2+}] derived from our new ΔH_f[UO_2^{2+}(g)] is ~250 kJ mol^{-1} more exothermic than ΔH_{hyd}[U^{2+}],[20] whereas the previous value was ~70 kJ mol^{-1} less exothermic than ΔH_{hyd}[U^{2+}].[20] Rösch and co-workers[76] have carried out a density functional study of the hydration properties of UO_2^{2+}. The following relationship allows direct comparison of their calculated ΔE_{hyd}[UO_2^{2+}] = −1766 kJ mol^{-1} [76] with our experimental result: $\Delta H_{hyd}[UO_2^{2+}] = \Delta E_{hyd}[UO_2^{2+}] + \Delta^*[UO_2^{2+}] + T\Delta S_{hyd}[UO_2^{2+}]$. In this relationship Δ^*[UO_2^{2+}] ≈ 209 kJ mol^{-1} [76] is the estimated difference between the calculated hydration energy and the free energy of hydration at 298 K.[76] Using ΔS_{hyd}[UO_2^{2+}] = 400 J K^{-1} mol^{-1}[20] and T = 298 K, the theoretically determined ΔH_{hyd}[UO_2^{2+}] is −1676 kJ mol^{-1}.[76] This calculated value is very close to our experimental value of ΔH_{hyd}[UO_2^{2+}] = −1665 ± 64 kJ mol^{-1}.

From ΔH_f[PuO_2^{2+}(g)] = 1727 ± 66 kJ mol^{-1} and ΔH_f[PuO_2^{2+}(aq)] = −822 ± 7 kJ mol^{-1},[19] we obtain ΔH_{hyd}[PuO_2^{2+}] = −1671 ± 67 kJ mol^{-1}, which is essentially the same as the value obtained for UO_2^{2+}. These two ΔH_{hyd}[AnO_2^{2+}] values of approximately −1670 kJ mol^{-1} compare with ΔH_{hyd}[U^{2+}] = −1413 kJ mol^{-1}, ΔH_{hyd}[Pu^{2+}] = −1452 kJ mol^{-1}, ΔH_{hyd}[U^{3+}]

$= -3371$ kJ mol^{-1} and $\Delta H_{hyd}[Pu^{3+}] = -3447$ kJ mol^{-1}.[20] As predicted by Marcus and Loewenschuss,[67] the hydration enthalpies of the AnO_2^{2+} are similar to those of the An^{2+}. The $\sim$250 kJ mol^{-1} more favorable (i.e., more negative) hydration enthalpies for the two AnO_2^{2+} compared with the corresponding bare An^{2+} might be attributed to a charge greater than +2 at the metal center in the actinyl ions.[20] Assuming that $\Delta H_{hyd}[NpO_2^{2+}] \approx \Delta H_{hyd}[AmO_2^{2+}] \approx -1670$ kJ mol^{-1}, and using $\Delta H_f[NpO_2^{2+}(aq)] = -861 \pm 5$ kJ mol^{-1} and $\Delta H_f[AmO_2^{2+}(aq)] = -652 \pm 2$ kJ mol^{-1} from Morss,[19] we obtain $\Delta H_f[NpO_2^{2+}(g)] \approx 1687$ kJ mol^{-1} and $\Delta H_f[AmO_2^{2+}(g)] \approx 1896$ kJ mol^{-1}.

Hydration enthalpies can also now be derived for the monopositive dioxo ions, AnO_2^+, that are found in aqueous solution.[14,19] Using the revised $\Delta H_f[UO_2^+(g)] = 115 \pm 50$ kJ mol^{-1} and $\Delta H_f[PuO_2^+(g)] = 270 \pm 54$ kJ mol^{-1} given above, together with $\Delta H_f[UO_2^+(aq)] = -1033 \pm 6$ kJ mol^{-1} and $\Delta H_f[PuO_2^+(aq)] = -915 \pm 6$ kJ mol^{-1},[19] the following hydration enthalpies are obtained using eq 5, and the values for $\Delta H^0_f[H^+(g)]$ and $\Delta H^0_{hyd}[H^+(aq)]$ cited above (after eq 5): $\Delta H_{hyd}[UO_2^+] = -709 \pm 51$ kJ mol^{-1} and $\Delta H_{hyd}[PuO_2^+] = -746 \pm 55$ kJ mol^{-1}. From the bond dissociation energies, BDE[OAn^+-O], previously estimated for NpO_2^+ (580 ± 70 kJ mol^{-1})[12] and AmO_2^+ (390 ± 40 kJ mol^{-1}),[13] $\Delta H_f[AnO_2^+]$ can be derived from the following relationship: $\Delta H_f[AnO_2^+] = \{\Delta H_f[AnO^+] + \Delta H_f[O] - \text{BDE}[OAn^+\text{-}O]\}$. Using the $\Delta H_f[AnO^+]$ in Table 4 and $\Delta H_f[O] = 249$ kJ mol^{-1},[53] we obtain $\Delta H_f[NpO_2^+(g)] = 215 \pm 82$ kJ mol^{-1} and $\Delta H_f[AmO_2^+(g)] = 410 \pm 50$ kJ mol^{-1}. Using $\Delta H_f[NpO_2^+(aq)] = -978 \pm 5$ kJ mol^{-1} and $\Delta H_f[AmO_2^+(aq)] = -805 \pm 5$ kJ mol^{-1},[19] the following hydration enthalpies can then be derived: $\Delta H_{hyd}[NpO_2^+] = -754 \pm 83$ kJ mol^{-1} and $\Delta H_{hyd}[AmO_2^+] = -776 \pm 51$ kJ mol^{-1}. The four $\Delta H_{hyd}[AnO_2^+]$ are in reasonable agreement within the reported uncertainties. A general trend of more exothermic hydration upon proceeding from UO_2^+ to AmO_2^+ is in line with the derived hydration enthalpies. The $\Delta H_{hyd}[AnO_2^{2+}]$ values are more than twice as negative as are the corresponding $\Delta H_{hyd}[AnO_2^+]$ values. However, the decrease in hydration enthalpy between the corresponding +2 and +1 dioxo ions is smaller than the decrease generally associated with bare +2 and +1 metal ions.[77] For example, $\Delta H_{hyd}[Cs^+] = -263$ kJ mol^{-1} vs $\Delta H_{hyd}[Ba^{2+}] = -1304$ kJ mol^{-1};[77] the latter is very close to $\Delta H_{hyd}[Ac^{2+}]$ and is $\sim$100−200 kJ less negative than most other $\Delta H_{hyd}[An^{2+}]$ values.[20] That the $\Delta H_{hyd}[AnO_2^+]$ are significantly more negative than predicted based on the analogy with bare metal ions might be due to the electron withdrawing effect of the oxo-ligands, which produces a greater effective charge at the metal center. The effect of the oxo-ligands appears to be smaller for the +2 dioxo ions, as indicated by the fact that the $\Delta H_{hyd}[AnO_2^{2+}]$ are closer to the typical values for bare +2 metal ions.

The estimated $\Delta H_f[NpO_2^+(g)] = 215 \pm 82$ kJ mol^{-1} from the preceding paragraph can be combined with $\text{IE}[NpO_2^+] = 15.1 \pm 0.4$ eV to derive $\Delta H_f[NpO_2^{2+}(g)] = 1671 \pm 91$ kJ mol^{-1}. This is close to the value of $\Delta H_f[NpO_2^{2+}(g)] \approx 1687$ kJ mol^{-1} that was derived above by assuming $\Delta H_{hyd}[NpO_2^{2+}] \approx -1670$ kJ mol^{-1}, in support of the assignment of this hydration enthalpy for neptunyl.

Intrinsic Stabilities of the Dipositive Actinyl Ions. The AnO_2^+ ionization energies are important in predicting the potential for a Coulombic explosion of bare AnO_2^{2+} into $\{AnO^+ + O^+\}$ or into $\{An^+ + O_2^+\}$, which would be indicative of the intrinsic instability of the bare AnO_2^{2+}. Coulombic explosion of an AnO_2^{2+} into $\{AnO^+ + O^+\}$ will be exothermic if the following quantity is negative: $\{\text{BDE}[OAn^+\text{-}O] + \text{IE}[O] - \text{IE}[AnO_2^+]\}$. Using IE[O] = 13.618 eV,[47] the lower limit of $\text{BDE}[OU^+\text{−}O] \geq 632$ kJ mol^{-1},[12] and our $\text{IE}[UO_2^+] = 14.6$ eV, we conclude that the bare UO_2^{2+} should be stable relative to $\{UO^+ + O^+\}$ by at least 5.6 eV. Using $\text{BDE}[OAn^+\text{-}O] \geq 498$ kJ mol^{-1} [12] and $\text{IE}[AnO_2^+] \approx 15.1$ eV for An = Np and Pu, both NpO_2^{2+} and PuO_2^{2+} are predicted to be stable relative to $\{AnO^+ + O^+\}$ by at least 3.7 eV.

The Coulombic explosion of an AnO_2^{2+} ion into $\{An^+ + O_2^+\}$ will be exothermic if $\{\text{BDE}[OAn^+\text{-}O] + \text{BDE}[An^+\text{-}O] + \text{IE}[O_2] - \text{BDE}[O\text{−}O] - \text{IE}[AnO_2^+]\}$ is negative. Using IE[O_2] from Table 1, the lower limits of BDE[OAn^+-O] indicated above, the lower limits of $\text{BDE}[An^+\text{-}O] \geq 752$ kJ mol^{-1} for An = U and Np,[12] and of $\text{BDE}[Pu^+\text{−}O] \geq 632$ kJ mol^{-1},[12] and our values of IE[AnO_2^+], we conclude that UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+} are stable relative to $\{An^+ + O_2^+\}$ by at least 6.6, 4.8, and 3.5 eV, respectively.

Coulombic explosion is a process where the unresolved issue of the role of entropy in gas-phase ion chemistry under low-pressure conditions may be pertinent.[48,78] If the entropies of AnO_2^{2+}, AnO^+, and An^+ are comparable, then the favorable entropy changes associated with Coulombic dissociation will be dominated by the formation of the atomic oxygen ion, $-T.S[O^+] = -46$ kJ mol^{-1} (−0.48 eV) at 298 K,[79] or of the molecular oxygen ion, $-T.S[O_2^+] = -61$ kJ mol^{-1} (−0.64 eV) at 298 K,[79] according to the classical approach of Irikura.[48] Even if the potential 0.5 or 0.6 eV entropic destabilizations are included in the assessment, bare UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+} are still predicted to be thermodynamically stable species at room temperature.

Aqueous thermochemistry can be employed to estimate IE[AmO_2^+] and the stability of bare AmO_2^{2+} ion. The electrochemical half-reaction given by eq 6 corresponds to the "ionization" of hydrated AnO_2^+.

$$AnO_2^+(aq) \rightarrow AnO_2^{2+}(aq) + e^- \qquad (6)$$

The relative enthalpies for eq 6, $\Delta H_f[AnO_2^{2+}(aq)] - \Delta H_f[AnO_2^+(aq)]$, are 0.15 ± 0.07 eV for UO_2^+; 1.21 ± 0.07 eV for NpO_2^+; 0.96 ± 0.09 eV for PuO_2^+; and 1.59 ± 0.05 eV for AmO_2^+.[19] If it is assumed that the change in enthalpy of hydration associated with eq 6, $\Delta H_{hyd}[AnO_2^{2+}] - \Delta H_{hyd}[AnO_2^+]$, is nearly constant for these four An, it would then follow that IE[UO_2^+] should be $\sim$1.06 ± 0.10 eV less than IE[NpO_2^+], and $\sim$0.81 ± 0.11 eV less than IE[PuO_2^+]. It was concluded from the gas-phase electron-transfer results that this difference from IE[UO_2^+] is actually 0.5 ± 0.6 eV for both IE[NpO_2^+] and IE[PuO_2^+]. The values in aqueous solution are consistent with the trend in the gas-phase values obtained above, $\text{IE}[UO_2^+] < \text{IE}[PuO_2^+] \approx \text{IE}[NpO_2^+]$. Accordingly, it can be concluded that $\text{IE}[AmO_2^+] > \text{IE}[PuO_2^+]$ and a difference of 0.6 eV between these two quantities can be estimated, leading to $\text{IE}[AmO_2^+] = 15.7 \pm 0.9$ eV, where the large uncertainty primarily reflects potential variations in the enthalpies of hydration. From this estimate for IE[AmO_2^+] and the estimate of $\Delta H_f[AmO_2^+(g)] = 410 \pm 50$ kJ mol^{-1} given above, we conclude that $\Delta H_f[AmO_2^{2+}(g)] = 1924 \pm 100$ kJ mol^{-1}. This latter value compares favorably with $\Delta H_f[AmO_2^{2+}(g)] \approx 1896$ kJ mol^{-1} that was obtained above by assuming $\Delta H_{hyd}[AmO_2^{2+}] \approx -1670$ kJ mol^{-1}, the same hydration enthalpy as for the other actinyl ions. This agreement between the two $\Delta H_f[AmO_2^{2+}(g)]$ further supports the conclusion that $\Delta H_{hyd}[AnO_2^{2+}] \approx -1670$ kJ mol^{-1} for An = U, Np, Pu, and Am.

Using the estimated $\text{IE}[AmO_2^+] = 15.7$ eV, $\text{BDE}[OAm^+\text{−}O] \geq 354$ kJ mol^{-1} [13] and $\text{BDE}[Am^+\text{−}O] \geq 532$ kJ mol^{-1},[13] it is predicted that AmO_2^{2+} will be stable relative to $\{AmO^+ + O^+\}$ by at least 1.6 eV and to $\{Am^+ + O_2^+\}$ by at least 0.4 eV. If the estimated BDE[OAm^+-O] = 390 kJ mol^{-1} and BDE[Am^+-O] = 560 kJ mol^{-1} from ref 13 are employed, rather than the lower limits of these quantities, AmO_2^{2+} is therefore predicted to be stable by 2.0 eV relative to $\{AmO^+ + O^+\}$ and by 1.0 eV relative to $\{Am^+ + O_2^+\}$. Considering the 0.9 eV uncertainty in IE[AmO_2^+] and the possibility of up to a 0.6 eV entropic destabilization, bare AmO_2^{2+} is still predicted to be an intrinsically stable dipositive ion relative to $\{AmO^+ + O^+\}$, but it remains uncertain whether it is stable relative to $\{Am^+ + O_2^+\}$.

Summary

In the work reported here, FTICR-MS has been employed to study gas-phase reactions of bare, oxo-ligated, and hydroxo-ligated dipositive ions of five actinides, Th, U, Np, Pu, and Am, with several oxidants, N_2O, C_2H_4O, H_2O, O_2, CO_2, NO, and CH_2O. With the exception of some previous oxidation studies of U^{2+} and UO^{2+},[6,9] this work represents the first systematic study of such fundamental dipositive gas-phase actinide ion chemistry. Earlier efforts have addressed the corresponding reactions of the monopositive cations;[12,13] an extension to doubly charged ions is particularly significant in view of the role of multiply charged actinide ions, notably the dipositive actinyls, in condensed-phase chemistry. Pseudo-first-order reaction rate constants were measured for several of the reactions and are reported as absolute values and reaction efficiencies, k/k_{COL}.

Each of the five studied An^{2+} ions reacted with at least one of the oxidants to produce AnO^{2+}. The measured oxidation efficiencies, k/k_{COL}, ranged from 0.56 for the Th^{2+}/O_2 reaction down to 0.01 for the Am^{2+}/C_2H_4O reaction. For several An^{2+}/RO reactions the oxidation efficiency was below the detection limit of ~0.001. Lower limits were thereby established for each bond energy, and we arrived at estimates of these energies in the following order: BDE[Th^{2+}-O] > BDE[U^{2+}-O] > BDE-[Np^{2+}-O] > BDE[Pu^{2+}-O] > BDE[Am^{2+}-O]. This is consistent with the inert character of the quasi-valence 5f electrons at the actinide metal centers and the increasing energies needed to excite a 5f electron to a bonding outer valence 6d or 7s orbital when proceeding to an An^{2+} with a higher atomic number.[50] Heats of formation for the AnO^{2+} ions and the ionization energies for the AnO^+ ions were derived based on observed An^{2+}/RO oxidation reactions.

Each of the An^{2+} ions reacted with H_2O to produce $AnOH^{2+}$. The efficiencies for these reactions ranged from from $k/k_{COL} = 0.15$ for Th^{2+} to $k/k_{COL} = 0.001$ for Pu^{2+} and Am^{2+}. Reactions of the primary $AnOH^{2+}$ ion with a second H_2O molecule revealed different reactivities, which are consistent with known actinide redox behaviors.

Several reactions of AnO^{2+} ions with oxidants were studied. The bare dipositive actinyl ions, AnO_2^{2+}, were formed with An = U, Np, and Pu. While bare uranyl had been similarly produced in previous studies,[6,9] this work represents the first syntheses of bare neptunyl and plutonyl ions. All three AnO_2^{2+} ions resulted from the AnO^{2+}/N_2O reactions, whereas only uranyl and neptunyl formed from the AnO^{2+}/O_2 reactions. Lower limits for the BDE[OAn^{2+}-O] are deduced from the observed reactions. The kinetics of electron-transfer reactions from N_2O to the actinyls were used to arrive at the following second ionization energy estimates for the dioxo ions: IE[UO_2^+] = 14.6 ± 0.4 eV; IE[NpO_2^+] = 15.1 ± 0.4 eV; and IE[PuO_2^+] = 15.1 ± 0.4 eV. These ionization energies in conjunction with other thermodynamic information indicate that bare UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+} ions are thermodynamically stable as isolated dipositive ions. The derived enthalpies of hydration for UO_2^{2+} and PuO_2^{2+} ions were essentially the same as one another but are significantly more negative than the value previously reported for UO_2^{2+}.[20] If a constant enthalpy for actinyl hydration is assumed, $\Delta H_{hyd}[AnO_2^{2+}] \approx -1670$ kJ mol^{-1}, and based on established aqueous thermodynamics of the americyl ion, bare AmO_2^{2+} ion is estimated to be intrinsically stable by ~2.0 eV relative to dissociation into $\{AmO^+ + O^+\}$ and stable by ~1.0 eV relative to dissociation into $\{Am^+ + O_2^+\}$.

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