Gas-Phase Oxidation Reactions of Neptunium and Plutonium Ions Investigated via Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

Marta Santos,[†] Joaquim Marçalo,*,[†] António Pires de Matos,[†] John K. Gibson,*,[‡] and Richard G. Haire[‡]

Departamento de Química, Instituto Tecnológico e Nuclear, 2686-953 Sacavém, Portugal, and Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6375

Received: March 6, 2002; In Final Form: June 5, 2002

The first gas-phase ion chemistry studies of the transuranium actinides Np and Pu by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR-MS) have been performed. Reactions of An^+ and AnO^+ (An = Th, U, Np, and Pu) with N_2O, C_2H_4O (ethylene oxide), H_2O, O_2, CO_2, NO, and CH_2O have been studied, with a focus on the oxidation of transuranium ions. All the An^+ ions formed AnO^+ with all the oxidants studied, with the exception of Pu^+ with CH_2O, in accord with the known bond dissociation energies, BDE(An^+-O). The reaction efficiencies appear to correlate with the magnitude of the promotion energies from the ground states to reactive-state configurations of the An^+ ions. Only N_2O and C_2H_4O oxidized all AnO^+ to AnO_2^+; CO_2 and NO oxidized only UO^+; H_2O and O_2 oxidized UO^+, NpO^+, and PuO^+; and CH_2O was unreactive with all the AnO^+ ions. The observed formation of PuO_2^+ from the oxidants weaker than N_2O is in conflict with the literature values for BDE(OPu^+-O), which we conclude are significantly too low. Charge-transfer “bracketing” experiments to determine the ionization energy of PuO_2 were performed, from which a value of 7.03 ± 0.12 eV was obtained. This IE(PuO_2) is 2−3 eV lower than the literature values, but in accord with our observations for the oxidation thermodynamics.

Introduction

Reactivity studies of actinide (An) ions in the gas phase, based on the use of Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR-MS), have until now been limited to Th and U,[1−7] due to the highly radioactive nature of the other members of the series. A special experimental setup installed at Oak Ridge National Laboratory (ORNL), based on the Laser Ablation with Prompt Reaction and Detection (LAPRD) technique, made possible the first gas-phase chemistry studies of Np, Pu, Am, Cm, Bk, and Cf ions,[8−17] and preliminary studies with Pa and Es ions.[18] These LAPRD gas-phase chemistry studies of actinide ions, as well as earlier work, have been recently reviewed.[19] At Instituto Tecnológico e Nuclear (ITN), conditions for handling small amounts of highly radioactive samples in the FTICR-MS lab have been recently established to examine gas-phase chemistry of actinide ions other than Th and U, to complement the considerable LAPRD work. Since FTICR-MS is a more adequate technique to acquire information on kinetics, mechanisms, and energetics, with these studies we will try to obtain fundamental kinetic and thermodynamic data on gaseous actinide ions, gain a better insight into the potential 5f electron contribution to reactivity in the first half of the An series, and estimate energetic data for An species that may be of interest for condensed-phase processes. Comprehensive descriptions of FTICR-MS fundamentals[20−22] and of applications to gas-phase metal ion chemistry[22−26] are available. In the present work, we examine by FTICR-MS the reactions of An^+ and AnO^+ ions (An = Th, U, Np, Pu) with N_2O, C_2H_4O (ethylene oxide), H_2O, O_2, CO_2, NO, and CH_2O, with a focus on the oxidation of transuranium ions, expanding a previous study of Np^+ and Pu^+ with C_2H_4O by the LAPRD technique.[16] The latter effort revealed inconsistencies with the reported thermochemistry of Pu oxides. Reactions of Th^+ and U^+ ions with N_2O, H_2O, O_2, and CO_2 have been previously studied by Schwarz and co-workers.[6]

Experimental Section

All experiments were performed in a Finnigan FT/MS 2001-DT FTICR mass spectrometer, equipped with a 3 T superconducting magnet, a Spectra-Physics Quanta-Ray GCR-11 Nd:YAG laser operated at the fundamental wavelength (1064 nm), and a Finnigan Venus Odyssey data system.

The actinide samples consisted of alloys of ~5% of an actinide metal in a Pt matrix, prepared by direct melting of the An metal with Pt in arc-melting furnaces, using water-cooled copper crucibles under Ti-gettered high-purity argon atmospheres. The sample with natural Th was prepared at ITN, while the samples containing natural U, Np-237, and Pu-242 were prepared at ORNL.

The reagent gases N_2O, O_2, CO_2, and NO were obtained commercially and used as purchased (purity > 99%). C_2H_4O, obtained commercially (purity > 99%), was degassed prior to use. The H_2O was thoroughly deoxygenated by bubbling with high-purity N_2, and degassed prior to use. Dry, gaseous CH_2O was prepared from a commercial aqueous solution according to a literature procedure.[27] The reagents for the bracketing experiments were commercial products (purity > 98%) and used as acquired, except for the liquids, which were degassed prior to use. The reagents were checked in situ for their purity through

---

* Corresponding authors. (J. Marçalo) Fax: +351.21.994.1455. E-mail: jmarcalo@itn.pt. (J. K. Gibson) Fax: +1.865.574.4987. E-mail: gibsonjk@ornl.gov.

[†] Instituto Tecnológico e Nuclear.

[‡] Oak Ridge National Laboratory.

10.1021/jp025733f CCC: $22.00

TABLE 1: Bond Dissociation Energies (BDE) of the Oxidizing Reagents RO (in kJ/mol)[a]

RO	N_2O	C_2H_4O	H_2O	O_2	CO_2	NO	CH_2O
BDE(R−O)	167.1 ± 0.1	354.3 ± 0.6	491.0 ± 0.1	498.4 ± 0.1	532.2 ± 0.2	631.6 ± 0.4	751.5 ± 0.1

[a] Ref 34.

EI spectra. All 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.

The actinide metal ions were produced by direct laser desorption/ionization (LDI) of small pieces of the alloys, mounted on the solids probe of the instrument. Ion selection, namely isolation of the actinide metal ions from the abundant Pt ions formed in the LDI process and isolation of the actinide oxide ions after an initial formation period, was achieved using single-frequency, frequency-sweep, or SWIFT excitation.[28] In the "bracketing" experiments, PuO_2^+ was produced by reaction of Pu^+ with O_2 introduced into the instrument through pulsed valves; the charge-exchange reagents were introduced through a leak valve.

Neutral pressures, measured by a Bayard-Alpert type ionization gauge, were calibrated using standard reactions of methane[29] and acetone[30] ions, and included corrections for the different ionization efficiencies of the reagents, calculated according to Bartmess and Georgiadis,[31] based on experimental molecular polarizabilities.[32]

Rate constants (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; each decay was followed until the consumption of the reagent ion had reached less than one tenth of the sum of all ion intensities. The rate constants are reported as fractions of the Average Dipole Orientation collisional rates (k_{ADO}),[33] that is, as reaction efficiencies, k/k_{ADO}. Collisional rates were calculated using experimental molecular polarizabilities and dipole moments of the neutral reagents.[32] Due to uncertainties in the pressure measurements, we estimate absolute errors of ±50% in the k/k_{ADO} values, but relative errors lower than 20%.

Thermalization of the reactant ions was performed for all the reactions by collisions with argon, introduced in the instrument through pulsed valves to pressures of ca. 10^{-5} Torr or through a leak valve at a constant pressure in the range of $(1-5) \times 10^{-6}$ Torr. Linearity of semilogarithmic plots of the reactant ion signal magnitudes versus time was taken as the main indication of the effectiveness of the thermalization of the reactant ions. Effective thermalization was also indicated by reproducibility of the reaction kinetics for different collisional cooling periods or collision gas pressures; as well as by the absence of changes in the product distributions in those cases where there was more than one product ion.

For obvious reasons, special care was taken to minimize the interference of reactions with residual water and oxygen in the instrument. This was accomplished by allowing long pumping times with the solids probe inside the high-vacuum chamber before introducing the oxidizing reagents. Also, the validity of the oxidation results was verified by comparison with reactions which occurred under typical background conditions.

Results and Discussion

Reactions of An^+ Ions with Oxidants. All four An^+ ions, Th^+, U^+, Np^+, and Pu^+, produced AnO^+ ions with each oxidant studied (N_2O, C_2H_4O, H_2O, O_2, CO_2, NO, and CH_2O), except in the case of Pu^+ with CH_2O, where no reaction was observed. Other products besides AnO^+ were observed in the reactions with N_2O (formation of AnN^+ for An = Th, U, and Np, with 50%, 40%, and 25% relative abundances, respectively) and with H_2O (formation of $AnOH^+$ for An = Th, with 35% relative abundance; for An = U and Np, formation of $AnOH^+$ was also observed only under conditions where thermalization was not effective). The results obtained in the cases of Th^+ and U^+ with N_2O, H_2O, O_2, and CO_2 are in agreement with a previous work of Schwarz and co-workers.[6]

TABLE 2: Bond Dissociation Energies (BDE) of the AnO^+ Ions (in kJ/mol)

AnO^+	ThO^+	UO^+	NpO^+	PuO^+
BDE(An^+−O)	875 ± 16[a]	807 ± 22[a]	773 ± 43[a]	
	866 ± 21[b]	803 ± 25[b]		683 ± 55[b]
		801 ± 22[c]		618 ± 22[c]
this work:	≥751.5	≥751.5	≥751.5	≥631.6

[a] Ref 35. [b] Ref 36. [c] Ref 37.

TABLE 3: Efficiencies (k/k_{ADO}) of the Reactions of An^+ Ions with Oxidizing Reagents

	N_2O	C_2H_4O	H_2O	O_2	CO_2	NO	CH_2O
Th^+	0.68	0.37	0.20	0.86	0.35	0.49	0.61
U^+	0.47	0.34	0.13	0.72	0.29	0.46	0.53
Np^+	0.48	0.32	0.10	0.68	0.30	0.45	0.28
Pu^+	0.02	0.21	0.004	0.27	0.003	0.17	<0.001

The oxygen dissociation energies for the seven oxidants studied are shown in Table 1, designated as R−O bond dissociation energies (BDE(R−O)). Formation of AnO^+ with CH_2O suggests that each BDE(An^+−O) ≥ BDE(H_2C−O) = 751.5 kJ/mol, for An = Th, U, and Np, which is consistent with the literature values reproduced in Table 2. The lower limit obtained in our experiments for BDE(Np^+−O) ≥ 751.5 kJ/mol, effectively narrows down the uncertainty of the only value found in the literature (see Table 2). In the case of Pu^+, observation of PuO^+ in the reaction with NO implies that BDE(Pu^+−O) ≥ 631.6 kJ/mol, in agreement with the literature values shown in Table 2, if reported uncertainties are taken into account; the nonobservation of PuO^+ in the reaction with CH_2O is in accord with these data. Because of the possibility of a particular kinetic hindrance in oxidation reactions of Pu^+ due to its electronic structure and energetics (see below), the evident inability of CH_2O to oxidize Pu^+ under nearly thermoneutral conditions cannot confidently be interpreted to indicate an upper limit for BDE(Pu^+−O). The new thermochemical results derived from this work for NpO^+ and PuO^+ are included in Table 2.

In Table 3 we present the efficiencies, k/k_{ADO}, of the reactions studied. For Th^+ and U^+ with N_2O, H_2O, O_2, and CO_2 the values obtained are roughly in agreement with the previous work of Schwarz et al.;[6] specifically, the lower k/k_{ADO} found in the reaction with H_2O as compared with the values obtained for the other three oxidants. The reaction efficiencies for the different An^+ ions vary in nearly the same way with all the oxidants: Th^+ is slightly more efficient than U^+ and Np^+, and Pu^+ is clearly the least efficient of the An^+ ions studied. These differences appear to correlate with the magnitude of the promotion energies from the ground state to an excited-state configuration of the An^+ ion, where two unpaired non-f electrons are available, as shown in Table 4: Pu^+ has a sizable promotion energy of 1.08 eV, while Th^+, U^+, and Np^+, have

TABLE 4: Promotion Energies from the Ground-State Configurations to Reactive- State Configurations of the An^+ Ions (with terms in parentheses)[38]

An^+	ground-state configuration	promotion lenergy (eV)	reactive state configuration
Th^+	$6d^27s$ ($^4F_{3/2}$)	0.00	$6d^27s$ ($^4F_{3/2}$)
U^+	$5f^37s^2$ ($^4I^O_{9/2}$)	0.04	$5f^36d7s$ ($^6L^O_{11/2}$)
Np^+	$5f^46d7s$ ($^7L_5$)	0.00	$5f^46d7s$ ($^7L_5$)
Pu^+	$5f^67s$ ($^8F_{1/2}$)	1.08	$5f^56d7s$ ($^8K^O_{7/2}$)

[a] Ref 38.

TABLE 5: Efficiencies (k/k_{ADO}) of the Reactions of AnO^+ with Oxidizing Reagents

	N_2O	C_2H_4O	H_2O	O_2	CO_2	NO	CH_2O
ThO^+	0.31	0.34	0.11	<0.001	<0.001	<0.001	<0.001
UO^+	0.08	0.30	0.009	0.45	0.004	0.11	<0.001
NpO^+	0.07	0.28	0.004	0.28	<0.001	<0.001	<0.001
PuO^+	0.003	0.15	0.002	0.07	<0.001	<0.001	<0.001

TABLE 6: Bond Dissociation Energies (BDE) of the AnO_2^+ Ions (in kJ/mol)

AnO_2^+	ThO_2^+	UO_2^+	NpO_2^+	PuO_2^+
BDE(OAn^+-O)	465 ± 21[a]	764 ± 24[a]		
	433 ± 30[b]	772 ± 56[b]		253 ± 77[b]
		772 ± 22[c]		261 ± 22[c]
this work:	≥354.3	≥631.6	≥498.4	≥498.4
			580 ± 70 (est.)	520 ± 20 (est.)

[a] Ref 35. [b] Ref 36. [c] Ref 37.

zero or near-zero promotion energies. The validity of this model in the elucidation of gas-phase actinide ion reactivity has been amply demonstrated in previous studies, as discussed in a recent review.[19]

Other factors definitely influence reaction efficiencies, namely, the neutral reagent can introduce kinetic restrictions beyond the exothermicity of the reactions. This is clearly the case for H_2O, which, as noted before by Schwarz and co-workers,[6] requires a considerable rearrangement to yield AnO^+ and H_2. It is interesting to note that this type of factor appears to have a more pronounced effect in the case Pu^+, which showed significantly lower reaction efficiencies with N_2O, H_2O, and CO_2. A similar diminution in reaction efficiency was previously found for Nd^+ when compared with Ce^+, most notably in reactions with CO_2.[6] Nd^+, like Pu^+, has a sizable promotion energy, 1.41 eV, whereas Ce^+, like the three other An^+ studied in the present work, has a negligible promotion energy.[39] It would appear that electronic excitation can play a significant role in oxidation kinetics for actinide and lanthanide metal ions. Accordingly, nonobservation of an oxidation reaction cannot necessarily be interpreted in a thermodynamic context.

Reactions of AnO^+ Ions with Oxidants. In the reactions of AnO^+ ions (An = Th, U, Np, and Pu) with the oxidizing reagents, formation of AnO_2^+ occurred with N_2O and C_2H_4O for all AnO^+ ions; with H_2O and O_2 for UO^+, NpO^+, and PuO^+; and with CO_2 and NO for UO^+. ThO^+ formed only ThO_2H^+ in the reaction with H_2O. All the AnO^+ ions were unreactive with CH_2O. The efficiencies k/k_{ADO} of the reactions are presented in Table 5. For ThO^+ and UO^+ with N_2O, H_2O, O_2, and CO_2, there is again a fair agreement with the previous work of Schwarz and co-workers.[6] Compared with the actinide metal ions, there is a general decrease in reactivity for all the monoxide ions, particularly in the cases where the reactions are thermodynamically favorable (see discussion below), revealing important kinetic restrictions. This decrease in reactivity is a general feature of the early actinides that has been seen in previous studies, as discussed in a recent review.[19] The strong An^+-O bonds (see Table 2), the accessible oxidation states of the actinide elements, and the electronic structures of the AnO^+ ions all appear to be influential.

In Table 6 we show the available literature data for BDE(OAn^+-O). Taking into account the BDE(R−O) values of Table 1, we can see a reasonable agreement of our results with the thermochemical data in the cases of Th and U (ThO_2^+ forming only with N_2O and C_2H_4O, UO_2^+ forming with all oxidants except CH_2O). It should be noted that in view of a potential kinetic limitation, the nonobservance of UO_2^+ from the reaction of UO^+ with CH_2O cannot necessarily be taken to indicate an upper limit of 751.5 kJ/mol for BDE(OU^+-O).

The formation of NpO_2^+ from the reaction of NpO^+ with O_2 indicates that BDE(ONp^+-O) exceeds 498.4 kJ/mol, but there is only limited literature data available for comparison in this case. From the data reported in a study of neutral NpO_2,[40] a value of BDE(ONp−O) = 666 ± 41 kJ/mol can be estimated, which, together with the ionization energies (IE) of NpO and NpO_2 from the literature,[36] and using eq 1:

$$\mathrm{BDE}(\mathrm{OAn}^+-\mathrm{O}) = \mathrm{BDE}(\mathrm{OAn}-\mathrm{O}) + \mathrm{IE}(\mathrm{AnO}) - \mathrm{IE}(\mathrm{AnO_2}) \quad (1)$$

leads to BDE(ONp^+-O) = 733 ± 64 kJ/mol. This value seems rather high and in a previous work[16] an estimate for BDE(ONp^+-O) = 600 ± 100 kJ/mol was made, built on experimental evidence. From the results obtained in the present work, we believe that we can go beyond the established lower thermodynamic bound of 498.4 kJ/mol and the crude estimates indicated above. Based on the very inefficient oxidation of UO^+ by CO_2 (see Table 5), the absence of detectable NpO_2^+ from the reaction of NpO^+ with CO_2 is not interpreted to establish an upper limit of BDE(ONp^+-O) of 532.2 kJ/mol. It is entirely feasible, if not probable, that kinetic effects result in the nonobservance of oxidation of NpO^+ by CO_2. Oxidation of AnO^+ by NO is evidently rather more efficient than by CO_2, as observed in the case of UO^+ (see Table 5), and an upper limit for BDE(ONp^+-O) in the vicinity of BDE(N−O) = 631.6 kJ/mol is tentatively inferred on the basis of the nonobservation of NpO_2^+ from the reaction of NpO^+ with NO. From these considerations, we arrive at an estimated BDE(ONp^+-O) of 580 ± 70 kJ/mol. This value is in accord with the rather efficient oxidation of NpO^+ by O_2 and it should be noted that the lower limit of the uncertainty range for this estimated value (∼510 kJ/mol) is close to the thermodynamically established lower limit of 498.4 kJ/mol.

In the case of Pu, formation of PuO_2^+ with O_2 also indicates that BDE(OPu^+-O) exceeds 498.4 kJ/mol, in distinct conflict with the literature values (Table 6), but confirming and extending the observations of a previous work,[16] where an estimate of BDE(OPu^+-O) = 450 ± 100 kJ/mol was made. We believe that the low values cited for BDE(OPu^+-O) in the literature (see Table 6) can be traced to the anomalously high ionization energy of PuO_2 reported in the same sources; this interpretation derives from the relationship given in eq 1.

Reported values of IE(AnO_2) are given in Table 7. Although it is predictable from experimental evidence that IE(PuO_2) should be larger than IE(UO_2) and IE(NpO_2),[41] it is intriguing that the reported IE(PuO_2) is larger than IE(ThO_2) in view of the accessible oxidation states of Th (+4) and Pu (+6). It is also rather surprising to see, from our experimental results, that PuO_2^+ is, with such a low reported BDE(OPu^+-O), inert toward

TABLE 7: Ionization Energies (IE) of AnO_2

AnO_2	ThO_2	UO_2	NpO_2	PuO_2
IE (eV)	8.7 ± 0.15[a]	5.4 ± 0.1[a]		
	8.7 ± 0.2[b]	5.5 ± 0.5[b]	5.0 ± 0.5[b]	9.4 ± 0.5[b]
		5.4 ± 0.1[c]		10.1 ± 0.1[c]
				7.03 ± 0.12[d]

[a] Ref 35. [b] Ref 36. [c] Ref 37. [d] This work.

TABLE 8: Ionization Energies (IE) of the Reagents Used in the Bracketing Experiments[a]

	IE (eV)
toluene	8.828 ± 0.001
p-cresol	8.34 ± 0.03
triethylamine	7.53 ± 0.01
diphenylamine	7.19 ± 0.05
N,*N*-dimethylaniline	7.12 ± 0.02
N,*N*-dimethyl-*p*-toluidine	6.93 ± 0.02
1,4-phenylenediamine	6.87 ± 0.05
ferrocene	6.71 ± 0.08

[a] Ref 34.

substrates such as H_2O and C_2H_4O (and the organic reagents used in the "bracketing" experiments described below), while ThO_2^+ readily abstracts a hydrogen from H_2O and C_2H_4O (and other organic substrates[6]) to form ThO_2H^+. The larger BDE($OPu^+{-}O$) derived from the present results is in better accord with the general chemical behavior of PuO_2^+.

Schwarz and co-workers have addressed several issues which can be relevant for the present discussion, including the bonding schemes in metal dioxide cations and their relations to IE of the neutral species and the reactivity toward hydrocarbons. Of particular note are a very interesting study of the oxidation properties of early transition-metal dioxide cations in the gas phase,[42] a detailed study of the CeO_2^+ cation,[43] and their comparative study of oxo-ligand effects in lanthanide and actinide gas-phase ion chemistry.[6]

Ionization Energy of PuO_2. In view of the substantial inconsistencies found for the thermochemistry of PuO_2^+, and our proposition that this derives primarily from the abnormally large literature values for the plutonium dioxide ionization energy, we undertook to independently obtain an accurate value for IE(PuO_2) from charge-transfer "bracketing" experiments[25,26,43−45] with PuO_2^+. The occurrence or nonoccurrence of charge transfer, when reacting PuO_2^+ with compounds with well-known IEs, gives us lower and upper bounds for IE(PuO_2). For this study we used the compounds listed in Table 8.

Charge transfer with PuO_2^+ was observed for *N*,*N*-dimethyl-*p*-toluidine, 1,4-phenylenediamine, and ferrocene, while it was not for *N*,*N*-dimethylaniline, diphenylamine, triethylamine, *p*-cresol, and toluene. If charge-transfer reactions have to compete with other reactions pathways, the accuracy of the "bracketing" procedure can be influenced, since the relative efficiencies of the reactions may depend on other than thermodynamic factors.[43−44] However, in our case, due to the low reactivity of PuO_2^+, we only observed slow adduct formation besides charge transfer with all the compounds studied. Thus, we arrive at IE(PuO_2) = 7.03 ± 0.12 eV, based on the observed charge transfer with *N*,*N*-dimethyl-*p*-toluidine and the nonobservation of that process with *N*,*N*-dimethylaniline.

To confirm the validity of our working conditions in these "bracketing" experiments, we performed a determination of IE(Mo), using Mo^+ formed by LDI of a pure piece of Mo metal and thermalized by collisions with argon. IE(Mo) was "bracketed" between *N*,*N*-dimethyl-*p*-toluidine and diphenylamine (the reaction with *N*,*N*-dimethylaniline was inconclusive due to the fact that charge transfer is very sensitive to thermalization, and represents a minor channel when compared to bond activation), leading to a value of 7.06 ± 0.18 eV, in agreement with the literature value of 7.09243 ± 0.00004 eV.[34]

The value obtained in the present work for IE(PuO_2), although substantially lower than the literature values, is intermediate between IE(UO_2) and IE(ThO_2), as expected (see Table 7 and the discussion above). Using eq 1, our new value for IE(PuO_2) = 7.03 eV, and BDE($OPu{-}O$) = 6.2 ± 0.2 eV and IE(PuO) = 6.6 ± 0.1 eV from Capone et al.[37] gives an approximate value for BDE($OPu^+{-}O$) = 557 ± 23 kJ/mol. This value is in accord with the observations made in the oxidation reactions, BDE($OPu^+{-}O$) $\geq$ 498.4 kJ/mol, but is probably too high; it places BDE($OPu^+{-}O$) very close to BDE($ONp^+{-}O$), which does not seem consistent with the relative reaction efficiencies of NpO^+ and PuO^+ with O_2, if reasoning similar to the one used above when we estimated BDE($ONp^+{-}O$) is employed. With these considerations in mind, we tentatively estimate a BDE($OPu^+{-}O$) = 520 ± 20 kJ/mol and include it in Table 6.

The independent measurements in this work of the minimum bond dissociation energy $OPu^+{-}O$ and ionization energy for PuO_2 have provided interconsistent and, we expect, convincing new results, which differ substantially from those previously reported in the literature. We do not have any explanation for the values of IE(PuO_2) in the literature, particularly the one determined recently by Capone et al.,[37] to be 2−3 eV higher than ours. Doubts could arise concerning the possibility of an ineffective thermalization of the PuO_2^+ ions in the charge-transfer reactions, but, if this was the case, it would mean that IE(PuO_2) was even lower than the "bracketed" value. Electron impact (EI) ionization threshold methods have been recently reviewed[45,46] and it was pointed out that, for molecules that change geometries upon ionization, EI methods could lead to either the adiabatic or the vertical ionization energy; clearly, this is a question which deserves further study, both experimental and theoretical.

Conclusions

With this work, we have further demonstrated that FTICR-MS is an important technique in studying gas-phase actinide ion chemistry, and have extended this line of inquiry to transuranium actinides. The results of the present study have made contributions to characterization of actinide ion oxidation reaction kinetics and thermodynamics. Particularly noteworthy is the contribution to the thermodynamics of the scientifically and technologically important plutonium oxide system. We believe having demonstrated that the existing literature values for both BDE($OPu^+{-}O$) and IE(PuO_2) are inaccurate, and have obtained a new lower limit for the former and a refined value for the latter. Such fundamental information is crucial to extending our understanding of plutonium chemistry, as well as that of the actinides in general. Soon, we intend to pursue these gas-phase oxidation studies with other actinides, and also to study different aspects of actinide ion reactivity with organic molecules. The overall goal is to further improve our understanding of the chemistry along the actinide series, and particularly the distinctive role of the actinide 5f electrons.

Acknowledgment. This work was supported by Fundação para a Ciência e a Tecnologia (Contract POCTI/35364/QUI/2000), by Fundação Luso-Americana (Grant L-V-343/2001), and by the Division of Chemical Sciences, Geosciences, and Biosciences, U. S. Department of Energy (Contract DE-AC05-00OR22725 with ORNL, managed by UT-Battelle, LLC).

References and Notes

(1) Heinemann, C.; Cornehl, H. H.; Schwarz, H. *J. Organomet. Chem.* **1995**, *501*, 201.

(2) Heinemann, C.; Schwarz, H. *Chem. Eur. J.* **1995**, *1*, 7.

(3) Marçalo, J.; Leal, J. P.; Pires de Matos, A. *Int. J. Mass Spectrom. Ion Processes* **1996**, *157/158*, 265.

(4) Cornehl, H. H.; Heinemann, C.; Marçalo, J.; Pires de Matos, A.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 891.

(5) Marçalo, J.; Leal, J. P.; Pires de Matos, A.; Marshall, A. G. *Organometallics* **1997**, *16*, 4581.

(6) Cornehl, H. H.; Wesendrup, R.; Diefenbach, M.; Schwarz, H. *Chem. Eur. J.* **1997**, *3*, 1083.

(7) Vieira, M. C.; Marçalo, J.; Pires de Matos, A. *J. Organomet. Chem.* **2001**, *632*, 126.

(8) Gibson, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 2633.

(9) Gibson, J. K. *Organometallics* **1998**, *17*, 2583.

(10) Gibson, J. K. *Radiochim. Acta* **1999**, *84*, 135.

(11) Gibson, J. K. *Inorg. Chem.* **1999**, *38*, 165.

(12) Gibson, J. K.; Haire, R. G. *J. Phys. Chem. A* **1998**, *102*, 10746.

(13) Gibson, J. K. *J. Mass Spectrom.* **1999**, *34*, 1166.

(14) Gibson, J. K. *Int. J. Mass Spectrom.* **2000**, *202*, 19.

(15) Gibson, J. K.; Haire, R. G. *Int. J. Mass Spectrom.* **2000**, *203*, 127.

(16) Gibson, J. K. *J. Mass Spectrom.* **2001**, *36*, 284.

(17) Gibson, J. K.; Haire, R. G. *Radiochim. Acta* **2001**, *89*, 709.

(18) Gibson, J. K.; Haire, R. G. Unpublished results.

(19) Gibson, J. K. *Int. J. Mass Spectrom.* **2002**, *214*, 1.

(20) Marshall, A. G.; Hendrickson, C. L.; Jackson, G. S. *Mass Spectrom. Rev.* **1998**, *17*, 1.

(21) Amster, I. J. *J. Mass Spectrom.* **1996**, *31*, 1325.

(22) Freiser, B. S. In *Techniques for the Study of Ion−Molecule Reactions*; Farrar, J. M.; Saunders, W. H., Jr.,Eds.; Wiley: New York, 1988; Chapter 2.

(23) Eller, K.; Schwarz, H. *Chem. Rev.* **1991**, *91*, 1121.

(24) Beauchamp, J. L.; Martinho Simões, J. A. *Chem. Rev.* **1990**, *90*, 629.

(25) Freiser, B. S. In *Bonding Energetics in Organometallic Compounds*; Marks, T. J., Ed.; American Chemical Society: Washington, DC, 1990; Chapter 4.

(26) Freiser, B. S. *J. Mass Spectrom.* **1996**, *31*, 703.

(27) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, 1988.

(28) Guan, S.; Marshall, A. G. *Int. J. Mass Spectrom. Ion Processes* **1996**, *137/138*, 5.

(29) Bruce, J. E.; Eyler, J. R. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 727.

(30) Lin, Y.; Ridge, D. P.; Munson, B. *Org. Mass Spectrom.* **1991**, *26*, 550.

(31) Bartmess, J. E.; Georgiadis, R. M. *Vacuum* **1983**, *33*, 149.

(32) *CRC Handbook of Chemistry and Physics*, 75th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1994.

(33) Su, T.; Bowers, M. T. In *Gas-Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 1, Chapter 3.

(34) *NIST Chemistry Webbook* − NIST Standard Reference Database Number 69, July 2001 release (http://webbook.nist.gov/chemistry/).

(35) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

(36) Hildenbrand, D. L.; Gurvich, L. V.; Yungman, V. S. *The Chemical Thermodynamics of Actinide Elements and Compounds, Part 13: The Gaseous Actinide Ions*; International Atomic Energy Agency: Vienna, 1985.

(37) Capone, F.; Colle, Y.; Hiernaut, J. P.; Ronchi, C. *J. Phys. Chem. A* **1999**, *103*, 10899.

(38) Fred, M. S.; Blaise, J. In *The Chemistry of the Actinide Elements*, 2nd ed.; Katz, J. J.; Seaborg, G. T.; Morss, L. R., Eds.; Chapman and Hall: London, 1986; Vol. 2, Chapter 15.

(39) Martin, W. C.; Zalubas, R.; Hagan, L. *Atomic Energy Levels: The Rare-Earth Elements*; NSRDS-NBS 60; National Bureau of Standards (NIST): Washington, DC, 1978.

(40) Ackermann, R. J.; Faircloth, R. L.; Rauh, E. G.; Thorn, R. J. *J. Inorg. Nucl. Chem.* **1966**, *28*, 111.

(41) Gibson, J. K. *Radiochim. Acta* **1998**, *81*, 83.

(42) Harvey, J. N.; Diefenbach, M.; Schröder, D.; Schwarz, H. *Int. J. Mass Spectrom.* **1999**, *182/183*, 85.

(43) Heinemann, C.; Cornehl, H. H.; Schröder, D.; Dolg, M.; Schwarz, H. *Inorg. Chem.* **1996**, *35*, 2463.

(44) Zimmerman, J. A.; Bach, S. B. H.; Watson, C. H.; Eyler, J. R. *J. Phys. Chem.* **1991**, *95*, 98.

(45) Ervin, K. M. *Chem. Rev.* **2001**, *101*, 391.

(46) Hildenbrand, D. L. *Int. J. Mass Spectrom.* **2000**, *197*, 237.