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Review

New developments in gas-phase actinide ion chemistry

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Contents

Abstract

In this review, recent progress in the study of the chemistry of actinide ions in the gas phase is summarized. The new results, obtained using various mass spectrometric techniques, encompass reactivity studies of bare and ligated actinide ions with inorganic and organic molecules, thermochemical studies of neutral and ionic actinide oxides, and solvation studies of ionic actinide species. A few examples of the implications of this fundamental research to other aspects of actinide chemistry are presented. Potential future work in this area is briefly discussed.
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1. Introduction

The value of gas-phase metal ion chemistry derives, to a large extent, from the fact that it studies the physical and chemical properties of the ionic species in the absence of perturbing factors like solvation or lattice neighbors. At this fundamental level, the reactivity and bonding of the metal ions generally correlate directly with their electronic structures and energetics. These studies typically rely on the use of a variety of mass spectrome-try techniques. Gas-phase reactions of metal ions, d-block metal ions in particular, have been studied for more than three decades, and have been the subject of several excellent reviews [1–5]. The last two decades witnessed an expansion of the field to f-block metals, lanthanides (Ln) in particular, and the work involving the 4f elements has been reviewed recently [6,7]. For the 5f actinides (An), initial studies unsurprisingly focused on naturally occurring Th and U. These studies were later extended to several of the highly radioactive members of the actinide series, namely Np through Cf. These gas-phase actinide ion chemistry studies have been comprehensively reviewed [8]. There, the main tenets for understanding the chemical behaviour of actinide ions in the gas phase were thoroughly described, and the unique nature of the 5f elements as compared to their 4f homologues was emphasized.

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In the approximately four-year period since the previous review [8], new developments in the field of gas-phase actinide ion chemistry have appeared that justify an update. In the present report, we summarize the new results, relate them to the previous work and evaluate them in the context of prospects put forward in the previous review. Having in mind the characteristic audience of this journal, we will also draw some relationships with condensed-phase actinide chemistry. Specifically, we address reactivity studies of bare and ligated actinide ions with inorganic and organic molecules, thermochemical studies of actinide oxides, and solvation studies of actinide species; we present a few examples of the consequences of this research to actinide chemistry in general; we discuss potential future work.

2. Reactivity studies of bare and ligated actinide ions

2.1. Protactinium and einsteinium—from Th to Es by LAPRD

In the last few years, gas-phase reactivity studies of actinide ions experienced an extension to two more members of the actinide series, Pa and Es, with the technique that had been previously employed for the study of the transuranium actinides—laser ablation with prompt reaction and detection (LAPRD) [8].

Gibson and Haire reported on the reactions of Pa^+ and PaO^+ with neutral molecules [9]. They showed that Pa^+ is a very reactive actinide ion, using reagents as diverse as alkenes, ethylene oxide, and sulfur hexafluoride. Direct comparisons were made with U^+, Np^+, and the corresponding monoxide ions. The reaction of Pa^+ with ethylene oxide showed very efficient formation of PaO^+, which reacted also very efficiently to give PaO_2^+, in which Pa is in its very stable pentavalent oxidation state. Facile fluorination of Pa^+ up to PaF_4^+ was observed in the reaction with SF_6, again leading to a very stable Pa(V) species. Pa^+ was found to be highly reactive with ethene, propene, 1-butene, and iso-butene, inducing oligomerization of the alkenes; in the case of ethene, this corresponded to the formation of a presumed benzene complex, $PaC_6H_6^+$. The authors observed an exceptional reactivity for PaO^+, which induced efficient dehydrogenations of the four alkenes, and they attributed it to participation of the 5f electrons of PaO^+ in the activation process, either directly or through promotion/hybridization.

These same authors performed the first gas-phase reactivity studies with Es^+ [10]. Through direct comparisons with Bk^+, they were able to demonstrate the stability of the divalent state of Es in reactions with hexafluoropropene, where EsF^+ was the only product formed. Es^+ was inert towards propene, 1-butene, iso-butene, 1,5-cyclooctadiene, 1-methyl-1-cyclohexene, benzene, and butylamine, forming only the adduct ions in the cases of 1-butene, iso-butene, and butylamine. The alkene adducts constituted the first examples of organometallic complexes of Es. In the reaction with dimethylether, formation of the methoxide ion $EsOCH_3^+$ was observed, while in the reaction with 1,2-ethanedithiol EsS^+ was produced.

In a recent report, Gibson and Haire described the reactivity of Es^+ with 1,2,3,4,5-pentamethylcyclopentadiene (HCp^*) [11].

Cm^+ and Cf^+ were also studied for the first time with this reagent. Although Es^+ was previously found to be inert towards alkenes, it activated HCp^* to form $[EsCp^*]^+$, $[EsC_5(CH_3)_4(CH_2)]^+$, and $[EsC_5(CH_3)_4H]^+$, which were the first organoeinsteinium complexes derived from the activation of an organic substrate. Formation of a presumed metallocene complex $[EsCp^*_2]^+$, was also observed.

Besides the Pa and Es studies, reactions of selected An^+ and AnO^+ ions (An = Th, U, Np, Pu, Am) with silane, disilane, and germane were studied with LAPRD [12]. Dehydrogenation was the main reaction pathway observed, leading to silylenes, germylenes, and in a few cases, germanides. Experiments with the hydrocarbon homologs methane and ethane were also made for comparative purposes and only Th^+ was observed to react.

Gas-phase actinide ion chemistry studies carried out with the LAPRD technique have now probed the reactivity of An^+ ions from Th^+ to Es^+. Although LAPRD does not allow the measurement of reaction kinetics, which could put the relative reactivity of An^+ ions on a quantitative basis, all the experiments involved careful comparisons of the reactivity of pairs or triplets of An^+ ions (as well as comparisons with selected Ln^+ ions), thereby permitting a qualitative assessment of the relative reactivity of An^+ from Th^+ to Es^+. The studies that involved alkenes as substrates (with HCp^* a special case) were systematically made and were the most informative. Based on the LAPRD results the following ordering of reactivities can be presented:

$$Th^+ \geq Pa^+ \geq U^+ \approx Np^+ > Cm^+$$
$$\geq Pu^+ > Bk^+ > Am^+ \approx Cf^+ \geq Es^+$$
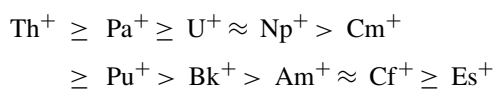
As has been shown in several studies and was described in detail in the previous review paper [8], the reactivity of An^+ ions (and of Ln^+ ions) towards hydrocarbons can be interpreted via a bond-insertion mechanism and generally correlates inversely with the promotion energies necessary to excite the ions from their ground states to "divalent" electronic configurations with two unpaired non-f electrons, of the type $[Rn]5f^{n-2}6d7s$ (where [Rn] represents the closed radon electronic core). In Fig. 1, we show a plot of the variation of these promotion energies along the actinide series, from which the inverse correlation with the reactivity can been perceived: the lower the An^+ reactivity according to the ordering stated above, the greater the promotion energy in Fig. 1. One notable feature of this type of correlation is that it leads to the conclusion that the spectroscopically determined promotion energy for Cf^+ [13] does not correspond to the lowest-lying such configuration; instead, an early estimate by Brewer [14] (used in Fig. 1) is in accord with the experimental observations of the comparative reactivities of Cf^+ and Es^+ with HCp^* [11]. Also presented in Fig. 1 is the variation of the promotion energies to the other pertinent "divalent" electronic configuration of the An^+ ions, $[Rn]5f^{n-2}6d^2$. It can be seen that the general trend is similar between the two sets of promotion energies, although they diverge as one progresses along the series. The reactivity of An^+ ions has usually been related to the need for a $6d7s$ configuration. The ordering of the An^+ reactivities presented above, particularly the relation $Am^+ \approx Cf^+ \geq Es^+$, indicates that it is the $6d7s$ configuration that
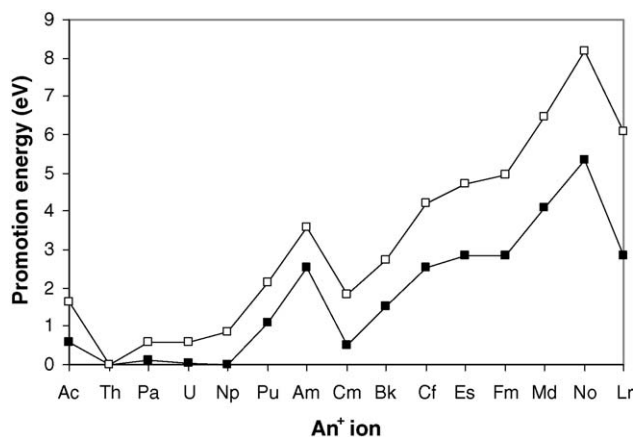
Fig. 1. Promotion energies of the An$^+$ ions from the ground states to configurations with two non-f electrons, [Rn]5f^{n-2}6d7s (filled squares) and [Rn]5f^{n-2}6d^2 (open squares). The ground states are: Ac$^+$, [Rn]7s^2; Th$^+$, [Rn]6d^{2}7s; Pa$^+$, [Rn]5f^{2}7s^2; U$^+$, [Rn]5f^{3}7s^2; Np$^+$, [Rn]5f^{4}6d7s; Pu$^+$, [Rn]5f^{6}7s; Am$^+$, [Rn]5f^{7}7s; Cm$^+$, [Rn]5f^{7}7s^2; Bk$^+$, [Rn]5f^{9}7s; Cf$^+$, [Rn]5f^{10}7s; Es$^+$, [Rn]5f^{11}7s; Fm$^+$, [Rn]5f^{12}7s; Md$^+$, [Rn]5f^{13}7s; No$^+$, [Rn]5f^{14}7s; Lr$^+$, [Rn]5f^{14}7s^2. The data are from ref. [13] except for Md$^+$, No$^+$, and Lr$^+$ that are estimates from ref. [14]. The promotion energy to the [Rn]5f^{n-2}6d7s configuration of Cf$^+$ is also from ref. [14].

is influential, at least in the case of hydrocarbons. This is in accord with the analogous requirement for a 5d6s configuration for hydrocarbon activation by the Ln$^+$ [6,7].

This type of systematization based on the promotion energies can also provide a guide for predicting the chemistry of neutral An and ultimately the condensed-phase behaviour of these elements. Gibson and Haire compared the promotion energies of An$^+$ with those of neutral An and were able to arrive at some conclusions regarding the stability of the oxidation states of the actinides in condensed phase [10]. As the authors indicated, these predictions can be particularly useful for the last part of the actinide series, Fm to Lr, where the minuscule quantities and very short half lives of the elements highly limit experimentation.

2.2. Trapped actinide ions—quantifying reactivity

Another recent advance in gas-phase actinide ion chemistry occurred through the use of trapped-ion mass spectrometry, namely Fourier transform ion cyclotron resonance mass spectrometry (FTICR/MS) and quadrupole ion trap mass spectrometry (QIT/MS), to study actinides, including transuranics by FTICR/MS. The trapped-ion mass spectrometric techniques allow the measurement of reaction kinetics, and the reaction rate constants (k) that can be obtained are normally compared with theoretical collisional rate constants (k_{COL}), which depend on the particular ion/neutral pair. The ratio of the two constants (k/k_{COL}) defines the so-called reaction efficiency, that is, the fraction of ion/neutral collisions that are effective in yielding reaction products, which is a useful measure of the relative reactivity of the ions. Other advantages of the ion traps as compared to a method like LAPRD include the capacity to analyse reaction sequences by isolating a primary reaction product and examining its subsequent reactions; to perform collision-induced dissocia-

Table 1
Efficiencies (k/k_{COL}) of the reactions of An$^+$ ions with oxidizing reagents

An$^+$	N$_2$O	C$_2$H$_4$O	H$_2$O	O$_2$	CO$_2$	NO	CH$_2$O
Th^{+a}	0.68	0.37	0.20	0.86	0.35	0.49	0.61
U^{+a}	0.47	0.34	0.13	0.72	0.29	0.46	0.53
Np^{+a}	0.48	0.32	0.10	0.68	0.30	0.45	0.28
Pu^{+a}	0.02	0.21	0.004	0.27	0.003	0.17	<0.001
Am^{+b}	0.004	0.21	0.001	0.32	0.001	<0.001	<0.001

[a] From ref. [15].
[b] From ref. [16] except CH$_2$O which is from ref. [22].

tion (CID) studies, in which the structures of ions are probed by translationally exciting the ions, allowing them to collide with an inert gas, and observing the fragment ions formed thereafter.

Reactions of An$^+$ and AnO$^+$ (An = Th, U, Np, Pu, Am) with several oxidants were studied by Santos et al. using FTICR/MS in conjunction with laser desorption ionization (LDI) to produce the actinide metal monopositive ions [15,16]. The oxidants employed were as follows, listed in decreasing order of thermodynamic oxidizing ability: N$_2$O > C$_2$H$_4$O (ethylene oxide) > H$_2$O > O$_2$ > CO$_2$ > NO > CH$_2$O. The authors observed that Th$^+$, U$^+$, and Np$^+$ produced AnO$^+$ for each oxidant; Pu$^+$ formed PuO$^+$ with all oxidants except CH$_2$O; Am$^+$ formed AmO$^+$ with all oxidants except CH$_2$O and NO. The reaction efficiencies of the An$^+$ ions obtained in the two studies are summarized in Table 1. The authors noted a correlation of the reaction efficiencies with the magnitude of the promotion energies from the ground states to reactive-state configurations of the An$^+$ ions. Comparison of the reaction efficiencies in Table 1 with the promotion energies in Fig. 1 appear in fact to indicate such a relationship, with Pu$^+$ and Am$^+$ being clearly less reactive than the earlier actinide ions. For the monoxide ions, AnO$^+$, a general decrease in reactivity, as compared with that of the metal ions, was observed by Santos et al. [15,16]: only C$_2$H$_4$O oxidized all the AnO$^+$ ions to AnO$_2^+$; N$_2$O oxidized all AnO$^+$ except AmO$^+$; H$_2$O and O$_2$ oxidized UO$^+$, NpO$^+$, and PuO$^+$; CO$_2$ and NO oxidized only UO$^+$; CH$_2$O was unreactive with all five studied AnO$^+$. In Table 2, we present a summary of the reaction efficiencies of the AnO$^+$ ions obtained by Santos et al. As the authors stated, in the case of the actinide monoxide ions it is more difficult to establish correlations with the electronic structures and energetics since these are virtually unknown.

In a very recent study, Gibson et al. used again FTICR/MS with LDI to probe the reactivity of doubly charged actinide ions,

Table 2
Efficiencies (k/k_{COL}) of the reactions of AnO$^+$ ions with oxidizing reagents

AnO$^+$	N$_2$O	C$_2$H$_4$O	H$_2$O^c	O$_2$	CO$_2$	NO	CH$_2$O
ThO^{+a}	0.31	0.34	0.11	<0.001	<0.001	<0.001	<0.001
UO^{+a}	0.08	0.30	0.009	0.45	0.004	0.11	<0.001
NpO^{+a}	0.07	0.28	0.004	0.28	<0.001	<0.001	<0.001
PuO^{+a}	0.003	0.15	0.002	0.07	<0.001	<0.001	<0.001
AmO^{+b}	<0.001	0.03	0.001	<0.001	<0.001	<0.001	–

[a] From ref. [15].
[b] From ref. [16]; CH$_2$O not studied.
[c] The ThO$^+$/H$_2$O reaction produced only ThO$_2$H$^+$ (presumably ThO(OH)$^+$); the AmO$^+$/H$_2$O reaction produced only AmO$_2$H$^+$ (presumably Am(OH)$_2^+$).

Table 3
Efficiencies (k/k_{COL}) of the reactions of An^{2+} ions with oxidizing reagents[a]

An^{2+}	N_2O	C_2H_4O	H_2O	O_2	CO_2	NO	CH_2O
Th^{2+}	0.41	0.28	0.15	0.56	0.55	0.42	0.18
U^{2+}	0.40	0.30	0.11[b]	0.53	0.38	0.29	0.10
Np^{2+}	0.25	0.25	0.05[b]	0.48	<0.001	0.20[b]	<0.001
Pu^{2+}	0.17	0.21	0.001[b]	<0.001	<0.001	0.23[b]	<0.001
Am^{2+}	<0.001	0.21	0.001[b]	<0.001	<0.001	0.22[b]	<0.001

[a] From ref. [17]; these are overall reaction efficiencies for oxidation and other reaction channels.

[b] The binary oxide, AnO^{2+}, was not observed as a product.

An^{2+} and AnO^{2+}, with the same oxidants used before with the singly charged ions [17]. Oxidation of the An^{2+} to AnO^{2+} with all seven oxidants was observed only in the case of Th^{2+}; U^{2+} was oxidized by the oxidants except H_2O and CH_2O; Np^{2+} was oxidized by N_2O, O_2, and C_2H_4O; Pu^{2+} was oxidized by N_2O and C_2H_4O; Am^{2+} was oxidized only by C_2H_4O. Other reaction channels, like electron transfer, were observed in some cases due to the fact that the second ionization energies of the actinides, all close to 12 eV [18], are higher than the ionization energies of C_2H_4O, CH_2O, and NO. In Table 3, we show the overall reaction efficiencies for oxidation and other reaction pathways of the An^{2+} ions [17]. The authors were not able to establish any direct correlation of the oxidation efficiencies of the An^{2+} ions with the electronic structures and promotion energies, this in contrast to the case of An^+ ions. In fact, all the An^{2+} except Th^{2+} have promotion energies from the ground states to "divalent" configurations with two unpaired non-f electrons that are rather high, ranging from 2.4 eV in the case of U^{2+} up to 8.7 eV in the case of Am^{2+} [13]. Gibson et al. examined only a restricted set of reactions of AnO^{2+} due to experimental limitations. It is particularly noteworthy that from the reactions of AnO^{2+} with N_2O for $An = U$, Np, and Pu, and with O_2 for $An = U$ and Np, it was possible to produce the bare gas-phase actinyl dipositive ions, AnO_2^{2+}, which in the cases of Np and Pu were identified for the first time (bare uranyl had previously been synthesized in similar experiments by Cornehl et al. [19]). It was verified that the bare actinyls UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+} are thermodynamically stable towards Coulomb dissociation to $\{AnO^+ + O^+\}$ or $\{An^+ + O_2^+\}$. It was predicted that the non-observed bare AmO_2^{2+} is also thermodynamically stable toward dissociation, albeit by only ca. 1 eV [17].

Santos et al. have continued to use FTICR/MS to extend the reactivity studies of actinide ions to hydrocarbon substrates. With indene (C_9H_8) it was verified that all the studied An^+ and AnO^+ ions ($An = Th$, U, Np, Pu, Am) were very reactive, eventually leading to the formation of An-bis(indenyl) species [20]. With alkanes (methane, ethane, propane, *n*-butane) and alkenes (ethene, propene, 1-butene), the experiments involved An^+ and An^{2+} ions ($An = Th$, U, Np, Pu, Am) and the preliminary results were interpreted in the context of the electronic structures and energetics of the An ions; for comparative purposes, experiments with the Ln^{2+} cations and the same hydrocarbons were performed [21].

Recently, Pires de Matos et al. added Pa to the group of An ions already studied by FTICR/MS, using both oxidants and

hydrocarbons as reagents [22]. These studies will allow a more thorough assessment of the relative reactivity of actinide cations in the first half of the series.

QIT/MS was also recently used to examine the reactivity of actinide ions. Jackson et al. studied reactions of U^+ and U^{2+} with oxygen and water, using a glow discharge source to produce the uranium ions [23]. The authors were able to measure the reaction efficiencies for the bare uranium metal ions and also for the corresponding monoxides. Although the results showed a general agreement with the results of FTICR/MS studies, a few differences were encountered in the reactions with water that were ascribed to the different pressure regimes of the two ion trap techniques: $\leq 10^{-6}$ Torr for FTICR/MS versus ca. 10^{-3} Torr for QIT/MS.

Jackson et al. explored the differences between QIT/MS and FTICR/MS in a study of the reactivity of Th^+, U^+, ThO^+, UO^+, and UO_2^+ with HCp^* [24]. The authors studied representative Ln^+ and LnO^+ ions for comparison with the actinide ions, and with a previous FTICR/MS study of the Ln^+ cations [25]. Based on CID studies and on variations of the bath gas pressure in the QIT/MS, it was confirmed that the different pressure regimes of the two ion traps were responsible for the differences in reactivity [24].

More recently, Jackson et al. studied the reactions of bare and ligated uranium ions with sulfur hexafluoride [26]. U^+ was found to produce UF_n^+ species ($n = 1$, 2, 3, 4) rather efficiently. The reactions with SF_6 of a number of ligated uranium ions, namely UO^+, UOH^+, and several UF_n^+ ions formed in the primary reactions, were also studied.

The use of the trapped-ion techniques undeniably provided new information on the gas-phase reactivity of actinide ions, although limitations exist in terms of the actinides that can be studied. Studies of Cm ion chemistry are a reasonable goal in view of the availability and relatively long half life (3.5×10^5 years) of the Cm-248 isotope. Trapped ion studies with later actinides present a much greater challenge, though it may ultimately prove feasible to carry out such experiments using small amounts of Cf-249, which has a 351 year half life.

3. Thermochemical studies of actinide oxides

3.1. Bond dissociation energies of ionic actinide oxides

Another dimension of the ion traps that has been explored is the capacity to provide quantitative information on ion and neutral molecular thermodynamics. If the reactant ions are properly thermalized, the reactions that are observed are either exothermic or athermic, although kinetic barriers may be present that preclude observation of an exothermic or athermic reaction at a detectable rate. If the ion/neutral reactions are carefully chosen, and the thermodynamic properties of some of the reactant partners are known, estimates can be obtained for the unknown energies of bonds being formed and/or broken. In particular cases, the reaction efficiencies can also be of use in such estimates. The experimental techniques and methodologies available for studying the thermochemistry of ions in the gas phase have recently been comprehensively reviewed [27].

Table 4
Bond dissociation energies (BDE) of ionic actinide oxides (kJ/mol)

An	BDE[An$^+$−O]	BDE[OAn$^+$−O]	BDE[An^{2+}−O]	BDE[OAn^{2+}−O]
Th	866 ± 21[a]	433 ± 30[a]	≥751[b]	–
U	803 ± 25[a]	772 ± 56[a]	690 ± 60[b]	560 ± 30[b]
Np	773 ± 43[c]	580 ± 70[d]	530 ± 30[b]	520 ± 20[b]
Pu	683 ± 55[a]	520 ± 20[d]	460 ± 50[b]	410 ± 100[b]
Am	560 ± 30[e]	390 ± 40[e]	400 ± 50[b]	260 ± 100[b]

[a] From ref. [18].
[b] From ref. [17].
[c] From ref. [28].
[d] From ref. [15].
[e] From ref. [16].

In the FTICR/MS oxidation studies mentioned in the previous section [15–17], the use of oxidizing reagents with a large range of oxygen dissociation energies allowed estimation of unknown An$^+$–O, An^{2+}–O, OAn$^+$–O, and OAn^{2+}–O bond dissociation energies (BDEs) and verification or correction of literature values obtained by other methods. In Table 4, we present a summary of the estimates obtained by Santos et al. [15,16] for BDE[An$^+$−O] and BDE[OAn$^+$−O] and by Gibson et al. [17] for BDE[An^{2+}−O] and BDE[OAn^{2+}−O], together with literature values that were substantiated by the oxidation studies. A particularly notable result of the FTICR/MS studies is the conclusion that the literature value for BDE[OPu$^+$−O] of ca. 250 kJ/mol [18] was too low by ca. 250 kJ/mol.

An assessment of the known bond dissociation energies of actinide (and lanthanide) neutral and singly charged monoxides was recently carried out [29]. A relationship was developed between the BDEs and the electronic structures and energetics of the isolated metal atoms and ions, that can be used in the estimation of unknown bond dissociation energies. Evidence was presented for the requirement of two unpaired d valence electrons on the metal center for effective bonding to an oxygen atom to be established. In the case of the ionic actinide monoxides, the relation could not be firmly demonstrated due to the lack and/or large uncertainties of the experimental BDEs, but the limited correlations that could be made appear to indicate the validity of the model for the AnO$^+$ ions. One interesting aspect of this assessment is that it points to the "divalent" 6d^2 configuration as the relevant one for oxide bond formation, this in contrast to the evidence for the importance of the 6d7s configuration in the reactivity of An$^+$ ions with hydrocarbons (see Fig. 1 and the associated discussion in the previous section). We propose that the evident requirement for a 6d^2 configuration for oxide bond formation and a 6d7s configuration for oxidative insertion might be rationalized on the basis of different metal-based orbital symmetry requirements for formation of the An$^+$=O double bond, versus formation of the two single bonds in the C−An$^+$−H or C−An$^+$−C activated intermediate.

3.2. Ionization energies of neutral and ionic actinide oxides

In an ion trap, the study of electron-transfer reactions can provide ionization energies (IEs) by means of "bracketing" experiments, in which the ions of interest are reacted with neutral compounds with well-known IEs. The occurrence or non-occurence of electron transfer from the neutrals establishes lower and upper limits for the ion electron affinities, which directly provide the ionization energies of the corresponding neutrals. Other ways of obtaining ionization energies are possible using FTICR/MS, basically involving the analysis of the thermodynamics of reactions with selected substrates.

From the reactions of AnO$_2$$^+$ ions with several compounds, mainly amines, and using FTICR/MS, Santos et al. determined IE[PuO$_2$] = 7.03 ± 0.12 eV [15] and IE[AmO$_2$] = 7.23 ± 0.15 eV [16], and, in a recent study, Gibson et al. obtained IE[NpO$_2$] = 6.33 ± 0.18 eV [30]. As the authors pointed out, the IE[PuO$_2$] value was significantly lower than the literature values, by ca. 2.5–3 eV, but was consistent with the observed oxidation reactions and derived plutonium oxide bond energies. The IE[NpO$_2$] value was more than 1 eV higher than the literature value; the IE[AmO$_2$] value was experimentally determined for the first time.

Heaven and coworkers [31–33] have recently made accurate photoionization measurements of the ionization energies of UO, UO$_2$, and ThO. The neutral oxide molecules were ionized by resonant absorption of two photons and the resulting oxide ions were mass spectrometrically resolved prior to detection. Their results are: IE[UO] = 6.0313 ± 0.0006 eV, IE[UO$_2$] = 6.128 ± 0.003 eV [31,32], and IE[ThO] = 6.6035 ± 0.0008 eV [33]. As discussed by the authors of this work [31–33], these new values represent significant corrections to the literature values [18].

Gibson et al. studied electron-transfer reactions of AnO$_2$$^{2+}$ ions (An = U, Np, Pu), that allowed estimation of the second ionization energies of AnO$_2$ species [17]. For these estimates, the authors used an adaptation of the "bracketing" technique for electron-transfer reactions involving doubly charged ions. The method is not as straighforward as for singly charged ions due to the fact that two positively charged species are formed in the electron-transfer reaction and an energy barrier arises due to the repulsive Coulombic interactions between the products. It was also possible to estimate the second ionization energy of AmO$_2$ from a comparative analysis of known aqueous phase thermodynamic data of actinide species in conjunction with the estimated second ionization energies of UO$_2$, NpO$_2$, and PuO$_2$ [17]. Estimates of the second ionization energies of AnO (An = U, Np, Pu, Am) were also made based on the thermodynamics of the studied oxidation reactions [17].

From the study of reactions of AnO$^+$ with 1,3-butadiene and isoprene, and using a model developed by Cornehl et al. for the lanthanides [34], Santos et al. estimated the ionization energies of PuO and AmO [16]. The authors were able to recommend one of two discrepant literature values of IE[PuO] and obtained IE[AmO] for the first time. Gibson et al. [30] have recently revised the IE[AnO] values as a consequence of the recent accurate spectroscopic determination of IE[UO] by Han et al. [31,32], which was ca. 0.3 eV higher than the literature value that had been used to "anchor" the IE values for PuO and AmO in the previous work [16]. A general assessment of the known first and second ionization energies of the actinide monoxides and dioxides has recently been presented

Table 5
First and second ionization energies (IE) of actinide oxides (eV)

An	IE[AnO]	IE[AnO$_2$]	IE[AnO$^+$]	IE[AnO$_2$$^+$]
Th	6.60[a]	8.7 ± 0.2[b]	≤12.8[c]	–
U	6.03[d]	6.13[d]	12.7 ± 0.8[c]	14.6 ± 0.4[c]
Np	6.1 ± 0.2[e]	6.33 ± 0.18[e]	13.8 ± 0.6[c]	15.1 ± 0.4[c]
Pu	6.1 ± 0.2[e]	7.02 ± 0.12[f]	13.7 ± 0.8[c]	15.1 ± 0.4[c]
Am	6.2 ± 0.2[e]	7.23 ± 0.15[g]	13.7 ± 0.6[c]	15.7 ± 0.9[c]

[a] From ref. [33]; the precise value is IE[ThO] = 6.6035 ± 0.0008 eV.
[b] From ref. [18].
[c] From ref. [17].
[d] From refs. [31,32]; the precise values are IE[UO] = 6.0313 ± 0.0006 eV and IE[UO$_2$] = 6.128 ± 0.003 eV.
[e] From ref. [30].
[f] From ref. [15].
[g] From ref. [16].

[30]. There, comparisons were made with the ionization energies of actinide atoms and with values for other relevant molecules, and systematic trends were considered. In Table 5, we present a summary of the first and second ionization energies of actinide oxides.

As mentioned in the previous section, Pires de Matos et al. recently added Pa to the group of An ions studied by FTICR/MS [22]. Preliminary experiments involving oxidation and electron-transfer reactions demonstrated that bare PaO$_2$$^+$ is a very stable species, reflected in a OPa$^+$−O bond energy larger than that for the analogous U species, and in an ionization energy higher than those for the Np and Pu dioxide cations. Another result of interest was the observation of bare "protactinyl", PaO$_2$$^{2+}$, formally a Pa(VI) species [22].

4. Solvation studies of ionic actinide species

4.1. From gas phase to solution phase

In aqueous solutions containing U, Np, Pu, and Am the actinyls, AnO$_2$$^{2+}$, hexavalent species of varying stability, can be important; the pentavalent dioxo ions AnO$_2$$^+$ can also be present under certain conditions. There is a considerable knowledge of the thermodynamic properties of these ions in aqueous solution, which combined with gas-phase data can lead to a more complete characterization of these species.

The gas-phase thermodynamic data obtained for the bare AnO$_2$$^{2+}$ ions (An = U, Np, Pu) have been employed in conjunction with the known aqueous thermochemistry of these actinyls to derive hydration enthalpies [17]. It was found that ΔH_{hyd}[AnO$_2$$^{2+}$] ≈ −1670 kJ/mol for these three actinides, a value that is substantially more negative than previously reported for uranyl. In the case of the singly charged AnO$_2$$^+$ ions, ΔH_{hyd}[AnO$_2$$^+$] values of −709 ± 51 kJ/mol for U, −754 ± 83 kJ/mol for Np, −746 ± 55 kJ/mol for Pu, and −776 ± 51 kJ/mol for Am were derived; these values are in reasonable agreement with one another within the indicated uncertainties.

Another way to probe the hydration properties of actinide ionic species is to study reactions of selected bare actinide ions with water. Gresham et al. used a QIT/MS to study reactions of UO(OH)$^+$, UO$_2$$^+$, and UO$_2(OH)^+$ ions with water [35]. The authors employed a ReO$_4$$^-$ ion gun to produce the UO(OH)$^+$ and UO$_2$$^+$ ions from solid UO$_3$, and generated the UO$_2$(OH)$^+$ ions by O$_2$ oxidation of UO(OH)$^+$ in the gas phase. It was demonstrated that UO(OH)$^+$ and UO$_2$$^+$ added up to four water molecules, while UO$_2$(OH)$^+$ added up to three, in all cases reaching a maximum of six ligands around the uranium center. The kinetics of the successive reactions were measured, with the first hydration step being slower than the second for the three reactant ions. Based on the kinetics studies, the authors concluded that the stability of the UO$_y$H$_x$(H$_2$O)$_n$$^+$ complexes increased with increasing n, until an optimum number of total ligands, five or six, was achieved: the higher the uranium oxidation state, the greater the ultimate degree of coordination.

4.2. From solution phase to gas phase

Electrospray ionization (ESI) is nowadays one of the most widely used ionization methods coupled to mass spectrometry, mainly because of its ability to probe ions directly from solution phase. The study of the solvation of metal ions is just one of the applications of the method that has been the focus of a number of studies. Stace has recently reviewed the main issues implicated in the gas-phase study of metal ion solvation [36].

Van Stipdonk, Groenewold, and co-workers recently initiated a systematic study of the solvation properties of uranyl via ESI-QIT/MS. In the first such study, Van Stipdonk et al. used CID to characterize the dissociation pathways of complexes formally composed of the uranyl ion, nitrate or hydroxide, and water or alcohol [37]. The authors observed that the uranyl complexes eliminated the coordinating water or alcohol molecules, leading ultimately to species formally composed of uranyl and an anion—hydroxide, nitrate, or alkoxide. The actual charge distribution in these (and other) monopositive "uranyl-anion" complexes is indeterminate, and it is probably not valid to consider them as gas-phase UO$_2$$^{2+}$·A$^-$ species where A$^-$ = hydroxide, nitrate, etc.

In a similar study, Anbalagan et al. used ESI to generate uranyl complexes containing halide (Cl, Br, I) or perchlorate as anions, together with water or alcohol as adducts, and examined the dissociation pathways via CID [38]. The authors found an intriguing difference between the decomposition of the hydrated complexes that contained bromide or perchlorate, which led to the bare "uranyl-anion" species, and those that contained chloride or iodide, which led to uranyl-hydroxide and hydrated UO$_2$$^+$. The authors also verified that the replacement of the water ligands by alcohol increased the tendency to eliminate the acid. These results were interpreted in the context of differing propensities for proton transfer within the hydrated complexes during CID [38].

Van Stipdonk et al. observed the oxidation of 2-propanol in a CID study of uranyl complexed by nitrate and the alcohol [39]. The authors identified the conversion of 2-propanol to acetone and of 2-propoxide to acetaldehyde, but did not observe corresponding transformations in the cases of 1-propanol or 2-methyl-2-propanol.

Chien et al. investigated the hydration of three uranyl-anion complexes of the type UO_2A^+ (A = acetate, nitrate, hydroxide) and found that the relative rates for the formation of the monohydrates followed the trend acetate > nitrate ≫ hydroxide [40]. The authors explained this observation in terms of the increasing donation of electron density to the uranyl metal center by the more basic hydroxide, which diminishes the Lewis acidity of the uranyl center and therefore reduces the rate of hydration, and also by the presence of increased degrees of freedom to accomodate excess energy from the hydration reaction in the acetate and nitrate ligands. Chien et al. also examined the successive formation of the dihydrates and the trihydrates and verified that only in the case of the hydroxide complex did the presence of the first water ligand result in an increase in the rate of addition of the second water.

Recently, Van Stipdonk et al. were able to produce uranyl complexes solvated only by neutral ligands, specifically acetone [41]. In all their previous ESI studies, Van Stipdonk, Groenewold, and co-workers had only been capable of generating singly charged "uranyl-anion" complexes, and ultimately the singly charged dioxouranium ion, UO_2^+. The authors studied the fragmentation pathways for the various uranyl–acetone complex ions formed but could not observe the formation of bare uranyl ion. Addition reactions with water or acetone were also investigated for ions with similar compositions but different charge states. A notable result from this work was that uranyl in the gas phase is coordinated by five acetone molecules. In aqueous solution, inner-sphere coordination by five water molecules occurs, so that the gas-phase results demonstrate a clear link to solution chemistry.

A recent major advance in fundamental understanding of uranyl speciation has come from the spectroscopic studies of Groenewold et al. [42] in which a tunable free electron laser is employed to obtain infrared vibrational spectra of gas-phase uranyl complexes. The uranyl complexes are produced by ESI as described in the preceding paragraph, and are then injected into an FTICR/MS. The vibrational spectra of mass-selected complexes are obtained by variable-wavelength infrared multiphoton dissociation (IRMPD)—the variation in the degree of photofragmentation as a function of the IRMPD wavelength provides a vibrational absorption spectrum that reveals aspects of bonding and structure for the uranyl complexes. Initial studies were on uranyl coordinated by acetone and acetonitrile, and the results were interpreted in the context of the nucleophilicity of the coordinating ligands.

The solvation studies of uranyl such as described above bear a special importance for the field of speciation of uranium (and other actinides) in the environment, in various stages of the nuclear fuel cycle, and in radiotoxicological problems. Recent years have witnessed the increased use of ESI, associated with different types of mass spectrometric techniques, for the study of actinide species, mainly uranium species. Moulin and co-workers have used ESI/MS to study the solution speciation of uranium [43] and thorium [44] and have summarized their work in this area in two recent reviews [45,46]. In a related report, Moulin and co-workers also used ESI/MS to study the interaction of uranyl with 1-hydroxyethane-1,1′-diphosphonic acid, a

compound that shows promise for the decorporation of uranium in humans [47].

Two other recent examples of ESI/MS studies of the complexation of uranyl by compounds of relevance in natural environments include work by Pasilis and Pemberton with citric acid [48], and work by Groenewold et al. with desferrioxamine siderophore [49].

5. Conclusions

We consider that the work summarized in this review represents clear progress for the field of gas-phase actinide ion chemistry. In the ca. four-year period since the previous review on the subject [8], some of the prospects put forward therein have materialized, namely the extension of fundamental reactivity studies to new members of the actinide series, and the increased use of trapped-ion mass spectrometry, with its advantages in terms of enabling detailed studies of the kinetics and energetics of ions, and complex reaction sequences. New studies using either FTICR/MS or QIT/MS can be expected in the near future. Another area which saw some progress was the chemistry of actinide cluster ions, through the work of Gibson and Haire with ternary plutonium oxide clusters [50]. The prospect of studies involving the heavy actinides and transactinides, presenting extreme challenges, has seen a modest but encouraging development in the work of Marx et al. with Ru^+ and Os^+ as model elements for future studies with Hs ions in the SHIPTRAP of GSI-Darmstadt [51].

As summarized in the previous section, another major advance in gas-phase actinide ion chemistry in recent years resulted from the utilization of ESI to generate actinide species directly from solution, thereby aproaching the important and more applied field of speciation of actinides. Another related area to which fundamental gas-phase actinide studies have recently contributed is the analytical chemistry of actinides. The generalization of the use of collision and reaction cells as components of inductively coupled plasma mass spectrometers (ICP/MS), with the purpose of increasing isotopic discrimination by chemical means [52,53], has led to the exploration of differences in reactivity of the An^+ ions with various substrates to resolve isobaric nuclides in the analysis of actinides [54,55]. Other recent work in the field of actinide elemental analysis, mainly with ICP/MS [56–58] – but also with thermal ionization mass spectrometry (TIMS) [59] – has confirmed the importance of the fundamental ion chemistry studies.

On the fundamental side, it should be remarked that the $\Delta H_{hyd}[AnO_2^{2+}]$ values obtained recently by Gibson et al. [17] (see previous section) showed remarkably close agreement with a recent theoretical study by Moskaleva et al. of the solvation of uranyl by water [60]. In fact, one of the interests in studying fundamental aspects of actinide chemistry, particularly physicochemical properties of actinide species in the gas phase, lies in its direct relevance to theoretical studies. The large number of electrons and the influence of relativistic effects in the actinides, that posed severe limitations in the past, have recently been largely surpassed by progress in quantum chemical methods and improved computational facilities. This has stimulated a

renewed interest in the area of computational actinide chemistry, which has led to a growing number of reliable theoretical studies on actinide systems of increasing complexity. Some of these studies, like that cited above [60], have employed gas-phase results as a reference and we anticipate that new experimental results will be of increasing use for theoreticians in the near future, to both develop and validate advanced theoretical approaches for the actinide-containing molecules.

Acknowledgments

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