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International Journal of Mass Spectrometry 228 (2003) 457–465

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

FTICR-MS study of the gas-phase thermochemistry of americium oxides

Marta Santos[a], Joaquim Marçalo[a], João Paulo Leal[a],
António Pires de Matos[a,*], John K. Gibson[b,1], Richard G. Haire[b]

[a] Departamento de Química, Instituto Tecnológico e Nuclear, 2686-953 Sacavém, Portugal
[b] Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6375, USA

Received 28 November 2002; accepted 18 March 2003

This paper is dedicated to Professor Helmut Schwarz on the occasion of his 60th birthday. The authors acknowledge with conviction his immense contribution for the development of gas-phase ion chemistry and will always remember his exciting lectures in MS meetings. The Actinide Chemistry Group at ITN would also like to recall the high energy he imparted to his students that came to Sacavém a few years ago to collaborate in generating the ubiquitous uranyl ion in the gas phase. A.P.M. and J.M. are grateful for the fine hospitality during their visits to Berlin. In one of the visits, A.P.M. remembers an excellent opera evening as well as the MS discussions in the laboratory.

Abstract

Gas-phase ion chemistry experiments with americium using Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) were performed for the first time. Reactions of Am^+ and AmO^+ with the oxidants N_2O, C_2H_4O (ethylene oxide), H_2O, O_2, CO_2, and NO have been studied. Am^+ formed AmO^+ with all the reagents except NO, while AmO^+ only reacted with C_2H_4O to form $AmO_2{}^+$ and other products. These results allowed us to estimate the previously unknown Am^+–O and OAm^+–O bond dissociation energies. The ionization energies (IE) of AmO and AmO_2 could also be determined by two different types of experiments: charge-transfer “bracketing” with $AmO_2{}^+$, yielding $IE(AmO_2) = 7.23 \pm 0.15$ eV, and AmO^+ reactivity with dienes, following a model developed by Helmut Schwarz and coworkers, leading to $IE(AmO) = 5.9 \pm 0.2$ eV. With this last method, we were also able to resolve the disagreement between the two literature values for the ionization energy of PuO.

Keywords: Actinide ions; Americium oxides; Plutonium oxide; Ionization energies; Thermochemistry

1. Introduction

We have recently reported on the first gas-phase ion chemistry studies of the transuranium actinides Np and Pu by Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS), in which contributions were made to the characterization of the oxidation reaction kinetics and thermodynamics of Np and Pu ions [1]. As can be appraised in a recent review paper [2], prior to this study, gas-phase ion chemistry experiments with the highly radioactive members of the actinide (An) series Pa, Np, Pu, Am, Cm, Bk, Cf, and Es had been based on the use of the laser ablation with prompt reaction and detection (LAPRD)

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[*] Corresponding author. Tel.: +351-21-994-6199; fax: +351-21-994-1455.
E-mail addresses: pmatos@itn.pt (A. Pires de Matos), gibsonjk@ornl.gov (J.K. Gibson).
[1] Co-corresponding author. Tel.: +1-865-576-4291; fax: +1-865-574-4987.

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doi:10.1016/S1387-3806(03)00138-6

technique [3–13], while FTICR-MS studies of An ions had been limited to Th and U [14–20]. Very recently, quadrupole ion trap mass spectrometry (QIT-MS) has also been shown to be an adequate technique to study An ion chemistry in the gas phase [21,22].

In the present work, we have employed the proven capabilities of FTICR-MS to acquire information on the kinetics, mechanisms, and energetics of gas-phase ion/molecule reactions [23–29], to try to obtain fundamental thermodynamic data on gaseous actinide species. We focus on the oxidation of transuranium ions and extend our previous study with Np and Pu by examining the reactions of Am^+ and AmO^+ ions with several oxidants, namely N_2O, C_2H_4O (ethylene oxide), H_2O, O_2, CO_2, and NO. Reactions of Am^+ ions with C_2H_4O have recently been studied using the LAPRD technique [11]. Due to the fact that the available thermochemical data for Am oxides are very scarce, we make an effort to further characterize these species, using the well-established charge-transfer "bracketing" method [28–32] to determine the ionization energy of AmO_2, and a model developed by Schwarz and coworkers [33] to estimate the ionization energy of AmO. In that important study [33], the reactivity of lanthanide (Ln) monoxide cations with dienes of different nucleophilicities [34] was correlated with the ionization energies of the neutral lanthanide monoxides. Schwarz and coworkers have rationalized this and other examples from gas-phase organometallic ion chemistry in a broader model of inner-sphere electron transfer [35]. We also try to substantiate the validity of the model for the actinide monoxide cations by performing experiments with Th, U, Np, and Pu, for which IE(AnO) are known.

2. Experimental

The experiments were performed in a Finnigan FT/MS 2001-DT FTICR mass spectrometer, equipped with a 3T 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 the An metal (2% in the case of Am, 5% in the cases of Th, U, Np, and Pu) 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 in Instituto Tecnológico e Nuclear (ITN), while the samples containing natural U, Np-237, Pu-242, and Am-243 were prepared at Oak Ridge National Laboratory (ORNL).

All the reagent gases O_2, N_2O, CO_2, NO, and C_4H_6 (1,3-butadiene) were obtained commercially and used as purchased (purity $>$ 99%). C_2H_4O (ethylene oxide), C_5H_8 (isoprene), $C_6H_{15}N$ (triethylamine), $C_8H_{11}N$ (*N*,*N*-dimethylaniline and 2,6-dimethylaniline), and $C_9H_{13}N$ (*N*,*N*-dimethyl-*p*-toluidine) were all obtained commercially (purity $>$ 99%) and degassed prior to use. H_2O was thoroughly deoxygenated by bubbling with high-purity N_2, and degassed prior to use. 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 checked in situ for their purity through EI spectra.

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. Isolation of the An metal ions from the abundant Pt ions formed in the LDI process was achieved using single-frequency, frequency-sweep, or SWIFT excitation [36]. The An oxide ions were either produced by LDI of the oxide layer on the surface of the samples or, in the case of the less oxophilic actinide metals, by reaction of the metal ion with O_2, N_2O, or C_2H_4O, introduced in the vacuum chamber through pulsed valves. Isolation of the An oxide ions was also achieved using single-frequency, frequency-sweep, or SWIFT excitation.

The reactant ions were thermalized by collisions with argon, introduced in the instrument through pulsed valves to pressures of *ca.* 10^{-5} Torr or through a leak valve with constant pressures of $(1–5) \times 10^{-6}$ Torr. The reproducibility of reaction kinetics as well as the linearity of semilog plots of normalized reactant ion intensities versus time were used as indications of thermalization of the reactant ions. In the cases where there was more than one product ion, the absence of changes in the product distributions for different collisional cooling periods or collision gas pressures was also considered as an indication of the effectiveness of the thermalization procedure.

Neutral pressures, measured by a Bayard–Alpert type ionization gauge, were calibrated using standard reactions of methane [37] and acetone ions [38], and included corrections for the different ionization efficiencies of the reagents, calculated according to Bartmess and Georgiadis [39], based on experimental molecular polarizabilities [40]. The rate constants (k) were determined from the pseudo-first-order decay of the reactant ion relative intensity as a function of time, at constant neutral reagent pressure. These constants are reported as reaction efficiencies, that is, as fractions of the average dipole orientation (ADO) theory collisional rates (k_{ADO}) [41], calculated using experimental molecular polarizabilities and dipole moments of the neutral reagents [40]. Uncertainties in the pressure calibration procedure may lead to errors in the absolute rate constants that we estimate to be ±50%, but relative magnitudes of the reaction efficiencies should have errors lower than 20%.

Special care was taken to ensure a low background and avoid reactions with residual water and oxygen by allowing long pumping times with the solids probe inside the high-vacuum chamber before introducing the reagents.

3. Results and discussion

3.1. Reactions of Am^+ and AmO^+ ions with oxidants

Am^+ ions reacted with the oxidants N_2O, C_2H_4O, H_2O, O_2, and CO_2, producing AmO^+ as the single primary product. With NO no reaction was observed. In Table 1 we show the efficiencies k/k_{ADO} for these reactions and, for the sake of comparison, we also present the corresponding values obtained for Th^+, U^+, Np^+, and Pu^+ in our previous work [1]. Am^+ shows the lowest reaction efficiencies with all the oxidants, compared with the other An^+ ions. This is consistent with a reduced reactivity of Am^+ due to a high promotion energy (2.54 eV) needed to achieve a reactive electronic configuration where two unpaired non-f electrons are available (see Table 2). This model has been productively used in other studies of gas-phase actinide ion reactivity, as described in a recent review [2]. As noted in our previous work [1], the neutral reagent can introduce kinetic restrictions beyond the exothermicities of the reactions and, therefore, influence the efficiencies. For instance, in the case of H_2O a considerable rearrangement is required to yield AnO^+ and H_2. As we can see in Table 1, very low reaction efficiencies were obtained in the reactions of Am^+ ions with N_2O, H_2O, and CO_2, which may be attributed to kinetic restrictions associated with these particular neutral reagents. This behavior of Am^+ indicates that, as pointed out in our previous work [1] for the case of Pu^+, the kinetic

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

An^+	N_2O	C_2H_4O	H_2O	O_2	CO_2	NO
Th^+ [a]	0.68	0.37	0.20	0.86	0.35	0.49
U^+ [a]	0.47	0.34	0.13	0.72	0.29	0.46
Np^+ [a]	0.48	0.32	0.10	0.68	0.30	0.45
Pu^+ [a]	0.02	0.21	0.004	0.27	0.003	0.17
Am^+ [b]	0.004	0.21	0.001	0.32	0.001	<0.001

[a] Ref. [1].

[b] This work.

Table 2
Promotion energies from the ground-state configurations to reactive-state configurations of the An^+ ions (with terms in parentheses)[a]

An^+	Ground-state configuration	Promotion energy (eV)	Reactive-state configuration
Th^+	$6d^27s$ ($^4F_{3/2}$)	0.00	$6d^27s$ ($^4F_{3/2}$)
U^+	$5f^37s^2$ ($^4I^\circ_{9/2}$)	0.04	$5f^36d7s$ ($^6L^\circ_{11/2}$)
Np^+	$5f^46d7s$ ($^7L_5$)	0.00	$5f^46d7s$ ($^7L_5$)
Pu^+	$5f^67s$ ($^8F_{1/2}$)	1.08	$5f^56d7s$ ($^8K^\circ_{7/2}$)
Am^+	$5f^77s$ ($^9S^\circ_4$)	2.54	$5f^66d7s$ ($J = 2$)

[a] Ref. [42].

Table 3
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
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

[a] Ref. [43].

restrictions are more apparent for those ions with sizable promotion energies (see Table 2).

In Table 3 we show the oxygen dissociation energies for the oxidants used, designated as R–O bond dissociation energies (BDE(R–O)). The formation of AmO^+ in the reaction of Am^+ with CO_2 indicates that $BDE(Am^+–O) \geq BDE(OC–O) = 532.2$ kJ/mol. To our knowledge, the only literature value for $BDE(Am^+–O)$ is 673 kJ/mol, which was indirectly inferred from the abundance of AmO^+ relative to Am^+ in an inductively coupled plasma (ICP) ion source [44]. Although the non-observation of a reaction cannot necessarily be interpreted thermodynamically, based on the following rationale, we consider that the lack of reaction between Am^+ and NO can be used to establish an upper limit for $BDE(Am^+–O)$. Specifically, the k/k_{ADO} values in Table 1 show that the reaction of Pu^+ with NO is reasonably efficient, indicating that for this reagent reduced kinetic restrictions occur, as compared for instance with CO_2. In the case of Am^+, the reaction efficiencies are rather similar to the ones obtained for Pu^+, with the exception of NO, and therefore we interpret the non-observation of AmO^+ with this reagent as having a thermodynamic origin. This upper limit of 631.6 kJ/mol for $BDE(Am^+–O)$ is in discord with the literature value cited above obtained in ICP experiments. With these lower and upper bounds, we could make a first estimate of $BDE(Am^+–O) = 580 \pm 50$ kJ/mol. However, the $BDE(An^+–O)$ along the actinide series should be related to the promotion energies from the ground states of the An^+ ions to states with two unpaired non-f electrons needed to form a double bond with oxygen. An equivalent type of relationship has been proposed for the case of BDE(An–O) [45]. Taking into account the promotion energies from Table 2, we could expect $BDE(Am^+–O)$ to be *ca.* 140 kJ/mol lower than $BDE(Pu^+–O) = 683 \pm 55$ kJ/mol [46], the literature value that better agrees with our earlier study of the thermochemistry of Pu oxides [1]. From these considerations, we then estimate $BDE(Am^+–O) = 560 \pm 30$ kJ/mol.

The reactivity of AmO^+ ions with N_2O, C_2H_4O, H_2O, O_2, CO_2, and NO was also studied and no reactions were observed for the cases of N_2O, O_2, CO_2, and NO. With H_2O, very slow addition ($k/k_{ADO} = 0.001$) of a water molecule to give $AmO_2H_2^+$ was the only process that occurred. With C_2H_4O, a slow reaction could be observed ($k/k_{ADO} = 0.03$), leading to four different primary products: AmO_2^+ (10%), $AmO_2H_2^+$ (20%), $AmO_2C_2H_2^+$ (60%), and $AmO_2C_2H_4^+$ (10%). In a previous study of the Am^+/C_2H_4O system by the LAPRD technique, these products could also be detected [11]. In contrast to AmO^+, the AnO^+ ions (An = Th, U, Np, Pu) studied before in our laboratories produced only AnO_2^+ in reactions with C_2H_4O [1].

The formation of AmO_2^+ in the reaction of AmO^+ with C_2H_4O shows that $BDE(OAm^+–O) \geq BDE(C_2H_4–O) = 354.3$ kJ/mol, but there is no literature data available for comparison in this case. The formation of AmO_2^+ as a minor product, as compared with the exclusive formation of AnO_2^+ in the case of the actinides studied previously [1], is interpreted as indicating that the thermodynamic driving force for formation of AmO_2^+ is small, and that $BDE(OAm^+–O)$ is close to the established lower limit of 354.3 kJ/mol. Moreover, the low reaction efficiency obtained in the case of AmO^+ ($k/k_{ADO} = 0.03$, being 0.003 the partial efficiency for the formation of AmO_2^+), when compared with the ones obtained before for other AnO^+ ions [1] (An = Th, $k/k_{ADO} = 0.34$; An = U, $k/k_{ADO} = 0.30$; An = Np, $k/k_{ADO} = 0.28$; An = Pu, $k/k_{ADO} = 0.15$), could also be interpreted in the context of a small thermodynamic driving force for formation of AmO_2^+, as no important kinetic restrictions are apparent in the reactions of C_2H_4O with AnO^+ ions, as well as with An^+ ions (see Table 1). The non-observation of AmO_2^+ in the reaction of AmO^+ with O_2 can be used to establish an upper limit for BDE(OAm^+–O), if similar reasoning to that used above for the estimation of BDE(Am^+–O) is applied. O_2 is a reagent for which no relevant kinetic restrictions appear to be present, as can be inferred from Table 1 and from the k/k_{ADO} values obtained in our earlier work [1] for the reactions of AnO^+ ions with O_2 (An = U, $k/k_{ADO} = 0.45$; An = Np, $k/k_{ADO} = 0.28$; An = Pu, $k/k_{ADO} = 0.07$). In conclusion, we think that we have confidently bracketed BDE(OAm^+–O) between 350 and 500 kJ/mol but, based on the above considerations on product distributions and oxidation kinetics, we tentatively place it in the lower half of the bracketing interval, that is, we estimate BDE(OAm^+–O) = 390 ± 40 kJ/mol. This value can be compared with the estimates of BDE(ONp^+–O) = 580 ± 70 kJ/mol and BDE(OPu^+–O) = 520 ± 20 kJ/mol made in our last work [1] and with a literature value [46] of BDE(OU^+–O) = 772 ± 56 kJ/mol. This decrease in BDE(OAn^+–O) from U to Am may reflect the known diminishing stability of the oxidation states higher than +4 across this part of the actinide series.

3.2. Ionization energies of AmO and AmO_2

In an effort to further characterize the Am oxides thermochemically, we performed charge-transfer "bracketing" experiments [28–32] to determine the ionization energy (IE) of AmO_2, with a procedure previously tested for PuO_2 [1]. We decided to start the "bracketing" experiments with reagents having IEs in the range used before for PuO_2, and in fact charge transfer with AmO_2^+ was observed for *N*,*N*-dimethylaniline (IE = 7.12 ± 0.02 eV [43]) and *N*,*N*-dimethyl-*p*-toluidine (IE = 6.93 ± 0.02 eV [43]), whereas it was not observed for 2,6-dimethylaniline (IE = 7.33 ± 0.05 eV [43]) and triethylamine (IE = 7.53 ± 0.01 eV [43]). Slow adduct formation occurred with all the amines studied. From the above results, we obtain IE(AmO_2) = 7.23 ± 0.15 eV, but there are no literature values to compare with. Our IE(AmO_2) value is slightly larger than IE(PuO_2) obtained in our previous work [1], substantially smaller than IE(ThO_2) = 8.7 ± 0.2 eV [46], and significantly larger than IE(UO_2) = 5.5 ± 0.5 eV [46] and IE(NpO_2) = 5.0 ± 0.5 eV [46]. With the exception of the anomalously low reported IE(NpO_2), lower than IE(NpO) = 5.7 ± 0.1 eV [46] in which Np is in a lower oxidation state, this relative ordering of the IE(AnO_2) seems to be in agreement with the experimental evidence gathered in a laser ablation study of AnO_2 (An = Th, U, Np, Pu, and Am) [47] and with the known accessibility of oxidation states of the actinides.

Concerning the ionization energy of AmO, it was argued in the laser ablation study of AnO_2 mentioned above [47] that IE(An) ≈ IE(AnO). Since IE(Am) = 5.9738 ± 0.0002 eV, as recently determined by resonance ionization mass spectroscopy (RIMS) [48], we can expect an IE(AmO) around 6 eV. For IEs of this magnitude, there are no adequate reagents to perform charge-transfer "bracketing" experiments [43]. Therefore, we decided to see if a model developed by Schwarz and coworkers to interpret the reactivity of lanthanide oxide ions with dienes [33] was valid in the case of the AnO^+ ions and could be used to estimate IE(AmO). According to this model, the reactivity increases with the nucleophilicity of the diene [35] and with the electrophilicity of LnO^+, thus with IE(LnO). We studied the reactions with the same dienes used by Schwarz and coworkers, 1,3-butadiene and isoprene, for An = Am and also for An = Th, U, Np, and Pu, to be able to compare the results with literature IE(AnO) values.

ThO^+ was the only AnO^+ ion that reacted with 1,3-butadiene, forming $ThOC_4H_6^+$ as the single primary product in a rather inefficient way (k/k_{ADO} = 0.02). With isoprene, all the AnO^+ ions were reactive, as can be seen in Table 4 where the primary product distributions and the reaction efficiencies obtained are presented. Formation of the condensation product $AnOC_5H_8^+$ was observed for all An, while

Table 4
Primary product distributions (in %) and efficiencies (k/k_{ADO}) of the reactions of AnO^+ ions with isoprene

AnO^+	$AnOC_5H_5^+$	$AnOC_5H_6^+$	$AnOC_5H_8^+$	k/k_{ADO}
ThO^+	25	40	35	0.17
UO^+	–	–	100	0.02
NpO^+	–	30	70	0.01
PuO^+	–	30	70	0.01
AmO^+	–	80	20	0.04

the dehydrogenation product $AnOC_5H_6^+$ formed for all An except U. In the case of ThO^+ ions, which are clearly the most reactive of the AnO^+, formation of a product formulated as $ThOC_5H_5^+$ was also observed.

In Table 5 we list the literature values of IE(AnO) which, at first glance, seem to be consistent with the reactivity results, according to the model put forward by Schwarz and coworkers [33]. The onset of reactivity of the LnO^+ ions with butadiene occurred for $IE(LnO) \approx 6.1$ eV, while with isoprene it corresponded to $IE(LnO) \approx 5.6$ eV. The literature value of 6.6 eV for IE(PuO) [50] appears to be too high and we would recommend the literature value of 5.8 eV [46], with an uncertainty that we believe we can narrow down now to 0.2 eV, as we indicate in Table 5. The fact that AmO^+ does not react with butadiene but does react with isoprene allows us to assign IE(AmO) in the range of 5.6–6.1 eV. The data in Table 4 shows that AmO^+ is more reactive with isoprene than are UO^+, NpO^+, and PuO^+, an observation that leads us to estimate $IE(AmO) = 5.9 \pm 0.2$ eV.

In view of the apparent agreement between our results for reactivities of several AnO^+ with dienes and the model developed by Schwarz and coworkers for LnO^+ reactivities [33], a few additional comments are in order. Previous studies of the reactivity of AnO^+ ions with unsaturated hydrocarbons have shown high reactivities for ThO^+ and UO^+ ions that were associated with their particular electronic structures, d-block character in the case of Th and eventual f-electron participation in the chemistry in the case of U [2,19,22]. Therefore, it is somewhat surprising that the results of the present work suggest that for butadiene and isoprene the activation mechanism proposed for LnO^+ by Schwarz and coworkers [33] also applies to ThO^+ and UO^+. The transuranium AnO^+ ions should be more lanthanide-like and therefore their reactivity with dienes would be expected to follow a trend similar to the one observed for LnO^+ ions.

To complete the study of the An/diene system, we also carried out the reactions of An^+ and AnO_2^+ ions (An = Th, U, Np, Pu, and Am) with 1,3-butadiene and isoprene. The primary product distributions and the reaction efficiencies obtained for the metal cations are presented in Table 6 for butadiene and in Table 7 for isoprene. The high reactivities of Th^+, U^+, and Np^+ with both dienes, compared with the lower reactivity of Pu^+, which reacts only with isoprene, and the inert character of Am^+, follow the trend defined by the promotion energies from the ground-state configurations to reactive-state configurations of the An^+ ions presented in Table 2. This is in agreement with previous reactivity studies of these actinide ions with alkenes and other organic molecules [2].

The ThO_2^+ ion reacted very efficiently with both dienes ($k/k_{ADO} = 1.60$ for butadiene and $k/k_{ADO} =$

Table 5
Ionization energies (IE) of AnO

AnO	ThO	UO	NpO	PuO	AmO
IE (eV)	6.1 ± 0.1[a] 6.1 ± 0.1[b]	5.7 ± 0.2[a] 5.65 ± 0.2[b] 5.6 ± 0.1[c]	5.7 ± 0.1[a] 5.7 ± 0.1[b]	5.8 ± 0.5[a] 6.6 ± 0.1[c] 5.8 ± 0.2[d]	5.9 ± 0.2[d]

[a] Ref. [46].
[b] Ref. [49].
[c] Ref. [50].
[d] This work.

Table 6

Primary product distributions (in %) and efficiencies (k/k_{ADO}) of the reactions of An^+ ions with 1,3-butadiene

An^+	$AnC_2H_2^+$	$AnC_3H_3^+$	$AnC_4H_2^+$	$AnC_4H_4^+$	$AnC_4H_6^+$	k/k_{ADO}
Th^+	65	5	10	20	–	0.80
U^+	80	–	–	10	10	0.75
Np^+	80	–	–	10	10	0.62
Pu^+	–	–	–	–	–	<0.001
Am^+	–	–	–	–	–	<0.001

1.53 for isoprene) by abstraction of a hydrogen atom to form the very stable species ThO_2H^+, a typical reactivity pattern for the thorium dioxide cation [19]. The remaining AnO_2^+ only formed the adducts in rather inefficient processes (k/k_{ADO} in the range 0.002–0.006 for butadiene and 0.03–0.05 for isoprene). The inert character of the UO_2^+ ions is in accord with the high value of BDE(OU^+–O) = 772 ± 56 kJ/mol [46] and with previous reactivity studies with organic molecules [2,18,19,22]. The reduced reactivity of NpO_2^+ and PuO_2^+ ions may also be a consequence of rather large BDE(OAn^+–O) values, that we estimated as BDE(ONp^+–O) = 580 ± 70 kJ/mol and BDE(OPu^+–O) = 520±20 kJ/mol in our earlier work [1]. We also showed [1] that the PuO_2^+ ions were inert towards different organic molecules. Considering the reactive nature of ThO_2^+ (BDE(OTh^+–O) = 433 ± 30 kJ/mol [46]), the inertness of AmO_2^+ would not be predicted from our estimated BDE(OAm^+–O) of only 390 ± 40 kJ/mol. The apparently discrepant behaviors of ThO_2^+ and AmO_2^+ can be rationalized based on a lower BDE(OAm^+–OH) compared with BDE(OTh^+–OH) (larger than BDE(H–OH) [19]) and the high stability of tetravalent Th.

We can now make some final tests of the thermochemistry of the Am oxides, as derived from the studies that we have been describing. Based on Eq. (1),

$$\mathrm{BDE}(\mathrm{Am^+–O}) - \mathrm{BDE}(\mathrm{Am–O}) = \mathrm{IE}(\mathrm{Am}) - \mathrm{IE}(\mathrm{AmO}) \tag{1}$$

and considering IE(Am) = 5.9738 ± 0.0002 eV [48] and our estimates of IE(AmO) = 5.9 ± 0.2 eV and of BDE(Am^+–O) = 560 ± 30 kJ/mol, we derive BDE(Am–O) = 553 ± 36 kJ/mol and see excellent agreement with the value of BDE(Am–O) = 550 kJ/mol estimated in earlier work on the neutral actinide oxides [45].

An analogous exercise based on Eq. (2),

$$\mathrm{BDE}(\mathrm{OAm^+–O}) - \mathrm{BDE}(\mathrm{OAm–O}) = \mathrm{IE}(\mathrm{AmO}) - \mathrm{IE}(\mathrm{AmO_2}) \tag{2}$$

and on our estimates of IE(AmO) = 5.9 ± 0.2 eV, IE(AmO_2) = 7.23 ± 0.15 eV, and BDE(OAm^+–O) = 390 ± 40 kJ/mol, leads to BDE(OAm–O) = 518 ± 47 kJ/mol. This value can be compared with BDE(OTh–O) = 684 ± 37 kJ/mol, BDE(OU–O) = 753 ± 76 kJ/mol, BDE(ON*p*–O) = 512 ± 86 kJ/mol, and BDE(OPu–O) = 639 ± 30 kJ/mol, calculated with Eq. (2) using data from the literature [46] and from our previous work [1]. With the exception of the value of Np, the trend in BDE(OAn–O) is in

Table 7

Primary product distributions (in %) and efficiencies (k/k_{ADO}) of the reactions of An^+ ions with isoprene

An^+	$AnC_2H_2^+$	$AnC_3H_2^+$	$AnC_3H_4^+$	$AnC_5H_4^+$	$AnC_5H_6^+$	k/k_{ADO}
Th^+	25	10	50	15	–	0.68
U^+	35	–	50	–	15	0.67
Np^+	25	–	55	–	20	0.48
Pu^+	–	–	50	–	50	0.13
Am^+	–	–	–	–	–	<0.001

agreement with the known decreasing stability of the An dioxides from U to Am. The anomalously low derived BDE(ONp–O) can be traced to the reported $\mathrm{IE(NpO_2)} = 5.0 \pm 0.5\,\mathrm{eV}$ [46], which is likely significantly lower than the actual value.

4. Conclusions

With this work, in which the gas-phase ion chemistry of americium has been probed for the first time using FTICR-MS, we confirm previous studies done with the LAPRD technique which showed that the reactivity of Am^+ ions correlated with the promotion energy from the ground-state to a reactive-state configuration, as for other actinide series ions. Moreover, we are able to contribute to the thermodynamic characterization of the americium oxide system, for which very few data were known. We have established definitive lower limits and made estimates for the Am^+–O and OAm^+–O bond dissociation energies, and determined the ionization energies of AmO and AmO_2. We have further shown that a model developed by Schwarz and coworkers [33] to interpret the gas-phase reactivity of lanthanide monoxide cations with dienes can be used productively for the estimation of the ionization energies of actinide monoxides. In the near future, we intend to continue gas-phase reactivity studies with the actinide ions, in an attempt to broaden our understanding of the chemistry along the actinide series.

Acknowledgements

This work was supported by Fundação para a Ciência e a Tecnologia (contract POCTI/35364/QUI/2000) and by Division of Chemical Sciences, Geosciences, and Biosciences, U.S. Department of Energy (contract DE-AC05-00OR22725 with ORNL, managed by UT-Battelle, LLC).

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