Inorg. Chem. **2002**, *41*, 5897–5906

Inorganic Chemistry

Article

Gas-Phase Chemistry of Bare and Oxo-Ligated Protactinium Ions: A Contribution to a Systematic Understanding of Actinide Chemistry

John K. Gibson* and Richard G. Haire

Chemical Sciences Division, Oak Ridge National Laboratory,
P.O. Box 2008, Oak Ridge, Tennessee 37831-6375

Received April 29, 2002

Gas-phase chemistry of bare and oxo-ligated protactinium ions has been studied for the first time. Comparisons were made with thorium, uranium, and neptunium ion chemistry to further the systematic understanding of 5f elements. The rates of oxidation of Pa^+ and PaO^+ by ethylene oxide compared with those of the homologous uranium ions indicate that the first and second bond dissociation energies, BDE[Pa^+–O] and BDE[OPa^+–O], are approximately 800 kJ mol^{-1}. The relatively facile fluorination of Pa^+ to PaF_4^+ by SF_6 is consistent with the high stability of the pentavalent oxidation state of Pa. Reactions with ethene, propene, 1-butene, and *iso*-butene revealed that Pa^+ is a very reactive metal ion. In analogy with U^+ chemistry, ethene was trimerized by Pa^+ to give $PaC_6H_6^+$. Reactions of Pa^+ with larger alkenes resulted in secondary and tertiary products not observed for U^+ or Np^+. The bare protactinium ion is significantly more reactive with organic substrates than are heavier actinide ions. The greatest difference between Pa and heavier actinide congeners was the exceptional dehydrogenation activity of PaO^+ with alkenes; UO^+ and NpO^+ were comparatively inert. The striking reactivity of PaO^+ is attributed to the distinctive electronic structure at the metal center in this oxide, which is considered to reflect the greater availability of the 5f electrons for participation in bonding, either directly or by promotion/hybridization with higher-energy valence orbitals.

Introduction

Protactinium occupies a key position in the periodic table, and the actinide series in particular. The energies of the vacant 5f orbitals of the preceding element, Th, are sufficiently high that in many regards it can be considered as a group IV d-block transition metal. However, the energies of the 5f orbitals relative to the 6d and 7s orbitals decrease dramatically with increasing nuclear charge, and the 5f orbitals of uranium are occupied and can participate in bonding (e.g., in the pure metal).[1] The bonding character of Pa, which lies between Th and U in the actinide series, is not always clear, and is dependent on the chemical environment. In elemental Pa, the 5f electrons are considered to have some involvement in bonding.[2] A contribution to bonding from the 5f electrons has also been proposed for some protactinium compounds, such as PaN and PaAs.[3]

The most prevalent oxidation state in compounds is Pa(V), where all of the valence electrons outside the [Rn] core are engaged in covalent and/or ionic bonding. Compounds and solutions of Pa(IV) are known,[4] but it is difficult to reduce Pa below the tetravalent state.[5] Protactinium is distinctive even among the actinides in its remarkable propensity toward hydrolysis and polymerization.[4] Maddock and Pires de Matos[6] noted the extensive polymerization of the ethoxide, $Pa(OC_2H_5)_5$, dissolved in benzene.

Although several protactinium solid inorganic compounds and organic complexes in aqueous solution have been reported for Pa, limited information is available regarding its organometallic chemistry.[4,7,8] The tetravalent π-bonded cyclopentadienyl (Cp) compound, $Pa(C_5H_5)_4$, was prepared

---

* Corresponding author. E-mail: gibsonjk@ornl.gov.

[1] Katz, J. J.; Morss, L. R.; Seaborg, G. T. In *The Chemistry of the Actinide Elements*, 2nd ed.; Katz, J., Seaborg, G. T., Morss, L. R., Eds.; Chapman and Hall: New York, 1986; pp 1121−1195.

[2] Smith, J. L.; Kmetko, E. A. *J. Less-Common Met.* **1983**, *90*, 83−88.

[3] Brooks, M. S. S.; Calestani, G.; Spirlet, J. C.; Rebizant, J.; Müller, W.; Fournier, J. M.; Blaise, A. *Physica* **1980**, *102B*, 84−87.

[4] Kirby, H. W. In *The Chemistry of the Actinide Elements*, 2nd ed.; Katz, J. J., Seaborg, G. T., Morss, L. R., Eds.; Chapman and Hall: New York, 1986; pp 102−168.

[5] Mikheev, N. B.; Kamenskaya, A. N.; Kulykhin, S. A.; Rumer, I. A. *Mendeleev Comm.* **1993**; 198−199.

[6] Maddock, A. G.; Pires de Matos, A. *Radiochim. Acta* **1972**, *18*, 71−73.

10.1021/ic025683t CCC: $22.00

by Baumgärtner et al. in 1969.[9] Subsequently, three other tetravalent π-bonded organometallic compounds of Pa were reported: protactinocene, $Pa(C_8H_8)_2$;[10,11] its tetramethyl-substituted analogue, Pa-bis(η^8-1,3,5,7-tetramethylcyclooctatetraene);[12] and $Pa(MeCp)_4$, where MeCp represents methylcyclopentadienyl.[13] The role of the 5f electrons in bonding in these organometallics is not well-established, and an understanding of (hypothetical) σ-bonded Pa organometallics is even less known. Kot and Edelstein provided a summary of basic protactinium chemistry,[13] including similarities of it to that of the group V d-block transition metals, Nb and Ta, and have reported the preparation and characterization of $Pa(BH_3CH_3)_4$.

Gas-phase metal ion chemistry is a well-established tool for elucidating fundamental aspects of d-block transition metal chemistry, particularly the role of electronic structures and energetics.[14] This line of inquiry has also been extended fruitfully to the 4f lanthanide elements.[15−22] The initial studies of actinide ion chemistry were limited to thorium and uranium[23−29] but have been extended to more radioactive actinides in recent years.[30−37] Some of the actinide results have suggested a greater role for the 5f electrons for the early members of the series. The chemistry described here for Pa^+ and PaO^+ further illuminates essential aspects of the chemistry of this rare and distinctive element.

Experimental Section

The experimental approach and procedures used have been described in detail elsewhere,[21,30,31] and only a general discussion and specific details relevant to the protactinium experiments are included here. The approach of laser ablation with prompt reaction and detection (LAPRD) is well-suited to studying fundamental aspects of the comparative chemistry of gas-phase metal ion chemistry.

The samples consist of one or more metal oxides mixed with copper powder and pressed into a pellet. A net composition corresponding to a few atomic percent of the metal(s) of interest relative to the copper matrix is used. A pulsed excimer laser (λ = 308 nm; pulse duration $\approx$ 15 ns) is focused onto the target, generating M^+, MO^+, and, in some cases, MO_2^+ ions. Owing to the relatively high ionization energy of atomic copper, 7.7 eV, only minuscule amounts of Cu^+ are ablated compared with the primary ions of interest. A pulsed valve injects volatile reagent gases into the path of ablated ions. The transient pressure in the 3 cm long reaction zone is indeterminate, but the results indicate multiple ion−molecule collisions. It is certain that very large temporal and spatial pressure gradients occur in the reaction zone, and it is impractical to reasonably estimate the actual local pressure during the reaction period. The goal of these experiments with this specialized radioactive mass spectrometer was to directly compare the chemistries of different actinides under identical experimental conditions, not to obtain absolute reaction rates. Both the unreacted and product positive ions are injected into the source region of a reflectron time-of-flight mass spectrometer (RTOF-MS), $\sim$35 μs after the laser pulse. The sampled ions typically have an average velocity of $\sim$1 km s^{-1}, which corresponds to a kinetic energy of $\sim$120 kJ mol^{-1} for an actinide ion.

For the organic reagents, the maximum center-of-mass collisional energy (KE_{CM}) is in the range 10 kJ mol^{-1} (methane) to 20 kJ mol^{-1} (butene). Although all LAPRD reactions are carried out under somewhat hyperthermal conditions, it has been established that substantially endothermic reactions are not enabled. Comparative reactivities of simultaneously studied ions are particularly reliable. It has been demonstrated that electronically excited state metal ion chemistry is not important under these experimental conditions,[21,30−37] possibly because of the use of relatively slow, low-energy ions in the tail of the ablation plume.

Three oxide-in-copper matrix targets containing Pa were studied in the work reported here, Pa alone, Pa/U/Ta, and Pa/Np. The latter two multielement targets were particularly useful for assessing the comparative chemistry of Pa ions with those of U and Np. In the Pa/U/Ta target, Ta was included as a prototypical "heavy" group V d-block transition metal element. However, only very minor amounts of Ta ions were generally ablated, presumably because of the relatively high ionization energy of Ta (7.9 eV vs 5.9 eV for Pa).

The isotopes used in this work were Pa-231, with a 33 000 year (y) half-life ($t_{1/2}$), natural U (99.3% U-238; $t_{1/2} = 4.5 \times 10^9$ y),

---

(7) Marks, T. J.; Streitweiser, A., Jr. In *The Chemistry of the Actinide Elements*, 2nd ed.; Katz, J., Seaborg, G. T., Morss, L. R., Eds.; Chapman and Hall: New York, 1986; pp 1547−1587.

(8) Marks, T. J. In *The Chemistry of the Actinide Elements*, 2nd ed.; Katz, J., Seaborg, G. T., Morss, L. R., Eds.; Chapman and Hall: New York, 1986; pp 1588−1628.

(9) Baumgärtner, F.; Fischer, E. O.; Kanellakopulos, B.; Laubereau, P. *Angew. Chem., Int. Ed.* **1969**, *8*, 202.

(10) Starks, D. F.; Parsons, T. C.; Streitweiser, A., Jr.; Edelstein, N. *Inorg. Chem.* **1974**, *13*, 1307−1308.

(11) Goffart, J.; Fuger, J.; Brown, D.; Duyckaerts, G. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 413−419.

(12) Solar, J. P.; Burghard, H. P. G.; Banks, R. H.; Streitweiser, A., Jr.; Brown, D. *Inorg. Chem.* **1980**, *19*, 2186−2188.

(13) Kot, W. K.; Edelstein, N. M. *New J. Chem.* **1995**, *19*, 641−654.

(14) *Organometallic Ion Chemistry*; Freiser, B. S., Ed.; Kluwer: Dordrecht, The Netherlands, 1996.

(15) Schilling, J. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 15−24.

(16) Sunderlin, L. S.; Armentrout, P. B. *J. Am. Chem. Soc.* **1989**, *111*, 3845−3855.

(17) Yin, W. W.; Marshall, A. G.; Marçalo, J.; Pires de Matos, A. *J. Am. Chem. Soc.* **1994**, *116*, 8666−8672.

(18) Heinemann, C.; Schröder, D.; Schwarz, H. *Chem. Ber.* **1994**, *127*, 1807−1810.

(19) Cornehl, H. H.; Heinemann, C.; Schröder, D.; Schwarz, H. *Organometallics* **1995**, *14*, 992−999.

(20) Marçalo, J.; Pires de Matos, A.; Evans, W. J. *Organometallics* **1996**, *15*, 345−349.

(21) Gibson, J. K. *J. Phys. Chem.* **1996**, *100*, 15688−15694.

(22) Marçalo, J.; Pires de Matos, A.; Evans, W. J. *Organometallics* **1997**, *16*, 3845−3850.

(23) Armentrout, P. B.; Hodges, R. V.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 3162−3163.

(24) Armentrout, P. B.; Hodges, R. V.; Beauchamp, J. L. *J. Chem. Phys.* **1977**, *66*, 4683−4688.

(25) Liang, Z.; Marshall, A. G.; Pires de Matos, A.; Spirlet, J. C. In *Transuranium Elements: A Half Century*; Morss, L. R., Fuger, J., Eds.; American Chemical Society: Washington, DC, 1992; pp 247−250.

(26) Heinemann, C.; Cornehl, H. H.; Schwarz, H. *J. Organomet. Chem.* **1995**, *501*, 201−209.

(27) Marçalo, J.; Leal, J. P.; Pires de Matos, A. *Int. J. Mass Spectrom. Ion Processes* **1996**, *157/158*, 265−274.

(28) Gibson, J. K. *Organometallics* **1997**, *16*, 4214−4222.

(29) Marçalo, J.; Leal, J. P.; Pires de Matos, A.; Marshall, A. G. *Organometallics* **1997**, *16*, 4581−4588.

(30) Gibson, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 2633−2640.

(31) Gibson, J. K. *Organometallics* **1998**, *17*, 2583−2589.

(32) Gibson, J. K.; Haire, R. G. *J. Phys. Chem. A* **1998**, *102*, 10746−10753.

(33) Gibson, J. K. *Inorg. Chem.* **1999**, *38*, 165−173.

(34) Gibson, J. K. *Radiochim. Acta* **1999**, *84*, 135−146.

(35) Gibson, J. K. *Int. J. Mass Spec.* **2000**, *202*, 19−29.

(36) Gibson, J. K.; Haire, R. G. *Int. J. Mass Spectrom.* **2000**, *203*, 127−142.

(37) Gibson, J. K. *J. Mass Spectrom.* **2001**, *36*, 284−293.

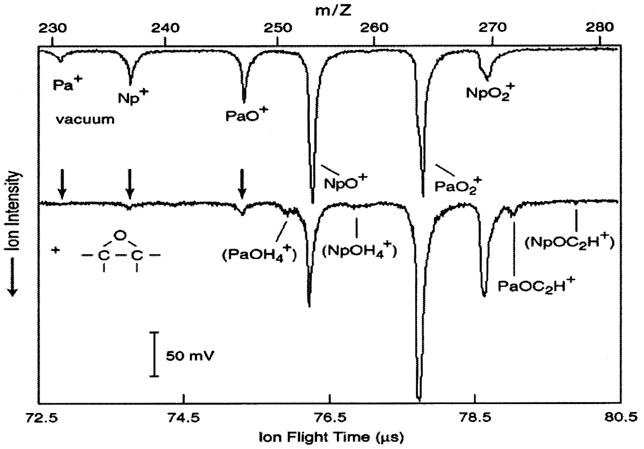

Figure 1. Mass spectra for ablation of protactinium oxide and neptunium oxide into vacuum (top spectrum) and into ethylene oxide (bottom spectrum). The PaO_2^+ peak in the bottom spectrum is off-scale. The peaks corresponding to "$PaOH_4$" and "$NpOH_4^+$" are attributed to collision-induced dissociation of PaO_2^+ and NpO_2^+ in the RTOF-MS; no hydride products are alleged.

and Np-237 ($t_{1/2} = 2.1 \times 10^6$ y), all of which α-decay. The Ta-181 is a naturally occurring stable isotope. Each of the gaseous reagents had a purity of at least 99%.

Results and Discussion

Reactions with Ethylene Oxide and Dimethyl Ether. The reactions of protactinium and neptunium ions with ethylene oxide are shown in Figure 1. The upper mass spectrum in Figure 1 shows a vacuum ablation spectrum, and the bottom spectrum shows all the ions (unreacted and products) after introduction of the reagent gas. It was found that the oxidation reactions 1 and 2 proceed under the nearly thermoneutral LAPRD conditions for the three actinides, An = Pa, U, Np. It is inferred that both reactions 1 and 2 are

$$An^+ + C_2H_4O \rightarrow AnO^+ + C_2H_4 \qquad (1)$$

$$AnO^+ + C_2H_4O \rightarrow AnO_2^+ + C_2H_4 \qquad (2)$$

exothermic, indicating that the $An^+{-}O$ and $OAn^+{-}O$ bond dissociation energies (BDEs) each exceed 354 kJ mol^{-1}.[38] Reaction 1 proceeds efficiently for the three actinides. Nearly all of the bare Pa^+, U^+, and Np^+ disappeared after addition of ethylene oxide. Previous results for oxidation of An^+ and AnO^+ by ethylene oxide[37] have indicated that the rates for reactions 1 and 2 correlated with BDE[$An^+{-}O$] and BDE[$OAn^+{-}O$], respectively. The present results suggest that BDE[$An^+{-}O$] values are comparable for PaO^+, UO^+, and NpO^+.

The value of BDE[$U^+{-}O$] is 803(25) kJ mol^{-1},[39] and BDE[$Np^+{-}O$] has been estimated as ~790 kJ mol^{-1}.[37] Accordingly, BDE[$Pa^+{-}O$] can be estimated to be ~800 kJ mol^{-1}; this is comparable to BDE[$Ta^+{-}O$] = 790(60) kJ mol^{-1}[40] and smaller than BDE[$Th^+{-}O$] = 862(21) kJ mol^{-1}.[39] Kleinschmidt and Ward[41] have determined BDE[Pa−O] = 788(17) kJ mol^{-1}. The evidently small difference between BDE[Pa−O] and BDE[$Pa^+{-}O$] suggests that the ionization energies, IE[Pa] and IE[PaO], are similar. Such similarity between metal atom and monoxide IEs is also characteristic of the lanthanides.[42]

As is evident in Figure 1, PaO^+ efficiently reacts with ethylene oxide, with oxidation to PaO_2^+ being the primary channel. The rate of oxidation of PaO^+ is substantially faster than that of NpO^+, and at least as fast as that of UO^+. Whereas most of the ablated PaO^+ was depleted, a significant amount of NpO^+ remained unreacted (Figure 1); the degree of depletion of UO^+ was evidently somewhat less than that of PaO^+. On the basis of the correlation between oxidation rates and BDEs, it is concluded that BDE[$OPa^+{-}O$] ≥ BDE[$OU^+{-}O$] = 770(60); the resulting estimate for BDE[$OPa^+{-}O$] is ~800 kJ mol^{-1}. As with uranium, the second metal−oxygen bond, $OPa^+{-}O$, is essentially as strong as the first bond, $Pa^+{-}O$. In contrast, BDE[$OTa^+{-}O$] is approximately 200 kJ mol^{-1} less than BDE[$Ta^+{-}O$]. In ThO_2^+, the thorium metal center is in a formally pentavalent state that is normally unstable, and BDE[$OTh^+{-}O$] is only 426(30) kJ mol^{-1}.[39]

The stabilities of the protactinium oxide ions can also be estimated from the vacuum ablation mass spectra from the relative amounts of directly ablated bare and oxo-ligated ions.[43] Vacuum spectra, such as those included in Figures 1 and 3, suggest the following ordering of bond energies: BDE[$Pa^+{-}O$] ≈ BDE[$U^+{-}O$] ≈ BDE[$Np^+{-}O$]; and BDE[$OPa^+{-}O$] > BDE[$OM^+{-}O$] (M = U, Np). Although the differences cannot be quantified, the pentavalent PaO_2^+ species is apparently somewhat more robust than UO_2^+ and NpO_2^+.

Both experimental[44] and theoretical[45] studies of the comparative solution complexation behavior of Nb, Ta, Pa, and Db have revealed that Pa is chemically disparate from these three bona fide group V elements. The present results suggest that PaO^+ exhibits a greater propensity to "coordinate" to a second O-atom when compared with TaO^+. It is interesting to compare the dissociation energies (in kJ mol^{-1}) for the neutral, group 5 metal oxides:[41,46] BDE[Pa−O] ≈ 788; BDE[Ta−O] ≈ 838; BDE[Nb−O] ≈ 783; BDE[OPa−O] ≈ 772; BDE[OTa−O] ≈ 642; BDE[ONb−O] ≈ 648. The differences between the first and second dissociation

---

[38] Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *Gas-Phase Ion and Neutral Thermochemistry*; American Chemical Society: Washington, DC, 1988.

[39] Hildenbrand, D. L.; Gurvich, L. V.; Yungman, V. S. *The Chemical Thermodynamics of Actinide Elements and Compounds, Part 13: The Gaseous Actinide Ions*; IAEA: Vienna, 1985.

[40] Schröder, D.; Schwarz, H.; Shaik, S. In *Metal-Oxo and Metal-Peroxo Species in Catalytic Oxidations*; Meunier, B., Ed.; Springer: Berlin, 2000; pp 91−123.

[41] Kleinschmidt, P. D.; Ward, J. W. *J. Less-Common Met.* **1986**, *121*, 61−66.

[42] Chandrasekharaiah, M. S.; Gingerich, K. A. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Jr., Eyring, L., Eds.; North-Holland: Amsterdam, 1989; Vol. 12, pp 409−431.

[43] Gibson, J. K. *J. Vac. Sci. Technol., A* **1995**, *13*, 1945−1958.

[44] Paulus, W.; Kratz, J. V.; Strub, E.; Zauner, S.; Brüchle, W.; Pershina, V.; Schädel, M.; Schausten, B.; Adams, J. L.; Gregorich, K. E.; Hoffman, D. C.; Lane, M. R.; Laue, C.; Lee, D. M.; McGrath, C. A.; Shaughnessy, D. K.; Strellis, D. A.; Sylwester, E. R. *Radiochim. Acta* **1999**, *84*, 69−77.

[45] Pershina, V.; Bastug, T. *Radiochim. Acta* **1999**, *84*, 79−84.

[46] *NIST Chemistry WebBook. NIST Standard Reference Database Number 69*; Mallard, W. G., Ed.; U.S. Department of Commerce: Washington, DC, 2001; http://webbook.nist.gov/chemistry/.

energies, $\Delta BDE[MO_{1,2}] = \{BDE[M{-}O] - BDE[OM{-}O]\}$, are approximately 16, 196, and 135 kJ mol^{-1} for M = Pa, Ta, and Nb, respectively. The small $\Delta BDE[PaO_{1,2}]$ is consistent with results for the $PaO_{1,2}^+$ ions. The ordering of $\Delta BDE[MO_{1,2}]$, Ta > Nb ≫ Pa, is in parallel with comparative results from other types of chemical studies.[44]

Oxidation by C_2H_4O was the major reaction pathway for the three An^+, but minor products of reactions with ethylene oxide were $AnOC_2H^+$ (e.g., Figure 1). The yield of $PaOC_2H^+$ was slightly greater than that of UOC_2H^+, and substantially greater than that of $NpOC_2H^+$ (Figure 1). Additionally, a very small amount of $PaOC_2H_3^+$ was definitively identified, a type of product not previously seen for reactions of other actinide ions with ethylene oxide.[37] Such products can be presumed to be stabilized by an interaction between the metal center of the OAn^+ moiety and the π-electron system of the radical organic ligand.[47] For each of the studied actinides, small amounts of $AnO_3C_2H_4^+$ products were identified, presumably association complexes, $AnO_2^+{-}C_2H_4O$, reflecting the low reactivity of the formally pentavalent metal centers in the AnO_2^+. Peaks corresponding in flight time to "$PaOH_4^+$" and "$NpOH_4^+$" in Figure 1 are attributed to collision-induced dissociation of AnO_2^+.[48]

All three An^+ reacted efficiently with dimethyl ether to produce complex products, essentially completely depleting the ablated bare An^+. Additionally, PaO^+ was highly reactive with dimethyl ether: the ablated PaO^+ peak nearly vanished, while UO^+ and NpO^+ exhibited little reactivity. For protactinium, major products were $PaOC_2H^+$ and $PaO_2CH_3^+$. The most striking aspect of the reactions with dimethyl ether was the very high reactivity of PaO^+ in contrast to the relatively inert character of both UO^+ and NpO^+.

Reactions with Sulfur Hexafluoride. Whereas sulfur hexafluoride is generally inert under most conditions because of steric congestion, thermodynamic considerations suggest it as a rather effective fluorinating agent: $BDE[F{-}SF_5] = 384$ kJ mol^{-1}.[38] Fluorination of metal ions by F-donors generally proceeds by an abstraction versus insertion mechanism,[49] so these processes should not be inhibited as a result of the kinetic restrictions typically applicable to SF_6, as direct access to a S−F bond is not necessary.

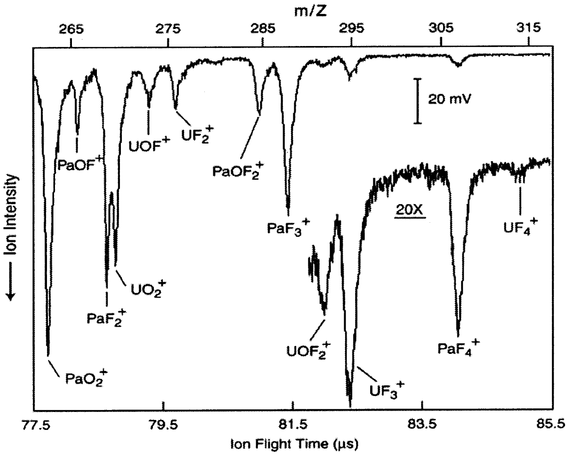

Figure 2. Mass spectrum showing polyatomic ions resulting from ablation of protactinium oxide and uranium oxide into sulfur hexafluoride. The amounts of ablated Pa^+, PaO^+, and PaO_2^+ were roughly twice those of the corresponding uranium ions (the PaO_2^+ and UO_2^+ peaks are shown in the mass spectrum). Not shown are the PaF^+ and UF^+ product ion peaks that had intensities of ~10 and ~5 mV, respectively; this compares with intensities of ~80 and ~10 mV, respectively, for the PaF_2^+ and UF_2^+ peaks shown in the spectrum.

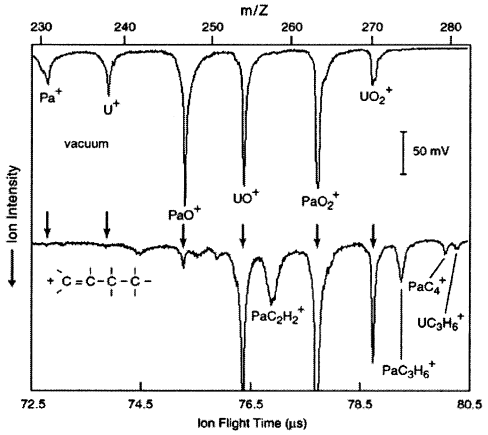

Figure 3. Mass spectra for ablation of protactinium oxide and uranium oxide into vacuum (top spectrum) and 1-butene (bottom spectrum). Reaction products heavier than $UC_3H_6^+$ (280 amu) are not shown.

Table 1. Product Abundances for Reactions with Sulfur Hexafluoride[a]

product ion	abundance, $A[I^+]$		
	M = Pa	M = U	M = Np
MF^+	10	10	10
MF_2^+	700	300	200
MF_3^+	70	50	80
MF_4^+	10	4	<1
MOF^+	20	15	<1
MOF_2^+	110	20	NA

[a] The relative ion abundances, $A[I^+]$, for the protactinium products from the three targets did not differ substantially. Approximate abundances are expressed as the peak intensity, I, of the product ion, as a percentage, relative to the anteceding fluoride: $A[MOF^+] = \{I[MOF^+]/I[MO^+]\} \times 100$; $A[MOF_2^+] = \{I[MOF^+]/I[M^+]\} \times 100$; $A[MF^+] = \{I[MF^+]/I[M^+]\} \times 100$; $A[MF_2^+] = \{I[MF_2^+]/I[MF^+]\} \times 100$; etc.

Products formed from the reaction of protactinium and uranium ions with SF_6 are shown in Figure 2, and representative results are given in Table 1. Previous experience[21] has indicated that all of the main reaction pathways are exothermic under the conditions of the LAPRD experiments, but even a semiquantitative thermochemical interpretation of the results must be presented with the caveat that a potential exists for somewhat endothermic processes. In assessing reactions with sulfur hexafluoride, the maximum available KE_{CM} of ~40 kJ mol^{-1} is not explicitly considered. The comparative results between Pa, U, and Np are entirely valid because the maximum KE_{CM} values are essentially identical for each ion.

The product ion abundances are defined in the footnote in Table 1; essentially, the abundance of a product ion is expressed as a percentage of its yield relative to the ion comprising one less F-atom. In the case of the sequential

---

(47) Cornehl, H. H.; Wesendrup, R.; Diefenbach, M.; Schwarz, H. *Chem. Eur. J.* **1997**, *3*, 1083−1090.
(48) Gibson, J. K. *Int. J. Mass Spectrom.* **2002**, *214*, 1−21.
(49) Cornehl, H. H.; Hornung, G.; Schwarz, H. *J. Am. Chem. Soc.* **1996**, *118*, 9960−9965.

abstraction of fluorine atoms from SF_6 molecules, these abundances reflect the comparative reactivities of the precursors. However, efficient abstraction of two (or more) F-atoms from an SF_6 (or other donors) might result in enhancement of difluoride (or polyfluoride) ions. Indeed, the abundances of the difluoride ions, AnF_2^+ and $AnOF_2^+$, were greater than those of the monofluorides, AnF^+ and $AnOF^+$. Two explanations for this are very efficient single F-atom abstractions by AnF^+ and $AnOF^+$ from SF_6, or concerted abstractions of two F-atoms by M^+ and MO^+. Because both bare M^+ and oxo-ligated MO^+ exhibited preferential formation of difluorides, concerted abstraction seems the more probable explanation and can be rationalized on the basis of thermodynamic considerations. Specifically, F-atom abstraction requires 384 kJ mol^{-1} for reaction 3 and only 308 kJ mol^{-1} per F-atom for reaction 4.[38]

$$SF_6 \rightarrow SF_5 + F \tag{3}$$

$$SF_6 \rightarrow SF_4 + 2F \tag{4}$$

The uranium fluoride ion bond dissociation energies (in kJ mol^{-1} at 298 K) have been determined previously as follows:[39] BDE[U^+-F] = 671(29); BDE[FU^+-F] = 552(44); BDE[F_2U^+-F] = 522(38); BDE[F_3U^+-F] = 385(19); BDE[F_4U^+-F] = 357(17); BDE[F_5U^+-F] = 22(27). The sequential, exothermic abstraction of F-atoms from SF_6 to produce UF_3^+ is expected on the basis of these values. The formation of UF_4^+ suggests that BDE[F_3U^+-F] > 384 mol^{-1}.

From the results of the present study, it can be concluded that BDE[F_nPa^+-F] exceeds 380 kJ mol^{-1} for $n = 0-3$. The greater rate of formation of PaF_4^+, as compared with UF_4^+, suggests that BDE[F_3Pa^+-F] > BDE[F_3U^+-F] $\gtrsim$ 384 kJ mol^{-1}, which is consistent with a greater stability of Pa(V) as compared to U(V). The thermodynamic data for protactinium compounds are sparse, but a comparison between the enthalpies of formation of the crystalline protactinium and uranium chlorides indicates a greater stability of Pa(V) versus Pa(IV) compared with U(V) versus U(IV).[50] We conclude that BDE[F_3Pa^+-F] > 400 kJ mol^{-1}. In analogy with UF_n^+, it can be presumed that BDE[F_nPa^+-F] values for $n = 0-2$ are substantially greater than for $n = 3$; for example, BDE[$F_{0-2}Pa^+-F$] > 450 kJ mol^{-1}. Just as UF_6^+ is barely stable toward F-elimination, it can be presumed that BDE[F_4Pa^+-F] must be very small if not negative.

The formation of substantial $AnOF^+$ indicates that BDE[OAn^+-F] > 384 kJ mol^{-1} for An = Pa and U. Although the appearance of $AnOF_2^+$ (An = Pa, U) suggests this same lower limit for the two BDE[$FOAn^+-F$] values, the possibility of concerted F-abstaction, eq 4, implies the possibility of a lower limit for BDE[$FOAn^+-F$] of only 232 kJ mol^{-1}. In accord with the greater stability of pentavalent Pa, the yield of $PaOF_2^+$ was found to be much greater than that of UOF_2^+. It can be inferred that BDE[$FOPa^+-F$] > BDE[FOU^+-F].

The Np^+ ion reacted with SF_6 at a comparable rate as Pa^+ and U^+ to produce the mono-, di-, and trifluorides, NpF_{1-3}^+. The appearance of $Np^{IV}F_3^+$ is consistent with the stability of tetravalent Np.[1] The pentavalent oxidation state of Np in aqueous solution is well-known, but NpF_4^+ was not detected here, implying that BDE[F_3Np^+-F] < 384 kJ mol^{-1}. Kleinschmidt et al.[51] reported approximate appearance potentials for the fragment ions of NpF_4, from which the following bond dissociation energies can be derived (in kJ mol^{-1}): BDE[Np^+-F] = 730(100); BDE[FNp^+-F] = 440(90); BDE[F_2Np^+-F] = 550(60); BDE[F_3Np^+-F] = 240(40). The diminished stability of pentavalent Np (in NpF_4^+) is clearly evident from the last value and the absence of NpF_4^+. The dissociation energies for thorium fluoride ions are as follows (in kJ mol^{-1}):[39] BDE[Th^+-F] = 664(36); BDE[FTh^+-F] = 701(47); BDE[F_2Th^+-F] = 630(47); BDE[F_3Th^+-F] = 26(35). The bonding in ThF_{1-3}^+ is robust, but the instability of pentavalent ThF_4^+ is clearly manifested.

It is evident that protactinium gas-phase ions are more reactive with SF_6 than are those of uranium and neptunium, particularly with regard to the formation of pentavalent products. Both Pa^+ and PaO^+ react with SF_6 to generate appreciable amounts of the pentavalent species, PaF_4^+ and $PaOF_2^+$. In contrast, much smaller yields of UF_4^+ and UOF_2^+ were obtained, and neither NpF_4^+ nor $NpOF_{1,2}^+$ were detected. The results can be rationalized on the basis of the greater thermodynamic stability of Pa(V) compared with U(V) and Np(V).

Reactions with Hydrocarbons. Protactinium ions were apparently inert toward activation of methane and ethane. The reaction of Pa^+ with CH_4 to give $PaCH_2^+$ did not occur at a sensitivity of <1% relative to the amount of ablated Pa^+.

In contrast to their inert behavior toward small alkanes, protactinium ions were highly reactive with the four studied alkenes: ethene, propene, 1-butene, and *iso*-butene. A partial product mass spectrum for reaction with 1-butene is shown in Figure 3. The main reaction products of the actinide ions with propene and the butenes are given in Table 2. With Pa^+, a sequential dehydrogenation and/or cracking of two or three hydrocarbon molecules could be deduced from the product compositions. This confirms multiple ion−molecule collisions under these experimental conditions. Cracking was particularly significant for the C_3 and C_4 alkenes. The complexity of the product spectra increased from ethene to propene to 1-butene to *iso*-butene. The relatively simple ethene reaction substrate is emphasized as a model of the comparative reactivities of actinide ions (and Ta^+).

Ethene. All three An^+ studied here reacted with ethene. On the basis of the degree of depletion of the An^+ reactants, it is concluded that the overall reaction rates decreased in the order: $Pa^+ \geq U^+ > Np^+$. With ethene, the dehydrogenation/trimerization process outlined in Scheme 1 was the primary reaction pathway for Pa^+. The efficiency of formation of $PaC_2H_2^+$ was typically ~50% relative to ablated Pa^+,

---

(50) Morss, L. R. In *The Chemistry of the Actinide Elements*, 2nd ed.; Katz, J. J., Seaborg, G. T., Morss, L. R., Eds.; Chapman and Hall: New York, 1986; pp 1278−1360.

(51) Kleinschmidt, P. D.; Lau, K. H.; Hildenbrand, D. L. *J. Chem. Phys.* **1992**, *97*, 1950−1953.

Table 2. Main Reaction Products of An^+ and AnO^+ with Propene and Butenes[a]

primary reactions	sequential reactions
propene (C_3H_6)	
$\mathbf{AnC_3H_4}^+$; $\mathbf{PaC_2H_2}^+$; $\mathbf{PaC_2}^+$	$\mathbf{PaC_5H_{10}}^+$; $PaC_5H_6^+$; $\mathbf{AnC_6H_8}^+$; $\mathbf{AnC_6H_6}^+$; $PaC_8H_8^+$; $PaC_9H_{10}^+$; $PaC_9H_8^+$
$AnOC_3H_2^+$; $\mathbf{PaOC_3H_4}^+$; $PaOCH_2^+$	$PaOC_6H_8^+$; $\mathbf{PaOC_6H_6}^+$; $PaOC_6H_4^+$; $PaOC_9H_8^+$; $PaOC_9H_6^+$
1-butene ($1\text{-}C_4H_8$)	
$\mathbf{AnC_4H_6}^+$; $PaC_3H_6^+$; $\mathbf{PaC_2H_2}^+$; PaC_4^+	$\mathbf{PaC_6H_{12}}^+$; $PaC_7H_{12}^+$; $\mathbf{PaC_8H_{12}}^+$
$PaOC_4H_6^+$	
iso-butene (*i*-C_4H_8)	
$AnC_4H_6^+$; $AnC_3H_6^+$;[b] $PaC_3H_2^+$; $\mathbf{AnC_2H_2}^+$;[c] PaC_4^+	$\mathbf{PaC_6H_{12}}^+$; $AnC_8H_{12}^+$;[d] $PaC_8H_{10}^+$; $PaC_8H_8^+$; $PaC_{12}H_{14}^+$
$\mathbf{PaOC_4H_6}^+$; $UOC_4H_8^+$;[e] $NpOC_4H_8^+$[e]	$PaOC_8H_{12}^+$
$PaO_2C_4H_8^+$;[e] $UO_2C_4H_8^+$[e]	

[a] Only the main products are included. The three An^+ were highly reactive; net reactivities of UO^+ and NpO^+ were small compared with PaO^+. "An" indicates a product observed for Pa, U, and Np. The most abundant products are indicated in bold. [b] Abundant product for Pa only. [c] $NpC_2H_2^+$ is isobaric with PaO_2^+. [d] Abundant for Pa only. [e] Association products with *i*-butene for AnO^+ and AnO_2^+ (no reaction).

that of $PaC_4H_4^+$ was typically ~10% relative to $PaC_2H_2^+$ product, and that of $PaC_6H_6^+$ was typically ~15% relative to $PaC_4H_4^+$.

Heinemann et al.[26] have examined the reaction of U^+ with ethene, identified the analogous trimerization process, and demonstrated that the $UC_6H_6^+$ product was a uranium–benzene complex. For uranium, the secondary dehydrogenation step may not result in ethene coupling and was the bottleneck in the overall U^+-mediated trimerization of ethene to benzene.[26] Our results suggest that this secondary step is also slower than the tertiary trimerization process for Pa^+. With uranium in the present study, the efficiency of initial ethene dehydrogenation was almost as great as for Pa^+, but the U^+-induced secondary dehydrogenation occurred with an efficiency of only 0.5%; because of the very low yield of the $UC_4H_4^+$ precursor, the $UC_6H_6^+$ product was not detected. The uranium results are in accord with the k_{capt} values of 100%, 1%, and 20% reported by Heinemann et al.[26] for the first, second, and third steps in the trimerization process. The comparative results indicate that the initial dehydrogenation of ethene proceeds at comparable rates for both Pa^+ and U^+ but that secondary dehydrogenation is much more efficient for $PaC_2H_2^+$, suggesting that the protactinium metal center is more chemically active than is the uranium metal center in the initial acetylene complexes. Because $NpC_2H_2^+$ is isobaric with PaO_2^+, the former could not be definitively identified, but the reaction of Np^+ with ethene was studied previously[30] and $NpC_2H_2^+$ was produced. The secondary $NpC_4H_4^+$ product was not detected to <0.3% of the amount of ablated Np^+, whereas the conversion of Pa^+ to $PaC_4H_4^+$ was ~7% when Pa^+ was studied concurrently. Marçalo et al.[27] examined the reaction of Th^+ with ethene and found efficient dehydrogenation as the primary process. In close analogy with both Pa^+ and U^+, secondary dehydrogenation to $ThC_4H_4^+$ occurred much less efficiently, and tertiary dehydrogenation to $ThC_6H_6^+$ was of intermediate efficiency. The reactivities of Th^+, Pa^+, and U^+ toward ethene would appear to be similar, in accord with the availability of at least two non-5f valence electrons in the ground-state configurations of each ion.

In one ethene experiment, conditions were such that sufficient Ta^+ was ablated with Pa^+ to allow comparison of the reactivities of Ta^+ and Pa^+. The yield of $TaC_2H_2^+$ was ~30%, and its conversion efficiency to $TaC_4H_4^+$ was ~2%; only an upper limit of <50% could be assigned for the final step in the trimerization process to the undetected $TaC_6H_6^+$ product. Buckner et al.[52] previously reported that Nb^+ sequentially dehydrogenates up to six ethene molecules to ultimately produce $NbC_{12}H_{12}^+$, a Nb^+-bis(benzene) sandwich complex. These authors performed a less comprehensive study of Ta^+ ion chemistry and reported $TaC_4H_4^+$ as the main secondary product of the Ta^+/ethene reaction.[52] On the basis of the present results, the ethene dehydrogenation reactivity of Ta^+ is comparable to that of Pa^+, but $TaC_2H_2^+$ is evidently less reactive than $PaC_2H_2^+$. The extreme reactivity of Pa^+ is also exhibited by the appearance of very small amounts of additional products not seen with the other actinide ions, notably $PaC_6H_4^+$ and PaC_4^+.

Whereas UO^+ and NpO^+ were inert to the detection limit, both PaO^+ and TaO^+ efficiently dehydrogenated ethene to give $PaOC_2H_2^+$ and $TaOC_2H_2^+$. The dehydrogenation reactivity of UO^+ was <1% of that of PaO^+. Very minor amounts of $PaOC_4H_4^+$ and $PaOC_4H_6^+$ were also detected, with the secondary dehydrogenation proceeding at a rate of the order of 0.1% relative to primary dehydrogenation. Cornehl et al.[53] have presented a mechanism for alkene activation by lanthanide monoxide ions, LnO^+, that involves electrophilic attack on the π-system. Accordingly, reactivity directly correlates with the oxide ionization energy, IE[LnO]. Although IE[PaO] is not known, IE[TaO] = 8.6 eV is significantly greater than IE[UO] = 5.7 eV.[46] The type of mechanism proposed by Cornehl et al. might explain the much greater reactivity of TaO^+ compared with UO^+. However, IE[M] and IE[MO] are generally similar for a given actinide or lanthanide.[42] Because IE[Pa] = 5.9 eV is slightly smaller than IE[U] = 6.2 eV,[50] it would not be predicted that IE[PaO] would be substantially greater than IE[UO]. If IE[PaO] were greater than IE[UO], the yield of ablated PaO^+ should have been less than that of UO^+: this was not the case. A more plausible explanation for the high reactivity of PaO^+ is the availability of chemically active valence electrons at the metal center, which enables C–H activation.

In Scheme 2[54,55] are shown the very small energies, ≤0.1 eV (1 eV = 96.4 kJ mol^{-1}), needed to excite Pa^+, U^+, and Np^+ from their ground states ($5f^{n-2}7s^2$ for Pa^+ and U^+, and $5f^46d\,7s$ for Np^+) to the "divalent" $5f^{n-2}6d7s$ configurations with two non-5f valence electrons, which are suitable for

---

(52) Buckner, S. W.; MacMahon, T. J.; Byrd, G. D.; Freiser, B. S. *Inorg. Chem.* **1989**, *28*, 3511–3518.

(53) Cornehl, H. H.; Wesendrup, R.; Harvey, J. N.; Schwarz, H. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2283–2291.

(54) Blaise, J.; Wyart, J.-F. *International Tables of Selected Constants, 20. Energy Levels and Atomic Spectra of Actinides*; Tables Internationales de Constantes: Paris, 1992.

(55) Brewer, L. *J. Opt. Soc. Am.* **1971**, *61*, 1666–1682.

Scheme 1

$$\mathrm{Pa}^+ \xrightarrow{+\mathrm{C_2H_4}-\mathrm{H_2}} \mathrm{PaC_2H_2}^+ \xrightarrow{+\mathrm{C_2H_4}-\mathrm{H_2}} \mathrm{PaC_4H_4}^+ \xrightarrow{+\mathrm{C_2H_4}-\mathrm{H_2}} \mathrm{PaC_6H_6}^+$$

Scheme 2

$$\begin{array}{lllll}
\mathbf{Th^+}: & 6d^2 7s & \xrightarrow{0.77\ \mathrm{eV}} 5f\,6d\,7s & \xrightarrow{-0.77\ \mathrm{eV}} 6d^2\,7s \\
\mathbf{Pa^+}: & 5f^2 7s^2 & \xrightarrow{0.10\ \mathrm{eV}} 5f^2\,6d\,7s & \xrightarrow{0.49\ \mathrm{eV}} 5f\,6d^2\,7s \\
\mathbf{U^+}: & 5f^3 7s^2 & \xrightarrow{0.04\ \mathrm{eV}} 5f^3\,6d\,7s & \xrightarrow{1.67\ \mathrm{eV}} 5f^2\,6d^2\,7s \\
\mathbf{Np^+}: & 5f^4 6d\,7s & \xrightarrow{0\ \mathrm{eV}} 5f^4\,6d\,7s & \xrightarrow{(2.9\ \mathrm{eV})} 5f^3\,6d^2\,7s \\
\mathbf{Pu^+}: & 5f^6 7s & \xrightarrow{1.08\ \mathrm{eV}} 5f^5\,6d\,7s & \xrightarrow{3.86\ \mathrm{eV}} 5f^4\,6d^2\,7s \\
\mathbf{Ce^+}: & 4f\,5d^2 & \xrightarrow{0.30\ \mathrm{eV}} 4f\,5d\,6s & \xrightarrow{4.39\ \mathrm{eV}} 5d^2\,6s
\end{array}$$

facile insertion into a C−H or C−C bond. In view of the generally inert character of the 5f electrons, it is evident why Pa^+, U^+, and Np^+ are among the most reactive An^+ toward hydrocarbon activation.[30] Ground state Th^+ ($6d^27s$) is particularly reactive and is the only actinide ion known to activate methane.[56]

In assessing the higher reactivity of PaO^+ compared with UO^+ and other AnO^+, the potential role of the 5f electrons is of central interest. Cornehl et al.[47] interpreted the reactivity of UO^+ as reflecting the participation of the 5f electrons in bond formation. In a photoelectron and theoretical assessment of the electronic structures of uranium oxide molecules, Allen et al.[57] cautioned that 5f/6d hybridization may be significant. Any interpretation of actinide oxide ion chemistry in the context of unperturbed atomic orbitals is only approximate. Although interactions of 5f orbitals with π-systems of organometallic ligands have been established,[58,59] substantial σ-type covalent 5f bonding of actinides in organometallic systems has not been demonstrated. The absence of σ-type bonding for transuranic actinides is supported by the reduced activity of Pu^+ (and heavier An^+) toward hydrocarbon activation.[30] However, covalent bonding involving 5f orbitals is more plausible for the lighter actinides. Even if the 5f electrons may be ineffective at forming covalent bonds with carbon and hydrogen, they can be promoted to, or hybridized with, 6d, 7s, and/or 7p orbitals.[60] Such lower-symmetry and spatially extended orbitals are better suited for σ-type bonding for C−H and C−C activation in organometallic systems. Appropriate hybridization or promotion of the f-electrons is most facile when the 5f orbitals are spatially and energetically compatible with the outer valence orbitals. It is with the earlier members of the actinide series when these conditions are best met.[61]

The energy for exciting a 5f electron to a 6d orbital indicates the energetic proximity of the 5f orbitals to outer valence orbitals that can effectively participate in bonding. The second set of excitation energies in Scheme 2 are the energies necessary to promote a 5f electron to a 6d state in the monopositive ion exhibiting the "divalent" configuration ($5f^{n-2}6d7s$), which has two unpaired non-5f valence electrons (6d7s) that presumably participate in the $\mathrm{An^+{=}O}$ bond. The parenthetical value for Np^+ in Scheme 2 is an estimate,[55] whereas the others were derived from spectroscopic measurements.[54] The 6d and 7s electrons resulting from the first promotion are considered to be engaged in the actinide−oxygen bond. Although an atomic ion model is not valid, it can be expected that the probability for significant 5f−6d hybridization at the metal center in AnO^+ should at least approximately correlate with the magnitude of the 5f-to-6d promotion energies from the $5f^{n-2}6d7s$ "divalent" configuration. A monotonic increase in these 5f-to-6d promotion energies is evident across the series: $\Delta\Delta E \approx 1.2$ eV is found between adjacent actinides. In the case of Th^+, 5f orbitals are not occupied in the ground state, and the incongruous 5f-to-6d "promotion energy" is negative by 0.77 eV. The energetics for Ce^+, the lanthanide homologue of Th^+, are included in Scheme 2 to illustrate the substantially lower energy of the 4f electrons compared with the valence (5d and 6s) electrons: the 4f electrons of the lanthanides are localized and nonbonding under all but the most extreme conditions (e.g., very high pressures[61]).

In the present context, the most striking feature of the energies in Scheme 2 is the relatively small 5f-to-6d promotion energy for Pa^+ (0.5 eV) compared with that for U^+ (1.7 eV) and transuranium An^+ ions. On the basis of the rationale outlined previously, it is expected that one or more 5f electrons at the metal center in PaO^+ should be substantially more prone to hybridization and participation in bonding than those in the heavier AnO^+. Without speculating on a detailed activation mechanism, we attribute the high reactivity of PaO^+ to the energetic (and spatial) proximity of the remaining 5f electrons at the metal center to the chemically active, valence orbitals.

In a fully ionic model, the metal center in MO^+ might be considered as M^{3+}. Brewer[55] has estimated the energies necessary to excite a 5f electron from the $5f^n$ ground states of the free An^{3+} ions to a $5f^{n-1}6d$ configuration. In direct correlation with the An^+ energetics shown in Scheme 2, the 5f-to-6d promotion energies, $\Delta E[\mathrm{An}^{3+}]$, increase monotonically upon proceeding across the actinide series: $\Delta E[\mathrm{Th}^{3+}] \approx 1.1$ eV; $\Delta E[\mathrm{Pa}^{3+}] \approx 2.5$ eV; $\Delta E[\mathrm{U}^{3+}] \approx 3.7$ eV; $\Delta E[\mathrm{Np}^{3+}] \approx 4.7$ eV; and so forth. This assessment of AnO^+ reactivity in the context of a trivalent metal center with localized molecular orbitals of predominantly 5f character is similar to considerations presented by Cornehl et al.[47] and has been substantiated for UO^+ by calculations.[62] The present results indicate a substantially more dramatic effect for PaO^+ compared with UO^+.

---

(56) Marçalo, J.; Leal, J. P.; Pires de Matos, A. *Int. J. Mass Spectrom. Ion Processes* **1996**, *157/158*, 265−274.

(57) Allen, G. C.; Baerends, E. J.; Vernoojis, P.; Dyke, J. M.; Ellis, A. M.; Fehér, M.; Morris, A. *J. Chem. Phys.* **1988**, *89*, 5363−5372.

(58) Kaltsoyannis, N.; Bursten, B. E. *J. Organomet. Chem.* **1997**, *528*, 19−33.

(59) Li, J.; Bursten, B. *J. Am. Chem. Soc.* **1997**, *119*, 9021−9032.

(60) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley and Sons: New York, 1988; pp 980−984.

(61) Lindbaum, A.; Heathman, S.; Litfin, K.; Méresse, Y.; Haire, R. G.; Le Bihan, T.; Libotte, H. *Phys. Rev. B* **2001**, *63*, 214101-1−214101-10.

(62) Krauss, M.; Stevens, W. J. *Chem. Phys. Lett.* **1983**, *99*, 417−421.

The role of the 5f electrons in bonding in the isoelectronic Pa, U, and Np halide complexes, PaX_6^{2-}, UX_5^-, and NpX_4 (X = F, Cl, Br), has been theoretically assessed by Kaltsoyannis and Bursten.[63] Their results indicate that covalent bonding between the metal center and the halogen is derived from molecular orbitals containing contributions from the 5f and 6d atomic orbitals. Because of the very different nature of these theoretical complexes and the organometallic systems assessed in the present work, direct comparisons must be made with caution. The conclusion by Kaltsoyannis and Bursten[63] that “the 5f contribution to the bonding levels increases significantly from PaX_6^{2-} to UX_6^- to NpF_6” emphasizes the need to assess the electronic structure of AnO^+ with sophisticated modeling which includes hybridization. We similarly attribute the distinctively greater activity of PaO^+ to participation of the 5f electrons but do not speculate regarding the relative contributions of direct 5f participation versus promotion/hybridization with outer valence orbitals. Cornehl et al.[47] compared the reactivity of ThO^+ and UO^+ with 1-butene and found ThO^+ to be substantially more reactive than UO^+. The reactivity of ThO^+ was attributed to a mechanism that employs the sole remaining valence electron at the metal center.

The essential conclusion from our experimental results with ethene is that the energetic and spatial proximity of the 5f electrons to the more chemically active outer valence electrons results in an enhanced reactivity of PaO^+ as compared to that of UO^+ and heavier actinide oxide ions. The greater reactivity of UO^+ as compared to NdO^+ [47] and heavier AnO^+ [30] represents a subtle effect when compared to that seen for PaO^+, suggesting a particularly dramatic change in going from PaO^+ to UO^+. The results for reactions of PaO^+ with larger alkenes are consistent with this picture.

Propene and Butenes. We investigated reactions between actinide ions and propene, 1-butene, and *iso*-butene. Cracking was a significant reaction channel for Pa^+ with all three reactants, and for U^+ and Np^+ with *iso*-butene. A partial product mass spectrum for ablation of protactinium and uranium ions into 1-butene is shown in Figure 3; higher mass products such as $AnC_4H_6^+$ are not shown in this spectrum. All three of the bare An^+ were highly reactive with propene and the two butenes, and each An^+ was almost entirely depleted, except for the Np^+/propene reaction where ~50% of the ablated Np^+ reacted. In concurrence with the ethene results, PaO^+ was also quite reactive toward the larger alkenes, whereas UO^+ and NpO^+ were relatively inert (see Figure 3). The main primary and sequential reaction products are given in Table 2 for the bare and oxo-ligated actinide ions. Because it was generally not practical to quantify the relative product yields, only qualitative product distributions are given. In view of the large discrepancies between the chemistries of the three studied actinides, these results provide a sufficient basis to effectively compare their chemistries. Whereas the overall product yields for the three bare An^+ were roughly comparable, the product yields for UO^+ and NpO^+ were substantially smaller than that for PaO^+.

The discrepancy in reactivities between Pa^+ versus U^+ and Np^+ is evident from the results with propene. All three An^+ induced dehydrogenation, consistent with previous results for U^+ and Np^+.[30] Protactinium distinctively cracked propene; whereas the single dehydrogenation product, $AnC_3H_4^+$, was dominant for An = U and Np, $PaC_2H_2^+$ and PaC_2^+ were at least as abundant as $PaC_3H_4^+$. The predominant formation of $UC_3H_4^+$ is in agreement with FTICR-MS results from Heinemann et al.[26] The fragmentation induced by Pa^+ demonstrates its greater tendency to induce C−C activation and cleavage.

The formation of PaC_2^+ indicates a strong propensity toward formation of polar covalent bonds with electronegative ligands. The C_2 moiety exhibits chemical similarities to the O-atom[42] and exhibits an electron affinity of 3.4 eV, compared with 1.5 eV for atomic oxygen. Cleavage of propene to give acetylene and methane is endothermic by only 133 kJ mol^{-1},[38] and it is reasonable that the Pa^+−{HC≡CH} bond energy should exceed this value. The overall process of formation of $\{C_2 + CH_4 + H_2\}$ from propene requires 736 kJ mol^{-1},[38] suggesting that BDE[Pa^+−C_2] is comparable to BDE[Pa^+−O]. Comparison of BDE[Ln−O] with BDE[Ln−C_2][42] indicates that this is reasonable. Marçalo et al.[27] studied the reaction of Th^+ with propene and reported efficient reaction, with $ThCH_2^+$ the main primary product, and $ThC_3H_4^+$ and $ThC_3H_2^+$ minor products. Activation of propene by Th^+ and Pa^+ apparently occurs via entirely different pathways. All three of the studied An^+ (like Th^+ [27]) induced secondary reactions with propene to give the products shown in Table 2. Tertiary products such as $PaC_9H_{10}^+$ were observed only for protactinium.

Whereas both UO^+ and NpO^+ were minimally reactive, propene was efficiently dehydrogenated by PaO^+. Interestingly, only the double dehydrogenation products, $AnOC_3H_2^+$, were detected for UO^+ and NpO^+ whereas for protactinium the single dehydrogenation product, $PaOC_3H_4^+$, was dominant. However, the yield of $PaOC_3H_2^+$ was much greater than those of $UOC_2H_2^+$ and $NpOC_2H_2^+$. Cornehl et al.[47] reported that UO^+ is inert toward activation of propene, and it should be emphasized that the yield of $UOC_3H_2^+$ relative to ablated UO^+ was <1% in the present study. The corresponding yield of $PaOC_3H_2^+$ was at least an order of magnitude greater, and the yield of $PaOC_3H_4^+$ was even greater. As with bare Pa^+, PaO^+ sequentially dehydrogenated one, two, and three propene molecules.

Along with the dehydrogenations, PaO^+ activated the C−C bond of propene to produce $PaOCH_2^+$, presumably $O{=}Pa^+{=}CH_2$. The exothermic reaction of PaO^+ with propene to give this product requires that BDE[OPa^+−CH_2] exceed ~420 kJ mol^{-1}.[38] With the formation of $PaOCH_2^+$, PaO^+ would appear to exhibit some chemical similarity to Th^+.[27]

All three An^+ efficiently dehydrogenated 1-butene to produce $AnC_4H_6^+$ (Table 2). Heinemann et al.[26] had previously studied the U^+/1-butene reaction and similarly reported very efficient single dehydrogenation, with double dehydro-

---

[63] Kaltsoyannis, N.; Bursten, B. E. *Inorg. Chem.* **1995**, *34*, 2735−2744.

genation being a minor (<10%) alternate reaction channel. As with propene, only Pa^+ was found to significantly induce C−C activation in the present work, with $PaC_2H_2^+$ appearing as a major product (Figure 3). Minor products were $PaC_3H_6^+$ and PaC_4^+. In an earlier study of the reaction of Th^+ with 1-butene,[27] the only four primary products were $ThCH_2^+$, $ThC_2H_2^+$, $ThC_4H_6^+$, and $ThC_4H_4^+$. The complete dehydrogenation of 1-butene to C_4 requires ~970 kJ mol^{-1},[38] and the appearance of PaC_4^+ as a significant product is notable. It can be inferred here that BDE[Pa^+-C_4] exceeds ~970 kJ mol^{-1}. The tetracarbon species has been studied theoretically and experimentally because of its importance in both terrestrial and interstellar chemistry. The electron affinity of linear C_4 has been measured as 3.88 eV,[64] which is 0.5 eV greater than that of the atomic fluorine.[38] Strong bonding between an electropositive transition metal ion and C_4 should be facilitated by both electrostatic and covalent bonding. As discussed previously, for Pa^+ the energetic proximity of the quasivalence 5f electrons to the 6d orbitals enhances their ability to participate in covalent bonding with a ligand such as C_4.

Of the actinide oxide ions studied, only PaO^+ exhibited reactivity toward 1-butene, inducing single dehydrogenation to give $PaOC_4H_6^+$. Cornehl et al.[47] demonstrated that UO^+ dehydrogenates 1-butene, albeit at such a slow rate that this process would not be detected in the present experiments. The reactivity of UO^+ was attributed to "...participation of 5f electrons in bond formation".[47] The much greater reactivity of PaO^+ compared to that of UO^+, as demonstrated here, is consistent with greatly enhanced participation, direct or indirect, of the protactinium 5f electrons in bond formation. The much faster reaction of ThO^+ with 1-butene reported by Cornehl et al.[47] was attributed to an entirely different mechanism that involved only one electron at the metal center.

The reaction products of An^+ with *iso*-butene were qualitatively similar to those with linear 1-butene. However, a greater propensity toward C−C over C−H bond activation was exhibited with the branched isomer. Notably, $UC_2H_2^+$ was not observed upon reaction with 1-C_4H_8 but was a major product with *i*-C_4H_8. Because $NpC_2H_2^+$ is isobaric with PaO_2^+, it could not be determined whether this cracking channel also occurred for Np^+ with *i*-butene. Each of the An^+ was highly reactive with *iso*-butene, exhibiting nearly complete depletion of the bare reactant ions. Whereas, with 1-butene, secondary products were produced only for Pa^+, small amounts of $AnC_8H_{12}^+$ appeared also for An = U and Np with *iso*-butene. The tertiary product, $PaC_{12}H_{14}^+$ was also identified.

The disparate reactivity of PaO^+ compared with those of UO^+ and NpO^+ is particularly striking in the case of *iso*-butene. Minor amounts of the association products, $AnOC_4H_8^+$, appeared for UO^+ and NpO^+, whereas the dehydrogenation product $PaOC_4H_6^+$ was produced efficiently for PaO^+, together with a minor amount of the secondary product, $PaOC_8H_{12}^+$. The appearance of the adducts for UO^+ and NpO^+, absent any reaction products, clearly demonstrates the distinctively higher reactivity of PaO^+. The inert character of PaO_2^+ and UO_2^+ was demonstrated by the formation of only the adducts, $AnO_2C_4H_8^+$. The corresponding NpO_2^+ adduct was not detected, presumably because of the small amount of ablated NpO_2^+. The relatively inert character of UO_2^+ has been demonstrated previously.[47]

Concluding Remarks

There are significant variations between the chemistries of the early actinide elements, Th−Pu, due in part to the unique character of the quasivalence 5f electrons. It is important to illuminate the chemistry of protactinium, one of the least studied of the actinides in this region of the actinide series, to elucidate the role of the 5f electrons. Pa is the first of the actinides to have 5f electrons in its free atom and monopositive ion ground state configurations.

Both Pa^+ and PaO^+ were readily oxidized by ethylene oxide. On the basis of oxidation rates relative to U^+ and UO^+, and the comparative amounts of directly ablated PaO^+ and PaO_2^+, we estimate the following bond dissociation energies: BDE[Pa^+-O] ≈ BDE[OPa^+-O] ≈ 800 kJ mol^{-1}. Fluorination of Pa^+ (and PaO^+) by sulfur hexafluoride allows us to estimate lower limits for BDE[F_nPa^+-F]. Particularly notable was the significantly greater rate of formation of PaF_4^+, as compared to that of UF_4^+. This is taken to reflect the inordinate stability of the pentavalent state of Pa.

Minor products from the reaction of Pa^+ with ethylene oxide were consistent with the high organometallic reactivity of this ion. All three of the bare actinide ions studied were found to be highly reactive toward activation of ethene, propene, 1-butene, and *iso*-butene. The greater propensity of Pa^+ toward cracking and oligomerization indicates a greater reactivity as compared to U^+ and Np^+. Unusual products, such the binary carbides, PaC_2^+ and PaC_4^+, were not observed with the other actinides. The enhanced oligomerization by Pa^+ suggests a greater chemical activity of the metal center in the primary product complexes, $Pa^+-C_xH_y$. Like Pa^+, Th^+ exhibits a high reactivity with small alkenes;[27] the disparate product distributions may reflect 5f electrons in ground state Pa^+ but not Th^+.

The most striking result of the present work was the much greater dehydrogenation reactivity of PaO^+ compared with UO^+ and NpO^+. This is interpreted to indicate that the 5f electrons of Pa play a greater role in organometallic bond formation, consistent with the enhanced reactivity of the primary protactinium complex ions. The apparent role of the 5f electrons of PaO^+ may result from direct participation and/or promotion/hybridization with outer valence orbitals. Consideration of the metal center in PaO^+ as a free ion is an oversimplification but is a considered valid approach for qualitatively comparing the energy levels of the 5f orbitals across the actinide series. A rather high reactivity of ThO^+ has been reported, but it was concluded that its reactions with alkenes must occur by a mechanism that involves only one chemically active valence electron at the metal center.

---

(64) Arnold, D. W.; Bradforth, S. E.; Kitsopoulos, T. N.; Neumark, D. *J. Chem. Phys.* **1991**, *95*, 8753−8764.

The Pa metal center in PaO_2^+ is “valence saturated”, and both PaO_2^+ and UO_2^+ appeared to be essentially inert species.

The results of this first study of the gas-phase chemistry of protactinium ions have revealed behavior very different from that of uranium and transuranium actinide ions. Both the bare and oxo-ligated protactinium monopositive ions are extremely reactive. The very distinctive behavior of PaO^+, compared with heavier AnO^+, indicates that the 5f electrons participate either directly or via promotion/hybridization in the chemistry of PaO^+. Additional experimental and theoretical studies should further address the chemistry of this pivotal member of the actinide series.

Acknowledgment. Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

IC025683T