Can stable molecular compounds of Th(V) and Pa(VI) exist?
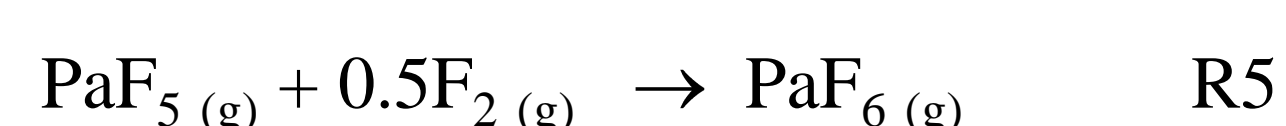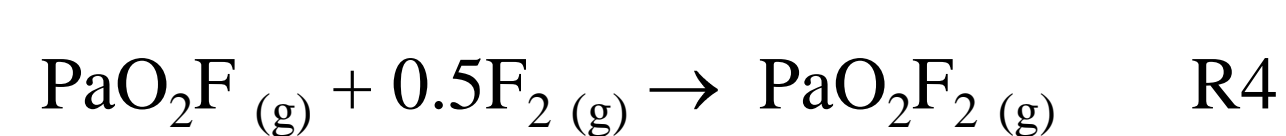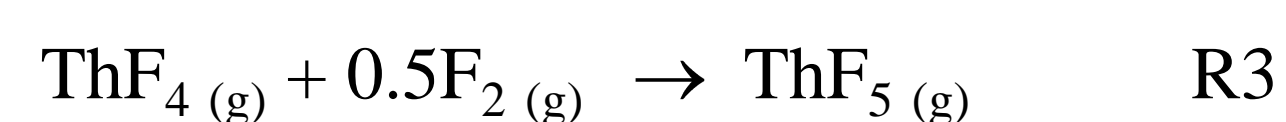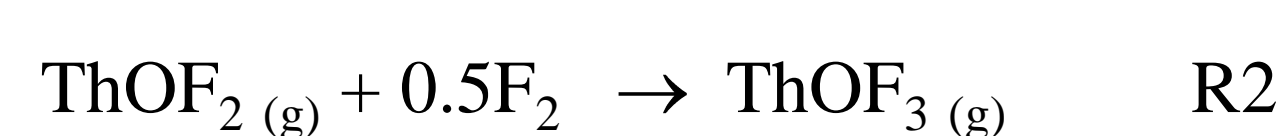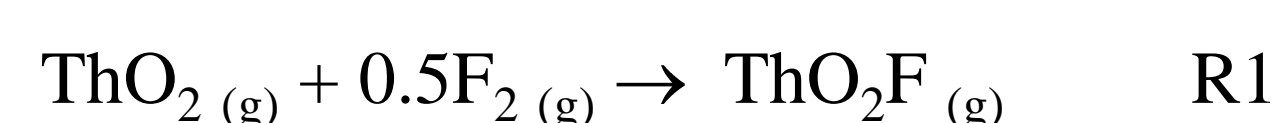
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Gibson and coworkers have recently shown that the PaO_2^{2+} ion, which formally contains Pa(VI), can be prepared in the gas phase.[1] As far as we are aware, this was the first report of the preparation of a "hypervalent" Pa compound. However, the energy necessary to produce this species is large, as the ionization energy of the "actinyl" ion PaO_2^+ that contains Pa(V) was calculated to be 16.6 eV. One would normally imagine that such high-energy species cannot exist as stable compounds. Yet the ionization energy of UO_2^+ is estimated [2] to be 15.2 eV, not much less than 16.6 eV, and the uranyl ion, UO_2^{2+}, which formally contains U(VI), is of course stable in both the solid state and in aqueous solution (at low pH). Since the ionization energy of ThO_2 is "only" 8.7 eV,[3] it is therefore worthwhile asking the question posed in the title: can stable molecular compounds of Th(V) exist? And are there any compounds of Pa(VI) that might be thermodynamically stable? We have used DFT to try to answer these questions, convinced that its application to actinide thermochemistry is relatively reliable.[4]

Gibson's paper [1] drew attention to the paucity of reliable thermodynamic data available for actinide compounds, even the most "simple" diatomic species. We have therefore decided to undertake a systematic survey of AnX and AnX_2 species (An = Th – Cm, X = H, C, N, O and F), both neutral molecules and their cations, to provide the beginning of a database. In view of the number of molecules that we wish to study, we shall use DFT methods. It has been known for some time that vibrational wavenumbers can be predicted to within a few percent, with high reliability.[6] Our experience for structures to date has been most encouraging [7] and we are not aware of any example where DFT has given "wrong" data for ground-state properties of these molecules. The margin of error that can be expected has yet to be established; the data below, for An = Th and Pa, together with other more fragmentary results for U, suggests that ionization energies and bond energies can consistently be determined to within about 50 kJ/mol (0.5 eV), and frequently substantially better. That is hardly "spectroscopic accuracy", but it is much better than plain ignorance, which is essentially the current state of affairs for several of the actinide elements.

Possible Th (V) and Pa (VI) Compounds

In general, high-oxidation state species are most stable as oxides, fluorides and oxide-fluorides. We therefore considered the gas-phase thermodynamic stability of compounds such as ThO_2F, $ThOF_3$ and ThF_5, all of which appear to contain Th(V), together with PaO_2F_2 and PaF_6 (Pa(VI)), relative to analogous compounds of Th(IV) and Pa(V), respectively. In other words, we calculated ΔE for the following reactions:

$$ThO_2 \text{ (g)} + 0.5F_2 \text{ (g)} \rightarrow ThO_2F \text{ (g)} \qquad R1$$

$$ThOF_2 \text{ (g)} + 0.5F_2 \rightarrow ThOF_3 \text{ (g)} \qquad R2$$

$$ThF_4 \text{ (g)} + 0.5F_2 \text{ (g)} \rightarrow ThF_5 \text{ (g)} \qquad R3$$

$$PaO_2F \text{ (g)} + 0.5F_2 \text{ (g)} \rightarrow PaO_2F_2 \text{ (g)} \qquad R4$$

$$PaF_5 \text{ (g)} + 0.5F_2 \text{ (g)} \rightarrow PaF_6 \text{ (g)} \qquad R5$$

Using standard DFT (B3LYP, small-core pseudopotentials for the actinides and TZP bases for O and F, we calculate the following reaction energy changes (kJ/mol, purely electronic energies, no zero-point or other thermal effects):

R1, -308: R2, -273; R3, +55; R4, -229; R6, +61.

Although it is clear that DFT reaction energies for actinide compounds cannot be expected to be accurate to within a few kJ/mol, we feel confident that reactions R1 and R2 are clearly exothermic. In other words, ThO_2F, $ThOF_3$ and PaO_2F_2 appear to be potentially stable molecular compounds of Th(V) or Pa(VI), since they are clearly thermodynamically stable compared to their Th(IV) precursors. However, the fluorides ThF_5 and PaF_6 are not stable, especially as entropic factors mean that ΔG for these reactions is less favourable than ΔE.

Why do we limit ourselves here to "molecular" compounds? Because we know that ThO_2 (s) is much more stable than ThO_2 (g), by about 670 kJ/mol;[5] it is clear that the lattice energies of ThO_2F, $ThOF_3$ and PaO_2F_2 will be large, but since we cannot calculate them with any useful accuracy, we refrain from any predictions about the stability of these new "hypervalent" compounds in the solid state.

As a method check, we also studied reaction R1 at the more reliable CCSD(T) level of theory, using larger basis sets (TZ+2df on F and O, TZ+2gh on Th), at the geometries obtained with DFT. We obtain ΔE = -279 kJ/mol for R1 at both the CCSD and CCSD(T) levels of theory. These values are so close to the DFT result that the latter is confirmed. Henceforth, we rely on DFT energies (see also right-hand column).

The Nature of these New Compounds

What can we say about the nature of these new compounds? Do they "really" contain Th(V) or Pa(VI)? Although the stoichiometry appears to say "yes", other aspects incite caution. For example, the Th-O distance in $ThOF_3$ is 2.215 Å, whereas in $ThOF_2$ it is only 1.882 Å. The unpaired electron in $ThOF_3$ is almost completely localized (98%) on the O atom, which is hardly compatible with the presence of Th (V) and a double bond between Th and O. In ThO_2F and PaO_2F_2, the unpaired electron is more evenly spread, but is still extensively delocalized: 18% on Th and 39% on each O in ThO_2F, 26% on Pa and 32% on each O in PaO_2F_2.
Overall, we feel inclined to give the following answer to the question raised in our title: "perhaps, but we haven't proved it yet".

Computed Data (B3LYP) for Th and Pa Compounds

Species	r [a] pm	AE [b] kJ/mol	IE [c] kJ/mol	Species	r [a] pm	AE [b] kJ/mol	IE [c] kJ/mol
ThH	201.6	294	603	PaH	2.029	282	
ThH$^+$	199.9	280					
ThC	193.1	527	618	PaC	188.8	487	611
ThC$^+$	189.5	498		PaC$^+$	185.8	431	
ThN	180.7	683	616	PaN	176.2	654	607
ThN$^+$	177.0	655		PaN$^+$	173.0	602	
ThO	183.6	908	629	PaO	181.2	837	607
ThO$^+$	180.3	875	1180	PaO$^+$	179.6	785	1198
ThO^{2+}	176.6	858		PaO^{2+}	174.9	774	
ThF	203.6	701	594	PaF	204.0	685	598
ThF$^+$	200.5	687		PaF$^+$	200.6	685	
ThH$_2$	201.7	602	591				
ThH$_2^+$	199.0	600					
ThO$_2$	190.0	1574	829	PaO$_2$	180.7	1640	601
ThO$_2^+$	187.0	1342		PaO$_2^+$	176.8	1593	1634
				PaO$_2^{2+}$	177.4	1146	
ThF$_2$	205.6	1376	624				
ThF$_2^+$	201.1	2					
Th			589, 1163	Pa			555, 1187

[a] bond length   [b] atomization energy (to actinide cations for ions)   [c] ionization energy

Comments
: we note that cations are always more weakly bound than their neutral parent, even though the bonds are slightly shorter in the cations. In all the diatomic molecules, the Th-X bond is slightly stronger than Pa-X. For both actinides, the bond energies decrease in the order O > F > N > C > H. Work in progress will establish whether this order is consistently maintained for the heavier actinides.

Comparisons with experiment
, where possible, with estimated uncertainties if >1 in the last digit:

ThO: r 184.0 pm,[8] AE 860 (30) kJ/mol,[9] IE 637 kJ/mol:[10] our errors are 0.4 pm, 48 (30) and 8 kJ/mol, respectively.

ThO$^+$: r 180.7 pm:[10] our error is 0.4 pm.

ThO$_2$: AE 1544 (30) kJ/mol,[4] IE 839 (15) kJ/mol:[4] our errors are 32 (30) and 10 (15) kJ/mol, respectively.

Th IE 608 kJ/mol,[10] our error is 19 kJ/mol.

U IE 598 kJ/mol:[11] our error (not reported here) 36 kJ/mol.

UO IE 591 kJ/mol:[12] our error (not reported here) 7 kJ/mol.

In our opinion, these comparisons show that DFT calculations can and do provide data of useful reliability for actinide thermochemistry. Selected four-component calculations will be undertaken to check our opinion.

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