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Where Is the Limit of Highly Fluorinated High-Oxidation-State Osmium Species?

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The structures and stabilities of various osmium fluorides and oxyfluorides in high oxidation states have been studied by quantum-chemical calculations at DFT (B3LYP), MP2, CCSD, and CCSD(T) levels. The calculations indicate that the homoleptic fluorides all the way up to OsF_8 may exist, even though OsF_8 will be difficult to prepare. The last missing osmium oxyfluoride, $OsOF_6$, is computed to be thermochemically stable against mononuclear gas-phase elimination reactions. The problem with the nonexistence of such highly fluorinated complexes appears thus to be mainly in difficult synthetic access under typical condensed-phase conditions. Matrix-isolation techniques might provide a means to characterize the highly fluorinated Os^{VIII} and Os^{VII} species.

1. Introduction

The highest oxidation state +VIII of the 5d transition-metal osmium (in fact, of any element) is best exemplified by the tetroxide, OsO_4, which has achieved substantial importance as an oxidation agent, for example, in organic chemistry.[1−3] In contrast, the octafluoride, OsF_8, is presently unknown, despite a long speculative history: In 1913, Ruff and Tschirch[4] claimed the first synthesis of OsF_8. Forty-five years later, Weinstock and Malm[5] showed that the purported OsF_8 was in fact OsF_6. The isolation of OsF_7, reported in 1966,[6] also could recently not be reproduced under the indicated conditions[7] (reaction of metal powder with F_2 at 620 °C and 400 bar with subsequent rapid cooling). The highest binary osmium fluoride characterized beyond doubt is thus OsF_6 (see Figure 1).[8]

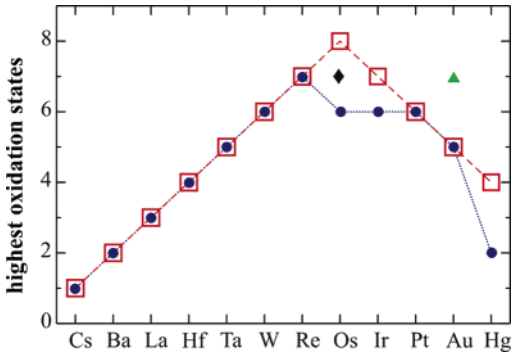

Figure 1. Maximum oxidation states of binary 5d transition-metal fluorides: (●) highest experimentally known MF_n species, (▲) incorrect experimental assignment, (♦) controversial experimental assignment, and (□) suggested maximum achievable oxidation states.

Figure 1 shows also that the decrease of the maximum oxidation states of the fluorides from group 8 through group 13 is irregular if we consider only the experimentally proven cases. Apart from OsF_8, the lack of IrF_7[9] and of HgF_4[10−13] prohibits a more regular trend (earlier reports on AuF_7 have recently been shown to be erroneous[14]).

To investigate the chances to prepare species like OsF_8 and OsF_7, we report here quantum-chemical calculations of

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structures and (gas-phase) stabilities. Additionally, we evaluate also the stabilities of heteroleptic Os^{VIII} oxyfluorides, to find out how they are affected by the number of fluorine atoms present. We will compare our results also to those of an earlier HF and MP2 study of osmium fluorides and oxyfluorides by Veldkamp and Frenking.[15] Notably, however, those authors had to rely on various isodesmic reactions to discuss stability, whereas the more refined and advanced computational methods available today allow us to discuss directly the relevant gas-phase elimination and bond-breaking reactions, and to evaluate also activation barriers for some key reactions.

2. Computational Methods

Structures were optimized using density-functional theory (hybrid B3LYP[16−19] functional), with the Gaussian 03[16] program. The transition-state optimizations were done using synchronous transit-guided quasi-newton (STQN) methods[20,21] according to the QST2 and QST3 keywords implemented in Gaussian 03. Optimizations were followed by single-point energy calculations at DFT, MP2, and high-level coupled-cluster (CCSD and CCSD(T)) levels. Quasirelativistic energy-adjusted, small-core "Stuttgart-type" pseudopotentials (effective-core potentials, ECPs) were used for the transition metals Os,[22] Au,[22] Pt,[22] and Ir.[22] The corresponding (8s7p6d)[6s5p3d] valence basis sets were augmented by one f-type polarization function[23] (exponent α: Os 0.886, Ir 0.938, Pt 0.993, and Au 1.050). Energy-adjusted 8-valence-electron pseudopotentials and (6s6p3d1f)/[4s4p3d1f] valence basis sets were used for the noble-gas atoms Ng = Kr, Xe.[24]

In the B3LYP-optimizations, a fluorine DZ+P all-electron basis set by Dunning[25] was used. Stationary points on the potential energy surface were characterized by harmonic vibrational frequency analyses at this level (providing also zero-point energy corrections to the thermochemistry). The subsequent single-point energy calculations had the fluorine basis replaced by a larger aug-cc-pVTZ basis set.[26] The post-HF calculations were carried out with the MOLPRO 2002.6[27] program package. Basis-set superposition errors (BSSE) were estimated by the counterpoise (CP)[28,29] procedure. We note that the methodology used here, in particular B3LYP optimizations followed by B3LYP or CCSD(T) single-point energy calculations with larger basis sets, is well established as a reliable tool for redox thermochemistry in the 5d transition-metal series, for example, in previous studies on Hg, Au, Pt, and Ir systems.[9,10,14] We have furthermore found excellent agreement with structures and relevant thermochemical data in test calculations on ReF_7 (the results will be reported elsewhere as part of a wider computational study on technetium and rhenium fluorides). We do not consider spin−orbit corrections in this work. Our previous studies indicated spin−orbit effects to have only a minor influence on the relevant thermochemical data or activation barriers, even when open-shell 5d species were involved.[9]

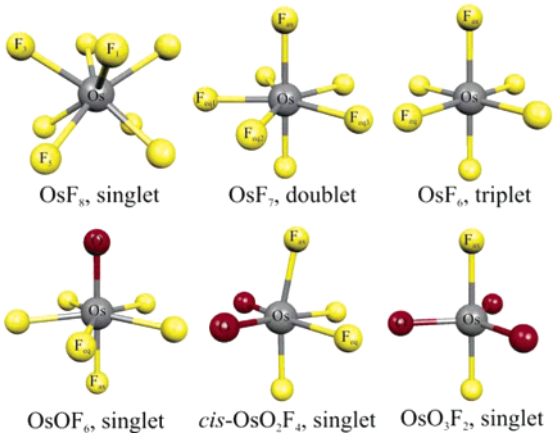

Figure 2. B3LYP-optimized minimum structures of OsF_8 (D_{4d}), OsF_7 (C_{2v}), OsF_6 (D_{4h}), $OsOF_6$ (C_{5v}), *cis*-OsO_2F_4 (C_{2v}), and OsO_3F_2 (D_{3h}). Distances and angles are in Table 1.

3. Results and Discussion

Figure 2 shows the B3LYP-optimized structures of OsF_8, OsF_7, and OsF_6. At this computational level, we find two minima for OsF_8. One is a distorted quadratic antiprism with D_{2d} symmetry and two different Os−F bonds (Table 1). The other is a regular quadratic antiprism with D_{4d} symmetry. The energies of the two minima differ only by less than 5 kJ mol^{-1}, and the calculations suggest a shallow potential energy surface around the two located minima. An earlier study at HF and MP2 levels indicated a pronounced dependence on computational method. At HF level (with a valence DZP basis for fluorine), a more distorted C_{2v} structure was obtained, whereas the less distorted antiprism of D_{2d} symmetry was found at MP2 level. OsF_8 may indeed be a fluxional species.

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Table 1. Experimental and B3LYP-Optimized Minimum Structures[a]

species	symmetry	species	symmetry	species	symmetry
OsF_8	D_{2d} (D_{4d})[b]	OsF_7	C_{2v}	OsF_6[c]	D_{4h}
$Os-F_1$	186.7 (188.2)	F_{ax}	183.9	F_{ax}	185.8
$Os-F_3$	189.9 (188.2)	F_{eq1}	185.6	F_{eq}	184.0
$Os-F_5$	1.867 (188.2)	F_{eq2}	189.0		
F_1-Os-F_2	104.0 (114.3)	F_{eq3}	186.9		
F_3-Os-F_4	123.8 (114.3)	$F_{eq1}-Os-F_{eq2}$	71.9		
F_1-Os-F_5	86.4 (78.2)	$F_{eq2}-Os-F_{eq3}$	72.2		
		$F_{eq3}-Os-F_{eq4}$	71.8		
$OsOF_6$	C_{5v}	*cis*-OsO_2F_4	C_{2v}	OsO_3F_2	D_{3h}
$Os-O$	167.8	$Os-F_{ax}$	186.1	$Os-F_{ax}$	189.3
$Os-F_{eq}$	188.6	$Os-O$	169.0	$Os-O$	169.7
$Os-F_{ax}$	186.1	$Os-F_{eq}$	188.8		
$O-Os-F_{eq}$	93.6	$F_{ax}-Os-O$	93.9		
$F_{eq}-Os-F_{eq}$	71.8	$F_{ax}-Os-F_{eq}$	85.3		
		$F_{ax}-Os-F_{ax}$	167.8		

[a] Distances in picometers and angles in degrees. See Figure 1 for atom numbering. [b] Values in parentheses are for the D_{4d} minimum; see text. [c] Experimental (X-ray single-crystal study)[39] bond lengths of OsF_6 are $Os-F_{ax1}$ 183.33(24), $Os-F_{eq1}$ 182.21(18), $Os-F_{ax2}$ 182.80(25), $Os-F_{eq2}$ 182.92(18). [d] Experimental bond lengths of OsO_2F_4 from gas-phase electron diffraction[35] are $Os-O$ 167.4(4), $Os-F_{ax}$ 184.3(3), $Os-F_{eq}$ 188.3(3).

Table 2. Computed Reaction Energies (in kJ mol^{-1})[a]

reaction	B3LYP	MP2	CCSD	CCSD(T)
(a) $OsF_8 \rightarrow OsF_6 + F_2$[b]	−79.1 (−97.3)	63.0	−150.8	−73.1
(b) $OsF_8 \rightarrow OsF_7 + F$[b]	6.6 (−7.8)	94.2	−38.4	14.4
(c) $OsF_7 \rightarrow OsF_5 + F_2$[b]	218.9 (206.8)	303.7	108.7	186.5
(d) $OsF_7 \rightarrow OsF_6 + F$[b]	69.6 (59.5)	142.4	12.0	65.2
(e) $OsF_6 \rightarrow OsF_5 + F$[b]	304.6 (296.4)	334.9	221.1	274.1
(f) $OsF_6 + KrF_2 \rightarrow OsF_8 + 2Kr$	43.4	−91.6	65.8	12.2
(g) $OsF_5 + KrF_2 \rightarrow OsF_7 + 2Kr$	−254.6	−332.2	−193.7	−247.4
(h) $[OsF_6]^- + [KrF]^+ \rightarrow OsF_7 + Kr$[c]	−688.7	−746.3	−552.7	−633.5
(i) $OsOF_6 \rightarrow OsOF_4 + F_2$	138.7	298.2	59.5	133.6
(j) $OsOF_6 \rightarrow OsF_5 + OF$	170.3	507.4	116.2	233.7
(k) $OsOF_6 \rightarrow OsF_6 + O$	97.5	390.0	73.7	164.7
(l) $OsOF_6 \rightarrow OsOF_5 + F$	54.2	150.1	4.1	54.8
(m) $OsO_2F_4 + 2F_2 \rightarrow OsF_8 + O_2$	−205.6	−129.2	−104.8	−110.2
(n) $OsO_2F_4 + 2KrF_2 \rightarrow OsF_8 + 2Kr + O_2$	−276.9	−186.3	−274.8	−232.1
(o) $OsO_4 + 4KrF_2 \rightarrow OsF_8 + 4Kr + 2O_2$	−836.9	−711.9	−921.3	−805.0
(p) $OsO_4 + 2KrF_2 \rightarrow OsO_2F_4 + 2Kr + O_2$	−560.0	−525.7	−646.5	−572.9
(q) $OsO_2F_4 + KrF_2 \rightarrow OsOF_6 + Kr + O$	96.7	95.0	28.6	71.5
(r) $OsO_2F_4 + F_2 \rightarrow OsOF_6 + O$	132.4	123.5	113.7	132.4
(s) $OsO_2F_4 + 2F_2 \rightarrow OsOF_6 + OF + F$	55.9	79.6	59.5	80.1
(t) $OsO_3F_2 + 2F_2 \rightarrow OsOF_6 + O_2$	−473.3	−387.2	−348.1	−337.9
(u) $KrF_2 \rightarrow Kr + F_2$[d]	−35.7	−28.5	−85.0	−60.9
(v) $F_2 \rightarrow 2F$[e]	155.3	173.6	124.4	152.7

[a] Reaction energies for singlet OsF_8, doublet OsF_7, triplet OsF_6, quartet OsF_5, singlet $OsOF_6$, singlet OsO_2F_4, singlet OsO_3F_2, and singlet OsO_4. [b] Values in parentheses are counterpoise and zero-point vibration corrected. [c] Energies for the separate steps are: (i) formation of the ion-pair complex −545.2 kJ mol^{-1}, and (ii) decomposition to OsF_7 and Kr −143.5 kJ mol^{-1} (B3LYP result). [d] The experimental value is -60.2 ± 3.4 kJ mol^{-1}.[40,41] [e] The experimental value is +158.3 kJ mol^{-1}.[42,43]

Unimolecular gas-phase F_2-elimination from OsF_8 to give OsF_6 is found to be exothermic (see Table 2, reaction a). However, the computed barrier for concerted elimination at B3LYP level is appreciable, 203.9 kJ mol^{-1}. The transition state has C_{2v} symmetry. A second potential channel for decomposition of OsF_8 involves the homolytic dissociation of an Os−F bond to give OsF_7. This reaction is endothermic (by 14.4 kJ mol^{-1} at CCSD(T) level; Table 2, reaction b) and exhibits an appreciable barrier of 144.0 kJ mol^{-1}, due to substantial nuclear reorganization. Bimolecular F_2-elimination to give OsF_7 (Table 3, reaction a) is strongly exothermic and may be a reason why OsF_8 has not been observed in typical condensed-phase reactions (computation of activation barriers of bimolecular reaction channels is outside the scope of the present work).

We note in passing the good agreement between B3LYP and CCSD(T) thermochemistry, whereas MP2 tends to overestimate and CCSD tends to underestimate the stabilities of the high-oxidation-state species significantly. These trends are consistent with appreciable differential nondynamical correlation effects and agree with our earlier experience on redox reactions of 5d transition-metal fluoride complexes.[9,10,12−14] We consider the B3LYP and CCSD(T) results to provide faithful estimates of the reaction energies. The good performance of B3LYP in this field of 5d-metal fluoride redox reactions (as compared to pure gradient-corrected functionals or hybrid functionals with larger exact-exchange admixtures[9,10,14]) is notable also in view of an apparently nonuniform quality of B3LYP in other areas of transition-metal thermochemistry.[30]

Moving to the next lower homoleptic fluoride, we find OsF_7 to exhibit a (doublet state) minimum with C_{2v} symmetry

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Table 3. Computed Bimolecular Decomposition Reactions (in kJ mol^{-1})[a]

reaction	B3LYP	MP2	CCSD	CCSD(T)
(a) $2OsF_8 \rightarrow 2OsF_7 + F_2$	−142.0	3.4	−212.2	−131.9
(b) $2OsF_7 \rightarrow 2OsF_6 + F_2$	−16.1	111.3	−100.4	−22.4
(c) $2OsF_6 \rightarrow 2OsF_5 + F_2$	453.9	496.1	317.7	395.4
(d) $2OsOF_6 \rightarrow 2OsF_6 + O_2$	−319.6	200.4	−295.5	−151.1
(e) $2OsOF_6 \rightarrow 2OsOF_5 + F_2$	−46.9	126.7	−116.2	−43.1
(f) $2OsO_2F_4 + 2F_2 \rightarrow 2OsOF_6 + O_2$	−249.7	−332.7	−215.6	−215.7
(g) $2OsO_2F_4 + 2KrF_2 \rightarrow 2OsOF_6 + O_2 + 2Kr$	−321.1	−389.7	−385.6	−337.5
(h) $2OsF_6 + KrF_2 \rightarrow 2OsF_7 + Kr$	−19.5	−139.8	15.4	−38.6

[a] See footnote 1 to Table 2.

Table 4. Computed Adiabatic First Ionization Potentials (in eV) of Neutral Osmium Fluoride Complexes and Decomposition Reaction Energies of Cationic Species (in kJ mol^{-1})[a]

reaction	B3LYP	MP2	CCSD	CCSD(T)
(a) $OsF_7 \rightarrow [OsF_7]^+$	12.6	11.4	13.3	12.5
(b) $OsOF_5 \rightarrow [OsOF_5]^+$	12.3	11.1	12.8	12.2
(c) $[OsF_7]^+ \rightarrow [OsF_6]^+ + F$	32.3	128.1	−24.5	33.5
(d) $[OsF_7]^+ \rightarrow [OsF_5]^+ + F_2$	88.3	257.9	−36.3	76.7
(e) $[OsOF_5]^+ \rightarrow [OsOF_4]^+ + F$	116.6	245.2	34.7	114.5
(f) $[OsOF_5]^+ \rightarrow [OsOF_3]^+ + F_2$	277.7	469.4	185.1	279.6

[a] Reaction energies for doublet OsF_7, singlet $[OsF_7]^+$, doublet $[OsF_6]^+$, triplet $[OsF_5]^+$, doublet $OsOF_5$, singlet $[OsOF_5]^+$, doublet $[OsOF_4]^+$, and triplet $[OsOF_3]^+$.

(Figure 2). Unimolecular F_2-elimination, $OsF_7 \rightarrow OsF_5 + F_2$, is now appreciably endothermic (by 186.5 kJ mol^{-1} at CCSD(T) level, Table 2). Homolytic bond cleavage costs 65.2 kJ mol^{-1} at the same level, with a relatively high barrier of 237.0 kJ mol^{-1}, due to extensive nuclear reorganization (B3LYP result). These results suggest appreciable stability for OsF_7 under typical gas-phase conditions. Notably, however, the bimolecular F_2-elimination (Table 3, reaction b) is exothermic. The characterization of OsF_7 in ref 6 was mainly based on an IR spectrum that differed from that of OsF_6. Our computed vibrational spectra (Table 5) suggest substantial differences between the two species but do not agree too well with the reported solid-state data on OsF_7. A recent attempt by Shorafa and Seppelt[7] to reproduce the reaction of ref 6 gave pure OsF_6 as sole product, as indicated by low-temperature Raman spectroscopy. Our computations do not allow us to interpret the experimental results of ref 6 at this point. In any case, OsF_7 appears to be a clearly more stable species and more easily accessible target (at least in gas-phase or matrix-isolation experiments) as compared to OsF_8. It is doubtful, however, whether the high-temperature condensed-phase conditions employed in the experiments would allow isolation of such a highly reactive species.

Previous attempts to prepare the higher homoleptic fluorides (OsF_7, OsF_8) by fluorinating $OsOF_5$ with KrF_2 have been unsuccessful, as neither oxygen elimination nor fluorination were observed.[31] Table 2 includes a number of reactions involving KrF_2 and KrF^+, as well as some isoelectronic xenon compounds. The oxidation reaction $OsF_6 + KrF_2 \rightarrow OsF_8 + Kr$ is calculated to be slightly endothermic (Table 2, reaction f). This indicates that preparation of OsF_8 will indeed be a great challenge. In contrast, oxidation of OsF_5 (Table 2, reaction g) or of OsF_6 (Table 3, reaction h) by KrF_2 is substantially exothermic. This holds even more so for the strongest presently known oxidative fluorinating agent KrF^+:[32] Formation of the $[KrF][OsF_6]$ ion-pair from (gas-phase) $[KrF]^+$ and quartet $[OsF_6]^-$ is highly exothermic (−545.2 kJ mol^{-1} at B3LYP level) and provides a local minimum on the potential energy surface. However, $[KrF][OsF_6]$ is calculated to decompose exothermically (by −143.5 kJ mol^{-1}) into OsF_7 and Kr. Reaction of the related $[XeF][OsF_6]$ is calculated to be endothermic (experimentally, this ion-pair complex decomposes at 20 °C according to $3[XeF][OsF_6] \rightarrow [Xe_2F_3][OsF_6] + 2OsF_6 + Xe$[33]).

Figure 3 shows the reaction energies $[NgF][MF_6] \rightarrow MF_7 + Ng$ for a range of ion pairs (Ng = Kr, Xe and M = Os, Ir, Pt, Au) at the corresponding computational level (note that these energies will be generally somewhat more positive in the condensed phase due to electrostatic stabilization of the ion-pair complexes). Reaction of $[KrF][IrF_6]$ to give IrF_7 is also exothermic and has recently been suggested as a possible pathway toward Ir^{VII}.[9] Figure 3 suggests analogous access to OsF_7. Interestingly, in contrast to several known $[KrF][MF_6]$ complexes of platinum and gold, and despite the existence of $[XeF][IrF_6]$,[33] the corresponding osmium $[NgF][OsF_6]$ and $[KrF][IrF_6]$ complexes have never been observed.

Veldkamp and Frenking[15] had discussed isodesmic fluorination reactions of Os^{VIII} oxofluorides as a possible pathway toward OsF_8. Unfortunately, experimental investigations suggest that these types of fluorinations, either with F_2 or with KrF_2, stop at the known OsO_2F_4 stage,[34−36] and further fluorination is unsuccessful. Thus, even $OsOF_6$ is not known (and a structure could not be located at HF or MP2 level in ref 15). Most likely, the reason is the increasing steric hindrance in the Os coordination sphere, leading to an increasing oxidizing power along the series $OsO_4 < OsO_3F_2 < OsO_2F_4$.[37] Interestingly, our computations (B3LYP or CCSD(T), Table 2) indicate exothermic fluorination, both with F_2 and with KrF_2, up to and including OsF_8 as product. Maybe the kinetics of these reactions are unfavorable (this

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Table 5. Experimental and Computed Fundamental Vibrational Frequencies (with IR and Raman Intensities) for OsF_7 and OsF_6[a]

	exp. IR freq. (solid-state)	exp. IR freq. (gas-phase)	exp. Raman freq.	comp. freq.	comp. IR inten.	comp. Raman activities
OsF_7	282			67		9
	336			193	9	
	366			268		4
	483			293	21	21
	550			303		4
	715			346	20	
				481		9
				500		4
				648		13
				661	150	
				680	150	
				706		46
				722	186	
OsF_6	628	268	252	159	4	
	700	728	632	204		4
			733	270	16	
				285		4
				468		11
				709	207	
				723		42

[a] Frequencies in cm^{-1}, computed IR-intensities in km mol^{-1}, computed Raman scattering activities in A^4 amu^{-1}. Experimental solid-state data for OsF_7 from ref 6 and for OsF_6 from ref 44. Gas-phase data for OsF_6 from ref 45.

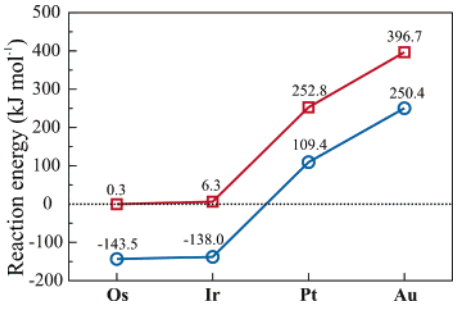

Figure 3. Computed energies (B3LYP) in kJ mol^{-1} for the (gas-phase) reactions $[NgF]^+[MF_6]^- \rightarrow MF_7 + Ng$ (Ng = Kr, Xe; M = Os, Ir, Pt, Au): (□) XeF^+ complexes, (○) KrF^+ complexes.

will be subject of future studies). Experimental evidence suggests in any case that homoleptic lower osmium fluorides provide a better starting point for the synthesis of the higher fluorides than do the Os^{VIII} oxyfluorides.

All attempts to synthesize the highest oxyfluoride $OsOF_6$ were unsuccessful (a claimed preparation was later shown to have led to OsO_2F_4[34,38]), and even the computational search for this complex failed.[15] In contrast to that older computational study, we have been able to locate a minimum for $OsOF_6$ at B3LYP level (a similar structure is obtained at HF or MP2 levels), a pentagonal bipyramidal structure (C_{5v} symmetry, Figure 2; a monocapped octahedral C_{3v} structure is a transition state at 61.6 kJ mol^{-1}, and the monocapped trigonal prism of C_{2v} symmetry is a second-order saddle point at 110.2 kJ mol^{-1} above the C_{5v} minimum). All unimolecular gas-phase decomposition channels of $OsOF_6$ are endothermic (Table 2), including homolytic Os−F bond-breaking to give $OsOF_5$ (doublet), or Os−O bond cleavage to give OsF_6 (triplet). Inclusion of bimolecular channels leads to exothermic decomposition pathways (Table 3, reactions d,e). As for OsF_8 or OsF_7, this suggests gas-phase or matrix-isolation techniques as preferred tools for the preparation of $OsOF_6$.

The cations $[OsF_7]^+$ and $[OsOF_5]^+$ are of particular interest as potential precursors for the missing targets OsF_8 and $OsOF_6$. Singlet $[OsF_7]^+$ exhibits a slightly compressed pentagonal bipyramidal structure (Os−F_{ax} 180.0 pm, Os−F_{eq} 184.7 pm). The adiabatic ionization potential $OsF_7 \rightarrow [OsF_7]^+$ is calculated to be appreciable at 12.5 eV (CCSD(T) result). Os−F bond homolysis and concerted F_2-elimination are computed to be endothermic (Table 4). $[OsOF_5]^+$ exhibits C_{4v} symmetry. Because of the trans influence of the oxo ligand, the axial Os−F bond is somewhat lengthened (Os−O 167.5 pm, Os−F_{ax} 183.9 pm, and Os−F_{eq} 181.2 pm). Unimolecular decomposition channels for this cation are all computed to be endothermic.

4. Conclusions

The evaluation of structures and stabilities of higher fluorides and oxyfluorides of osmium indicates that OsF_7 is a viable target for preparation. Yet, in view of potential exothermic bimolecular decomposition pathways, this might be better achieved in a gas-phase or matrix-isolation experiment than in an earlier[6] direct condensed-phase fluorination experiment that has recently been put into question.[7] OsF_8 is much less stable thermochemically but appears to exhibit appreciable activation barriers for its unimolecular decomposition pathways. Its experimental observation under matrix-isolation conditions appears thus also possible. The last missing Os^{VIII} oxyfluoride, $OsOF_6$, is even somewhat more

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stable against unimolecular decomposition. Overall, the highest fluorides and oxyfluorides do thus remain interesting challenges for matrix-isolation spectroscopists, or possibly for mass spectrometrical identification in the gas phase, whereas classical condensed-phase syntheses appear difficult.

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