Inorg. Chem. **2007**, *46*, 10016–10021

Inorganic Chemistry
Article

Heats of Formation of Krypton Fluorides and Stability Predictions for KrF_4 and KrF_6 from High Level Electronic Structure Calculations

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Received July 3, 2007

Atomization energies at 0 K and heats of formation at 0 and 298 K are predicted for KrF^+, KrF^-, KrF_2, KrF_3^+, KrF_4, KrF_5^+, and KrF_6 from coupled-cluster theory (CCSD(T)) calculations with effective core potential correlation-consistent basis sets for krypton. To achieve near chemical accuracy (±1 kcal/mol), three corrections were added to the complete basis set binding energies based on frozen core coupled-cluster theory energies: a correction for core-valence effects, a correction for scalar relativistic effects, and a correction for first-order atomic spin–orbit effects. Vibrational zero point energies were computed at the coupled-cluster level of theory. The calculated value for the heat of formation of KrF_2 is in excellent agreement with the experimental value. Contrary to the analogous xenon fluorides, KrF_2, KrF_4, and KrF_6 are predicted to be thermodynamically unstable with respect to loss of F_2. An analysis of the energetics of KrF_4 and KrF_6 with respect to fluorine atom loss together with calculations of the transition states for the intramolecular loss of F_2 show that fluorine atom loss is the limiting factor determining the kinetic stabilities of these molecules. Whereas KrF_4 possesses a marginal energy barrier of 10 kcal/mol toward fluorine atom loss and might be stable at moderately low temperatures, the corresponding barrier in KrF_6 is only 0.9 kcal/mol, suggesting that it could exist only at very low temperatures. Although the simultaneous reactions of either two or four fluorine atoms with KrF_2 to give KrF_4 or KrF_6, respectively, are exothermic, they do not represent feasible synthetic approaches because the attack of the fluorine ligands of KrF_2 by the fluorine atoms, resulting in F_2 abstraction, is thermodynamically favored over oxidative fluorination of the krypton central atom. Therefore, KrF_6 could exist only at very low temperatures, and even the preparation of KrF_4 will be extremely difficult.

Introduction

The first stable noble-gas compounds, the xenon fluorides, have been known[1,2] since the early 1960s beginning with the work of Bartlett,[3] who reported the first evidence for a xenon-containing compound, $XePtF_6$, which was subsequently shown to contain mixtures of XeF^+ salts that likely have PtF_6^-, $Pt_2F_{11}^-$, and $(PtF_5^-)_n$ as their anions. The syntheses of XeF_2, XeF_4, XeF_6, and $XeOF_4$ were described within a year of the original discovery.[4−6] There is a continuing chemistry of xenon, and a substantial variety of

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10.1021/ic701313h CCC: $37.00

xenon compounds have been synthesized and structurally characterized.[7,8] For krypton, on the other hand, many fewer compounds are known.[9] This is, in part, due to the difference in the ionization potentials of krypton (13.99961 ± 0.00001 eV) and xenon (12.12987 eV).[10,11] Krypton difluoride (KrF_2) was synthesized shortly after XeF_2 was made.[12,13] The first synthesis of a krypton compound was reported by Grosse et al.,[14,15] who claimed to have prepared KrF_4 by the use of a high voltage glow discharge through a Kr/F_2 mixture at −78 °C. Subsequent attempts to repeat the glow discharge synthesis of KrF_4 verified the formation of a krypton fluoride;[13] however, the vapor pressures and the ^{19}F NMR spectrum were very similar to those reported in the meantime for KrF_2.[16] Other workers have since failed to synthesize KrF_4 by the method of Grosse et al. or by any other method, producing only KrF_2. Turner and Pimentel[12] prepared KrF_2 by irradiation of Kr/F_2 mixtures at 20 K in an argon matrix and were the first to correctly identify KrF_2 and characterize it by infrared spectroscopy. Krypton difluoride has sufficient kinetic stability to permit its handling at ambient temperature over short periods of time.[13]

Krypton tetrafluoride and any krypton species in a higher oxidation state than +2 are still unknown. The neutral fluorides of krypton are presently limited to KrF_2, which is isolable in gram quantities using a variety of low-temperature synthetic approaches[8] and to the transient violet-colored $KrF^{\bullet}$ radical, which has been obtained by γ-irradiation of single crystals of KrF_2 with a ^{60}Co source at −196 °C.[17] The KrF^- anion has been studied in the gas phase using a Penning ion source with radical extraction and confirmed by observing the negative-ion mass spectrum of KrF_2.[18] Solid KrF_2 can be stored indefinitely at −78 °C, at which temperature its vapor pressure is negligible.

Krypton difluoride has a bond length of 1.875 ± 0.002 Å,[19] a heat of formation of 14.4 ± 0.8 kcal/mol,[1,20,21] and a total binding (atomization) energy of 21.9 kcal/mol. The vibrational frequencies of KrF_2 have also been measured.[19,22−24] All of the krypton compounds that have been synthesized in macroscopic amounts are derived from KrF_2. The KrF^+ and $Kr_2F_3^+$ ions have been formed by the reaction of KrF_2 with strong Lewis acid fluorides having high fluoride ion affinities. Hoffman et al.[25] used CCSD(T) (coupled cluster including single and double excitations with an approximate triples correction)[26] with polarized triple-ζ basis sets to study KrF_2 and KrF^+. They predicted a total binding energy of 17.8 kcal/mol and a bond distance of 1.89 Å for KrF_2. For KrF^+, they predicted a bond dissociation energy to $Kr^+ + F$ of 42.0 kcal/mol and a bond distance of 1.75 Å. Wilson and co-workers[27] have recently studied KrF_2 with all-electron, correlation-consistent basis sets at the CCSD(T) level up through aug-cc-pV5Z. They found an atomization energy of 20.8 kcal/mol at the CCSD(T)/aug-cc-pV5Z level with a Kr−F bond distance of 1.873 Å. Similarly, Curtiss and co-workers[28] obtained atomization energies of 21.3 kcal/mol at the G3 level and 20.6 at the G3X level.

Table 1. Dissociation Energy of Krypton and Xenon Fluorides into the $Ng + nF_2$ in Kcal/mol

reaction	Xe[a]	Kr
$NgF_2 \rightarrow Ng + F_2$	23.3	−14.8
$NgF_4 \rightarrow NgF_2 + F_2$	19.2	−26.8
$NgF_4 \rightarrow Ng + 2F_2$	42.5	−41.6
$NgF_6 \rightarrow NgF_4 + F_2$	13.4	−36.0
$NgF_6 \rightarrow NgF_2 + 2F_2$	32.6	−62.8
$NgF_6 \rightarrow Ng + 3F_2$	55.9	−77.6

[a] Ref 29.

We have recently performed extensive CCSD(T)/CBS (complete basis set) calculations on the xenon fluorides, predicted their heats of formation, and showed that the heats of formation need to be remeasured.[29] We also predicted the dissociation energies of the xenon fluorides into xenon and F_2 at 0 K and, as shown in Table 1, the XeF_x compounds are stable with respect to loss of F_2. We showed that XeF_6 is fluxional as a result of the presence of a sterically active, free valence electron pair on xenon. In the current work, we have calculated the same properties for the krypton fluorides KrF^-, KrF^+, KrF_2, KrF_3^+, KrF_4, KrF_5^+, and KrF_6 at the CCSD(T)/CBS level using the new effective core potential/correlation consistent basis sets developed by Peterson and

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Table 2. Calculated Geometry Parameters

molecule	method/basis set	r_e (Å)
KrF^+ ($C_{\infty v}$)	CCSD(T)/aVDZ	1.7892
	CCSD(T)/aVTZ	1.7478
	CCSD(T)/aVQZ	1.7397
KrF^- ($C_{\infty v}$)	CCSD(T)/aVDZ	3.0893
	q	3.0167
	CCSD(T)/aVQZ	2.9979
KrF_2 ($D_{\infty h}$)	CCSD(T)/aVDZ	1.9223
	CCSD(T)/aVTZ	1.8841
	CCSD(T)/aVQZ	1.8747
	Expt[19]	1.875 ± 0.002
KrF_3^+ (C_{2v})[a]	CCSD(T)/aVDZ	1.8350, 1.8255 (85.41°)
	CCSD(T)/aVTZ	1.7861, 1.7621 (85.45°)
KrF_4 (D_{4h})	CCSD(T)/aVDZ	1.9083
	CCSD(T)/aVTZ	1.8630
KrF_5^+ (C_{4v})[b]	CCSD(T)/aVDZ	1.8189, 1.8345 (85.03°)
	CCSD(T)/aVTZ	1.7615, 1.7602 (85.86°)
KrF_6 (O_h)	CCSD(T)/aVDZ	1.9193
	CCSD(T)/aVTZ	1.8664

[a] First bond distance is for the two equivalent $Kr-F_a$ bonds in the T-shaped structure. The second bond is the unique $Kr-F_e$ bond and the angle is $<F_a-Kr-F_e$. [b] First bond distance is for the four equivalent $Kr-F_e$ bonds in the C_{4v} structure. The second bond is the unique $Kr-F_a$ bond and the angle is $<F_a-Kr-F_e$.

Table 3. CCSD(T) Calculated Frequencies (cm^{-1})

molecule	symmetry	aVDZ	aVTZ
KrF_2[a]	σ_u^+ (589.9)	589.7	596.9
	σ_g^+ (449)	441.1	468.9
	π_u (233)	221.2	238.0
KrF_3^+	a_1	480.9	546.1
		467.1	519.9
		217.2	247.6
	b_1	216.8	231.5
	b_2	655.3	682.9
		301.4	343.7
KrF_4	a_{1g}	406.8	454.9
	b_{2g}	392.5	427.0
	b_{1g}	215.6	226.1
	a_{2u}	275.9	307.9
	b_{1u}	162.4	174.2
	e_u	597.8	610.9
		192.8	199.8
KrF_5^+	a_1	479.3	542.4
		449.1	522.4
		316.1	366.4
	b_1	271.8	309.3
	b_2	463.4	526.4
		199.6	229.4
	e	653.6	689.0
		324.4	380.0
		221.4	246.6
KrF_6	a_{1g}	348.2	433.2
	e_g	309.3	371.3
	t_{2g}	203.5	219.5
	t_{1u}	571.4	595.7
		204.7	208.1
	t_{2u}	169.9	169.6

[a] Experimental values in parentheses from refs 19, 22, 23, and 24.

co-workers.[30] These basis sets were developed in combination with effective core potentials from the Stuttgart/Köln group and enable us to study all of the main-group elements with high quality basis sets that can be extrapolated to the CBS limit.

Computational Methods

We used essentially the same approach for calculating the structures, frequencies, and energies for the krypton fluorides as used by us for the xenon fluorides.[29] The computational details are provided in the Supporting Information. Eq (1) describing the complete basis set extrapolation procedure and eq (2) summarizing the calculation of the total atomization energies are given in the Supporting Information.

Results and Discussion

The total energies used in this study are given as Supporting Information (Table S1). The calculated geometries and frequencies are given in Tables 2 and 3, respectively, where they are compared with the available experimental values.

The calculated bond distance in KrF_2 is in excellent agreement with the experimental value derived from an analysis of the rotation-vibration spectra.[19] Both our value and the spectroscopically derived value are shorter than the electron diffraction value of 1.889 ± 0.01 Å.[31] The calculated frequencies for KrF_2 can be compared with the experimental values. The calculated harmonic frequencies for KrF_2 at the CCSD(T)/aVTZ level are in excellent agreement with the experimental anharmonic values within 20 cm^{-1} and, as expected, are higher than the experimental values.[19,22−24] The calculated values for the σ_u^+ antisymmetric stretch, the σ_g^+ symmetric stretch, and the π_u bend are 7, 20, and 5 cm^{-1} too high, respectively. The CCSD(T)/aVDZ values are lower than the aVTZ basis set values with the largest differences for the σ_g^+ symmetric stretch and the π_u bend. The MP2 frequencies for KrF_2 are somewhat higher than the CCSD(T) values for a given basis set (Supporting Information, Table S2)

The KrF^+ harmonic frequency is predicted to be near 963.6 cm^{-1} and $\omega_e x_e = 10.4$ cm^{-1}. The comparable values for KrF^- are $\omega_e = 111.1$ cm^{-1} and $\omega_e x_e = 19.4$ cm^{-1}. The anharmonicity constant for KrF^- is almost double that for KrF^+ consistent with the very weak interaction between F^- and krypton discussed below.

The geometry of KrF_4 is D_{4h} as predicted for XeF_4 and observed experimentally for XeF_4. The geometry of KrF_6 was optimized in O_h symmetry, consistent with the geometry of BrF_6^-.[32] The structure of free XeF_6 is complicated and is most likely C_{3v}. It requires very large basis sets (at least aV5Z) at the CCSD(T) correlation level to predict the structure. The effect of the basis set on the a_{1g} and b_{1g} stretches in KrF_4 is much larger than the effect on the antisymmetric e_u stretch. The effect of the larger basis set is to make the frequencies larger. The e_u stretching frequency in KrF_4 is slightly above the antisymmetric stretching frequency in KrF_2, and the a_{1g} stretching frequency in KrF_4 is slightly below the σ_g^+ stretching frequency in KrF_2. The degenerate antisymmetric t_{1u} Kr−F stretching frequency in KrF_6 is comparable to the antisymmetric stretching frrequency in KrF_2 and slightly below that in KrF_4. The

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Table 4. CCSD(T) Atomization and Reaction Energies in kcal/mol[a]

molecule	CBS[b]	ΔE_{ZPE}[c]	ΔE_{CV}[d]	ΔE_{SR}[e]	ΔE_{SO}[f]	ΣD_0 (0K)[g]
$KrF^+ \rightarrow Kr + F^+$	121.61	1.37	−0.55	−0.02	−0.48	119.19
$KrF^+ \rightarrow Kr^+ + F\cdot$	47.30	1.37	0.03	0.02	−5.51	40.47
$KrF^+ + e^- \rightarrow Kr + F\cdot$	−279.64	1.37	−0.83	0.16	−0.39	−282.07
$KrF^- \rightarrow Kr + F\cdot + e^-$	82.90	0.15	0.11	−0.22	−0.39	82.25
$KrF^- \rightarrow Kr + F^-$	3.97	0.15	0.02	−0.06	0.0	3.78
$KrF_2 \rightarrow Kr + 2F\cdot$	25.42	2.11	−0.57	0.03	−0.78	21.99
$KrF_3^+ + e^- \rightarrow Kr + 3F\cdot$	−271.69	3.63	0.89	0.48	−1.17	−275.12
$KrF_3^+ \rightarrow Kr^+ + 3F\cdot$	55.25	3.63	1.72	0.35	−6.29	47.40
$KrF_3^+ \rightarrow KrF_2 + F^+$	104.19	1.79	1.61	0.20	−0.48	103.73
$KrF_4 \rightarrow Kr + 4F\cdot$	38.22	3.39	−1.13	0.11	−1.56	32.25
$KrF_5^+ \rightarrow KrF_4 + F^+$	103.01	1.99	−1.70	0.45	−0.48	99.29
$KrF_5^+ \rightarrow Kr^+ + 5F\cdot$	66.92	5.38	−2.03	0.75	−7.07	53.19
$KrF_5 + e^- \rightarrow Kr + 5F\cdot$	−260.02	5.38	−2.86	0.89	−1.95	−269.32
$KrF_6 \rightarrow Kr + 6F\cdot$	39.67	2.82	−1.45	0.13	−2.34	33.19

[a] The atomic asymptotes were calculated with the R/UCCSD(T) method. [b] Extrapolated by using eq 1 with aD, aT, aQ. [c] The zero point energies were obtained as follows: (1) For diatomics, the anharmonic ZPE's were computed as $0.5\omega_e - 0.25\omega_e x_e$; (2). For the polyatomics, the ZPE was taken as 0.5 the sum of the CCSD(T) harmonic frequencies. [d] Core-valence corrections were obtained with the cc-pwCVTZ (F) and cc-pwCVTZ-PP (for krypton) basis sets at the optimized CCSD(T)/aVTZ geometries. [e] The scalar relativistic correction is based on a CISD(FC)/ aVTZ MVD calculation and is expressed relative to the CISD result without the MVD correction, that is, including the existing relativistic effects resulting from the use of a relativistic effective core potential. [f] Correction as a result of the incorrect treatment of the atomic asymptotes as an average of spin multiplets. Values are based on C. Moore's Tables, ref 65. [g] The theoretical value of ΔD_0 (0 K) was computed with the CBS estimates.

Table 5. Calculated Heats of Formation (kcal/mol)

molecule	theory (0 K)	theory (298 K)
KrF^+	300.5	301.6
KrF^-	−63.8	−62.3
KrF_2	14.8	15.7
KrF_3^+	330.5	330.6
KrF_4	41.6	42.7
KrF_5^+	361.7	362.3
KrF_6	77.6	78.0

symmetric a_{1g} stretching frequency in KrF_6 decreases by ~20 cm^{-1} as compared to the a_{1g} symmetric stretching frequency in KrF_4.

The Kr−F stretches in KrF_3^+ also exhibit a substantial basis set effect with the larger basis set predicting higher frequencies. The Kr−F stretching frequencies in KrF_3^+ are significantly higher than those in KrF_2 for both the symmetric and antisymmetric modes. The e_u antisymmetric stretching frequency in KrF_5^+ increases slightly over the antisymmetric b_2 stretching frequency in KrF_3^+. The remaining stretches in KrF_5^+ are also higher than their counterparts in KrF_3^+. There is a substantial difference between the MP2 and CCSD(T) values, especially for the smaller basis set.

The energetic components for predicting the total molecular dissociation energies are given in Table 4. The core-valence corrections for the neutral molecules are negative, lowering the total bond dissociation energies. For KrF_3^+, ΔE_{CV} is positive for both channels, and for KrF^+ the correction is approximately 0 to −0.83 kcal/mol. The scalar relativistic corrections are not large, ranging in size from −0.25 to +0.9 kcal/mol. We estimate that the error bars for the calculated heats of formation for KrF^+, KrF^-, and KrF_2 are ±0.5 kcal/mol, considering errors in the energy extrapolation, frequencies, and other electronic energy components. The errors for KrF_3^+, KrF_4, KrF_5^+, and KrF_6 are estimated to be ±1.0 kcal/mol. An estimate of the potential for significant multireference character in the wavefunction can be obtained from the T_1 diagnostic[33] for the CCSD calculation. The value for the T_1 diagnostics for KrF_2, KrF_4, and KrF_6 are all about 0.02, showing that the wavefunction is dominated by a single configuration.

The calculated ionization potential for krypton is 13.987 eV, in excellent agreement with an experimental value of 13.99961 ± 0.00001. The calculated value for the dissociation energy of the higher energy channel for KrF^+ generating F^+ is 119.2 kcal/mol (5.17 eV) at 0 K, in good agreement with the value of 115.9 obtained at the lower local density functional theory level by us in our work on fluorocation detachment energies.[34] The channel for the formation of Kr^+ is at much lower energy, 40.5 kcal/mol (1.75 eV). This value is similar to the value of 1.81 eV predicted for $XeF^+ \rightarrow Xe^+ + F$. The fluoride ion affinity (FA) of krypton at 0 K is very small, 3.8 kcal/mol, and is significantly smaller than the value of 6.2 kcal/mol for FA(Xe).

The calculated heat of formation for KrF_2 at 298 K of 15.7 kcal/mol is in excellent agreement with the calorimetric experimental value of 14.4 ± 0.8 kcal/mol. The heat of formation of KrF^+ has been estimated to be 306.1 kcal/mol from the heat of formation of KrF_2 and the appearance potential of KrF^+ from KrF_2. We calculate a more reliable value of 300.5 kcal/mol at 0 K, in reasonable agreement with this estimated value.

The F^+ affinity of KrF_2 is 103.7 kcal/mol at 0 K and is smaller than that for krypton. The F^+ affinity of KrF_4 is even smaller, 99.3 kcal/mol at 0 K. These values are consistent with the trend predicted with lower-level density functional theory calculations[34] for the F^+ affinities of Xe, XeF_2, and XeF_4, where the F^+ affinities of the fluorides are predicted to be below that of the atom.

The calculated heats of formation can be used to calculate the dissociation energies of the krypton fluorides into krypton and F_2 at 0 K, as shown in Table 1. The loss of F_2 from KrF_2 results in a negative enthalpy of −14.8 kcal/mol, showing that KrF_2 is thermodynamically unstable with respect to krypton and F_2. Loss of one mol of F_2 from KrF_4 results in a value of −26.8 kcal/mol, almost double the exothermicity for the loss of F_2 from KrF_2. Loss of one F_2 from KrF_6 is another 9.0 kcal/mol more exothermic, giving a value of −36.0 kcal/mol. Thus, the addition of fluorine to these compounds becomes more difficult as the number of fluorine atoms is increased, most likely as a result of the increased steric interactions among the fluorine atom substituents and the valence lone pair as well as the decreasing Kr−F bond strengths (the average Kr−F bond energies in KrF_2, KrF_4, and KrF_6 are 11.0, 8.1, and 5.5 kcal/mol, respectively, at 0 K). In contrast, the losses of F_2 from XeF_2, XeF_4, and XeF_6 are endothermic processes. Similarly, but to a lesser degree, the average bond strengths in XeF_2, XeF_4, and XeF_6 decrease with increasing the oxidation state of xenon from 30.1 to 29.1 to 27.8 kcal/mol, respectively. The

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average bond energies decrease by 2.4 kcal/mol (∼8% of the average bond energy for XeF_6) from XeF_2 to XeF_6. In comparison, the average bond energies decrease by 5.5 kcal/mol (100% of the average bond energy for KrF_6) from KrF_2 to KrF_6. This shows that the steric crowding in the krypton fluorides is much greater than that in the xenon fluorides.

Although KrF_4 and KrF_6 are thermodynamically unstable with respect to the loss of F_2, significant barriers toward decomposition might impart sufficient kinetic stability to allow their synthesis and isolation. We first consider loss of a fluorine atom from KrF_4 and KrF_6 to form the KrF_3 and KrF_5 radicals, respectively. We can calculate the energy to break two Kr−F bonds at 0 K in KrF_6 from the reaction $KrF_6 \rightarrow KrF_4 + 2F$ as 0.9 kcal/mol. Most of this energy can be attributed to the breakage of the first bond because CCSD(T)/aVDZ calculations on KrF_5 show a highly dissociated complex with a fluorine atom barely interacting with closed-shell KrF_4, just as there is only a weak interaction of fluorine with krypton in KrF. Thus, there is only a small energy required to lose a fluorine atom from KrF_6 and, at most finite temperatures, KrF_6 is likely to quickly decompose to form $KrF_4 + 2F$. In addition, the free energy will always favor the loss of fluorine even at quite low temperatures because of the entropy term. This shows that the existence of KrF_6 will be highly improbable and might be possible only at very low temperatures.

In a similar fashion, we can calculate the energy for the reaction $KrF_4 \rightarrow KrF_2 + 2F$ at 0 K and obtain a value of 10.1 kcal/mol. Again, we optimized KrF_3 at the CCSD(T)/aVDZ level and found a dissociated complex between KrF_2 and fluorine with essentially zero bond energy. This shows that the first Kr−F bond energy in KrF_4 is approximately 10 kcal/mol and that, in contrast to KrF_6, KrF_4 might be marginally kinetically stable at low temperatures with respect to loss of a fluorine atom.

As a further test for the stability of KrF_4, we calculated the transition state for the intramolecular loss of a F_2 molecule at the density functional theory level with the B3LYP exchange-correlation functional[35,36] and the aVDZ and aVTZ basis sets. The barrier for a one-step concerted process for the loss of F_2 in the plane of KrF_4 to form linear KrF_2 is 60.2 kcal/mol with the aVDZ basis set and 64.3 kcal/mol with the aVTZ basis set. An intrinsic reaction coordinate[37] calculation showed that the transition state is connected to reactants and products. The barrier for the loss of F_2 in the plane perpendicular to the molecular plane is even higher, 76.1 kcal/mol at the B3LYP/aVDZ level. These high barriers show that although KrF_4 is unstable in a thermodynamic sense with respect to loss of F_2, it should be kinetically very stable with respect to the intramolecular elimination of an F_2 molecule. A similar situation is encountered for KrF_6. The barrier at 0 K for the elimination of F_2 from KrF_6 again is high, 53.8 kcal/mol at the B3LYP/aVDZ level and 57.8 kcal/mol at the B3LYP/aVTZ level, showing that KrF_6 is stable with respect to intramolecular F_2 elimination, but as discussed above, is barely stable with respect to loss of fluorine. The high barriers for the intramolecular F_2 elimination are above the F_2 bond dissociation energy of 36.9 kcal/mol at 0 K and are consistent with symmetry forbidden reactions. These considerations show that the loss of a fluorine atom from KrF_2, KrF_4, or KrF_6 have much lower activation energy barriers than the intramolecular F_2 eliminations and are the limiting factors determining their kinetic stabilities.

The predicted barrier of 10.1 kcal/mol for fluorine-atom elimination from KrF_4 and the exothermicity of the reaction of KrF_2 with two fluorine atoms suggest the simultaneous reaction of two fluorine atoms with KrF_2 as a possible synthetic pathway to KrF_4. However, a major issue with this approach is a competing attack of the fluorine ligands of KrF_2 by the fluorine atoms, leading to fluorine-atom abstraction and the formation of F_2 and KrF, with the latter rapidly decomposing to krypton and fluorine. From our heats of formation and assuming that the KrF bond energy is 0, the energy at 0 K for the reaction of $KrF_2 + F \rightarrow KrF + F_2$ can be calculated to be −15 kcal/mol, showing that the fluorine-atom abstraction is exothermic and is thermodynamically favored by about 5 kcal/mol over the oxidative fluorination of Kr in KrF_2. The same dilemma, but even more so, applies to the hypothetical synthesis of KrF_6 from KrF_2 and four fluorine atoms.

One can apply a similar type of analysis to the stability of KrF_5^+ and KrF_3^+. In this case, the ion can lose F^+ to form KrF_4 and KrF_2 respectively, lose F_2 to from KrF_3^+ and KrF^+ respectively, and fluorine to form KrF_4^+ and KrF_2^+, respectively. The first channel is the F^+ affinity given in reactions (3) and (4) at 0 K.

$$KrF_5^+ \rightarrow KrF_4 + F^+ \quad \Delta H = 99.3 \text{ kcal/mol} \tag{3}$$

$$KrF_3^+ \rightarrow KrF_2 + F^+ \quad \Delta H = 103.7 \text{ kcal/mol} \tag{4}$$

Thus, the ions are stable with respect to the loss of F^+. The loss of F_2 channels are given in reactions (5) and (6) and both channels are exothermic by about 30 kcal/mol at 0 K.

$$KrF_5^+ \rightarrow KrF_3^+ + F_2 \quad \Delta H = -31.2 \text{ kcal/mol} \tag{5}$$

$$KrF_3^+ \rightarrow KrF^+ + F_2 \quad \Delta H = -30.0 \text{ kcal/mol} \tag{6}$$

Thus these ions are unstable thermodynamically with respect to loss of F_2. Loss of a fluorine atom is shown in reactions (7) and (8).

$$KrF_5^+ \rightarrow KrF_4^+ + F \quad \Delta H = 13.8 \text{ kcal/mol} \tag{7}$$

$$KrF_3^+ \rightarrow KrF_2^+ + F \quad \Delta H = 1.3 \text{ kcal/mol} \tag{8}$$

The product ions in reactions (7) and (8) are formed by ionizing KrF_4 and KrF_2, respectively. We calculated the ionization potential for KrF_4 and KrF_2 using the procedure described above for the heats of formation. The results are shown in the Supporting Information. The CCSD(T)/CBS adiabatic ionization potential for KrF_4 is 13.68 eV at 0 K, and the heat of formation of KrF_4^+ is 357.0 kcal/mol at 0 K. Reaction (7) is endothermic, so KrF_5^+ is reasonably stable

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thermodynamically with respect to loss of fluorine. Ionization of KrF_4 is from an a_1 orbital.

The ionization of KrF_2 is complicated as noted by Brundle and Jones.[38] The Hartree Fock HOMO of the neutral is a σ_g with a π_u as the NHOMO. Experimentally vertical ionization occurs at 13.34 eV to yield a $^2\Pi_{3/2}$ state with ionization to the upper $^2\Pi_{1/2}$ spin-orbit component at 13.47 eV. Vertical ionization from the σ orbital is measured at 13.90 eV. The adiabatic ionization potential was estimated to be $\leq$13.16 eV. In the present theoretical work, the vertical ionization energy is calculated to be 13.60 eV for the $^2\Pi$ state and 13.99 eV for the $^2\Sigma^+$ state of the ion. Correction for spin-orbit effects using the experimental splitting gives a value of 13.53 eV for the vertical ionization potential, a difference of 0.2 eV as compared to experiment. Calculation of the adiabatic ionization energy for KrF_2 is complicated by the presence of the two low-lying states. We optimized the geometry of $D_{\infty h}$ KrF_2^+ in the $^2\Pi$ and $^2\Sigma^+$ states and found that the ionization potentials did not change much from the vertical values. Breaking the $D_{\infty h}$ symmetry for the $^2\Pi$ state led to the formation of a lower energy $C_{\infty v}$ structure that is a complex between KrF^+ and a fluorine atom with a short Kr−F^+ bond of 1.742 Å (0.002 Å longer than the KrF^+ bond length in the isolated ion) and a long F−Kr bond of 2.493 Å at the CCSD(T)/aug-cc-pVQZ level. This asymmetric complex is 13.9 kcal/mol lower in energy than the optimized $D_{\infty h}$ structure. Given the asymmetric complex, the adiabatic ionization potential is calculated to be 12.94 eV, which is consistent with the experimental value of $\leq$13.16 eV. We note that there is a very large change in the vertical and adiabatic ionization potentials due to the large change in the geometry. We use the energy of the asymmetric structure in reaction (8). Thus, KrF_3^+ is barely stable with respect to the loss of a fluorine atom. Finally, we can look at the reactions to lose two fluorine atoms from KrF_5^+ and KrF_3^+

$$KrF_5^+ \rightarrow KrF_3^+ + 2F \quad \Delta H = 5.7 \text{ kcal/mol} \tag{9}$$

$$KrF_3^+ \rightarrow KrF^+ + 2F \quad \Delta H = 6.9 \text{ kcal/mol} \tag{10}$$

These reactions are only slightly endothermic and at any reasonable finite temperature will be substantially exothermic due to the large entropy term arising from the production of two excess free particles as products.

Conclusions

We have predicted the heats of formation of the krypton fluorides: KrF^+, KrF^-, KrF_2, KrF_3^+, KrF_4, KrF_5^+, and KrF_6 at the CCSD(T)/CBS plus at an additional corrections level. The calculated value for the heat of formation of KrF_2 is in excellent agreement with the experimental value. Contrary to the analogous xenon fluorides, KrF_2, KrF_4, and KrF_6 are predicted to be thermodynamically unstable with respect to the loss of F_2. An analysis of the energetics of KrF_4 and KrF_6 with respect to fluorine-atom loss together with calculations of the transition states for the intramolecular loss of F_2 show that fluorine-atom loss is the limiting factor determining the kinetic stabilities of these molecules. Whereas KrF_4 possesses a marginal energy barrier of 10 kcal/mol toward fluorine-atom loss and might be stable at moderately low temperatures, the corresponding barrier in KrF_6 is only 0.9 kcal/mol, suggesting that it could exist only at very low temperatures and that even small entropy contributions would result in thermal decomposition. Although the simultaneous reactions of either two or four fluorine atoms with KrF_2 to give KrF_4 or KrF_6, respectively, are exothermic, they do not represent feasible synthetic approaches because attack of the fluorine ligands of KrF_2 by the fluorine atoms, resulting in F_2 abstraction and KrF formation, is thermodynamically considerably favored over oxidative fluorination of the krypton central atom. Therefore, KrF_6 may only exist at very low temperatures, and even the preparation of KrF_4 represents a formidable challenge to synthetic chemists. Similar conclusions as those for KrF_4 are reached for KrF_3^+ and KrF_5^+. Although both cations possess significant kinetic stability and barriers toward the loss of fluorine atoms, their exothermic syntheses from either KrF^+ and fluorine atoms, KrF_2 or KrF_4 and F^+ ions, or KrF_2 and F_2 in the presence of a strong Lewis acid will be impeded in the first two cases by F_2 abstraction and in the last case by the energetically favored rapid formation of the corresponding KrF^+ salt.

Acknowledgment. This research was supported, in part, by the U.S. Department of Energy, Office of Basis Energy Research, Chemical Sciences, in the catalysis program. This research was performed, in part, using the Molecular Science Computing Facility (MSCF) in the William R. Wiley Environmental Molecular Sciences Laboratory at the Pacific Northwest National Laboratory. The MSCF is a national user facility funded by the Office of Biological and Environmental Research in the U.S. Department of Energy. The Pacific Northwest National Laboratory is a multiprogram national laboratory operated by the Battelle Memorial Institute. K.O.C. is indebted to the Air Force Office of Scientific Research and the National Science Foundation for financial support. G.J.S. acknowledges the support of the Natural Sciences and Engineering Research Council of Canada in the form of a Discovery Grant.

Supporting Information Available: Computational details and complete references, total CCSD(T) energies (Table SM-1) as a function of basis set, MP2 calculated frequencies (Table SM-2) as a function of basis set, calculated geometry parameters (Table SM-3) for KrF_2^+ and KrF_4^+, CCSD(T)/aVTZ calculated frequencies (Table SM-4) for KrF_4^+, CCSD(T) atomization and reaction energies (Table SM-5) for KrF_2^+ and KrF_4^+, and calculated energies/heats of formation (Table SM-6) of KrF_2^+ and KrF_4^+. This material is available free of charge via the Internet at http://pubs.acs.org.

IC701313H

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