

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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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^- , $\text{Pt}_2\text{F}_{11}^-$, and $(\text{PtF}_5^-)_n$ 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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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 Pimentel¹² 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 approaches⁸ and to the transient violet-colored KrF^\cdot 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

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Table 1. Dissociation Energy of Krypton and Xenon Fluorides into the $\text{Ng} + n\text{F}_2$ in Kcal/mol

reaction	Xe ^a	Kr
$\text{NgF}_2 \rightarrow \text{Ng} + \text{F}_2$	23.3	-14.8
$\text{NgF}_4 \rightarrow \text{NgF}_2 + \text{F}_2$	19.2	-26.8
$\text{NgF}_4 \rightarrow \text{Ng} + 2\text{F}_2$	42.5	-41.6
$\text{NgF}_6 \rightarrow \text{NgF}_4 + \text{F}_2$	13.4	-36.0
$\text{NgF}_6 \rightarrow \text{NgF}_2 + 2\text{F}_2$	32.6	-62.8
$\text{NgF}_6 \rightarrow \text{Ng} + 3\text{F}_2$	55.9	-77.6

^a Ref 29.

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 $\text{Kr}^+ + \text{F}$ of 42.0 kcal/mol and a bond distance of 1.75 Å. Wilson and co-workers²⁷ 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-workers²⁸ obtained atomization energies of 21.3 kcal/mol at the G3 level and 20.6 at the G3X level.

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_c bond and the angle is <F_a–Kr–F_c. ^b First bond distance is for the four equivalent Kr–F_c bonds in the C_{4v} structure. The second bond is the unique Kr–F_a bond and the angle is <F_a–Kr–F_c.

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 KrF₂ 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 KrF₂ can be compared with the experimental values. The calculated harmonic frequencies for KrF₂ 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

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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
KrF ₄		301.4	343.7
	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
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
		348.2	433.2
KrF ₆	a_{1g}	309.3	371.3
	e_g	203.5	219.5
	t_{2g}	571.4	595.7
	t_{1u}	204.7	208.1
	t_{2u}	169.9	169.6

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

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 KrF₂ 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 $\omega_{eX_e} = 10.4$ cm⁻¹. The comparable values for KrF⁻ are $\omega_e = 111.1$ cm⁻¹ and $\omega_{eX_e} = 19.4$ 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 KrF₄ is D_{4h} as predicted for XeF₄ and observed experimentally for XeF₄. The geometry of KrF₆ was optimized in O_h symmetry, consistent with the geometry of BrF₆⁻.³² The structure of free XeF₆ 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 KrF₄ 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 KrF₄ is slightly above the antisymmetric stretching frequency in KrF₂, and the a_{1g} stretching frequency in KrF₄ is slightly below the σ_g^+ stretching frequency in KrF₂. The degenerate antisymmetric t_{1u} Kr–F stretching frequency in KrF₆ is comparable to the antisymmetric stretching frequency in KrF₂ and slightly below that in KrF₄. 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 ⁺ → Kr + F ⁺	121.61	1.37	-0.55	-0.02	-0.48	119.19
KrF ⁺ → Kr ⁺ + F [•]	47.30	1.37	0.03	0.02	-5.51	40.47
KrF ⁺ + e ⁻ → Kr + F [•]	-279.64	1.37	-0.83	0.16	-0.39	-282.07
KrF ⁻ → Kr + F [•] + e ⁻	82.90	0.15	0.11	-0.22	-0.39	82.25
KrF ⁻ → Kr + F ⁻	3.97	0.15	0.02	-0.06	0.0	3.78
KrF ₂ → Kr + 2F [•]	25.42	2.11	-0.57	0.03	-0.78	21.99
KrF ₃ ⁺ + e ⁻ → Kr + 3F [•]	-271.69	3.63	0.89	0.48	-1.17	-275.12
KrF ₃ ⁺ → Kr ⁺ + 3F [•]	55.25	3.63	1.72	0.35	-6.29	47.40
KrF ₃ ⁺ → KrF ₂ + F ⁺	104.19	1.79	1.61	0.20	-0.48	103.73
KrF ₄ → Kr + 4F [•]	38.22	3.39	-1.13	0.11	-1.56	32.25
KrF ₅ ⁺ → KrF ₄ + F ⁺	103.01	1.99	-1.70	0.45	-0.48	99.29
KrF ₅ ⁺ → Kr ⁺ + 5F [•]	66.92	5.38	-2.03	0.75	-7.07	53.19
KrF ₅ + e ⁻ → Kr + 5F [•]	-260.02	5.38	-2.86	0.89	-1.95	-269.32
KrF ₆ → Kr + 6F [•]	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 KrF₆ decreases by ~ 20 cm⁻¹ as compared to the a_{1g} symmetric stretching frequency in KrF₄.

The Kr–F stretches in KrF₃⁺ also exhibit a substantial basis set effect with the larger basis set predicting higher frequencies. The Kr–F stretching frequencies in KrF₃⁺ are significantly higher than those in KrF₂ for both the symmetric and antisymmetric modes. The e_u antisymmetric stretching frequency in KrF₅⁺ increases slightly over the antisymmetric b_2 stretching frequency in KrF₃⁺. The remaining stretches in KrF₅⁺ are also higher than their counterparts in KrF₃⁺. 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 KrF₃⁺, 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 KrF₂ are ± 0.5 kcal/mol, considering errors in the energy extrapolation, frequencies, and other electronic energy components. The errors for KrF₃⁺, KrF₄, KrF₅⁺, and KrF₆ 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 T₁ diagnostic³³ for the CCSD calculation. The value for the T₁ diagnostics for KrF₂, KrF₄, and KrF₆ 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⁺ → 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 KrF₂ 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 KrF₂ and the appearance potential of KrF⁺ from KrF₂. 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 KrF₂ is 103.7 kcal/mol at 0 K and is smaller than that for krypton. The F⁺ affinity of KrF₄ is even smaller, 99.3 kcal/mol at 0 K. These values are consistent with the trend predicted with lower-level density functional theory calculations³⁴ for the F⁺ affinities of Xe, XeF₂, and XeF₄, 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 F₂ at 0 K, as shown in Table 1. The loss of F₂ from KrF₂ results in a negative enthalpy of -14.8 kcal/mol, showing that KrF₂ is thermodynamically unstable with respect to krypton and F₂. Loss of one mol of F₂ from KrF₄ results in a value of -26.8 kcal/mol, almost double the exothermicity for the loss of F₂ from KrF₂. Loss of one F₂ from KrF₆ 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 KrF₂, KrF₄, and KrF₆ are 11.0, 8.1, and 5.5 kcal/mol, respectively, at 0 K). In contrast, the losses of F₂ from XeF₂, XeF₄, and XeF₆ are endothermic processes. Similarly, but to a lesser degree, the average bond strengths in XeF₂, XeF₄, and XeF₆ 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 XeF₆) from XeF₂ to XeF₆. In comparison, the average bond energies decrease by 5.5 kcal/mol (100% of the average bond energy for KrF₆) from KrF₂ to KrF₆. This shows that the steric crowding in the krypton fluorides is much greater than that in the xenon fluorides.

Although KrF₄ and KrF₆ are thermodynamically unstable with respect to the loss of F₂, significant barriers toward decomposition might impart sufficient kinetic stability to allow their synthesis and isolation. We first consider loss of a fluorine atom from KrF₄ and KrF₆ to form the KrF₃ and KrF₅ radicals, respectively. We can calculate the energy to break two Kr–F bonds at 0 K in KrF₆ from the reaction KrF₆ → KrF₄ + 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 KrF₅ show a highly dissociated complex with a fluorine atom barely interacting with closed-shell KrF₄, 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 KrF₆ and, at most finite temperatures, KrF₆ is likely to quickly decompose to form KrF₄ + 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 KrF₆ will be highly improbable and might be possible only at very low temperatures.

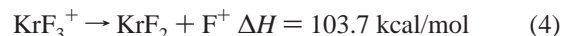
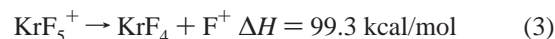
In a similar fashion, we can calculate the energy for the reaction KrF₄ → KrF₂ + 2F at 0 K and obtain a value of 10.1 kcal/mol. Again, we optimized KrF₃ at the CCSD(T)/aVDZ level and found a dissociated complex between KrF₂ and fluorine with essentially zero bond energy. This shows that the first Kr–F bond energy in KrF₄ is approximately 10 kcal/mol and that, in contrast to KrF₆, KrF₄ might be marginally kinetically stable at low temperatures with respect to loss of a fluorine atom.

As a further test for the stability of KrF₄, we calculated the transition state for the intramolecular loss of a F₂ 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 F₂ in the plane of KrF₄ to form linear KrF₂ is 60.2 kcal/mol with the aVDZ basis set and 64.3 kcal/mol with the aVTZ basis set. An intrinsic reaction coordinate³⁷ calculation showed that the transition state is connected to reactants and products. The barrier for the loss of F₂ 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 KrF₄ is unstable in a thermodynamic sense with respect to loss of F₂, it should be kinetically very stable with respect to the intramolecular elimination of an F₂ molecule. A similar situation is encountered for KrF₆. The barrier at 0 K for the elimination of F₂ from KrF₆ again is high, 53.8 kcal/mol at the B3LYP/aVDZ level and 57.8 kcal/mol at the B3LYP/aVTZ level, showing that KrF₆ is stable with respect to intramolecular F₂ elimination, but as discussed

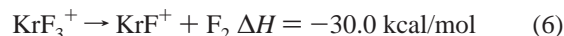
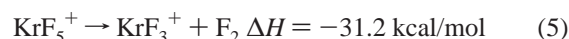
above, is barely stable with respect to loss of fluorine. The high barriers for the intramolecular F₂ elimination are above the F₂ bond dissociation energy of 36.9 kcal/mol at 0 K and are consistent with symmetry forbidden reactions. These considerations show that the loss of a fluorine atom from KrF₂, KrF₄, or KrF₆ have much lower activation energy barriers than the intramolecular F₂ eliminations and are the limiting factors determining their kinetic stabilities.

The predicted barrier of 10.1 kcal/mol for fluorine-atom elimination from KrF₄ and the exothermicity of the reaction of KrF₂ with two fluorine atoms suggest the simultaneous reaction of two fluorine atoms with KrF₂ as a possible synthetic pathway to KrF₄. However, a major issue with this approach is a competing attack of the fluorine ligands of KrF₂ by the fluorine atoms, leading to fluorine-atom abstraction and the formation of F₂ 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 KrF₂ + F → KrF + F₂ 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 KrF₂. The same dilemma, but even more so, applies to the hypothetical synthesis of KrF₆ from KrF₂ and four fluorine atoms.

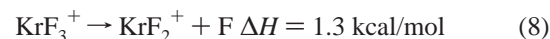
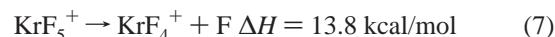
One can apply a similar type of analysis to the stability of KrF₅⁺ and KrF₃⁺. In this case, the ion can lose F⁺ to form KrF₄ and KrF₂ respectively, lose F₂ to form KrF₃⁺ and KrF⁺ respectively, and fluorine to form KrF₄⁺ and KrF₂⁺, respectively. The first channel is the F⁺ affinity given in reactions (3) and (4) at 0 K.



Thus, the ions are stable with respect to the loss of F⁺. The loss of F₂ channels are given in reactions (5) and (6) and both channels are exothermic by about 30 kcal/mol at 0 K.



Thus these ions are unstable thermodynamically with respect to loss of F₂. Loss of a fluorine atom is shown in reactions (7) and (8).



The product ions in reactions (7) and (8) are formed by ionizing KrF₄ and KrF₂, respectively. We calculated the ionization potential for KrF₄ and KrF₂ 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 KrF₄ is 13.68 eV at 0 K, and the heat of formation of KrF₄⁺ is 357.0 kcal/mol at 0 K. Reaction (7) is endothermic, so KrF₅⁺ is reasonably stable

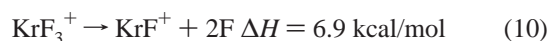
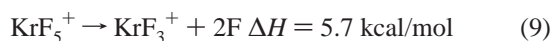
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thermodynamically with respect to loss of fluorine. Ionization of KrF_4 is from an a_1 orbital.

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 ≤ 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 ≤ 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^+



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.

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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>.

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