

# A Quantitative Scale for the Oxidizing Strength of Oxidative Fluorinators<sup>†,‡</sup>

Karl O. Christe\*<sup>§</sup> and David A. Dixon\*<sup>||</sup>

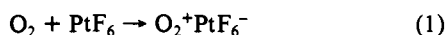
Contribution from Rocketdyne, A Division of Rockwell International Corporation, Canoga Park, California 91303, and The Central Research and Development Department, E. I. du Pont de Nemours and Company, Inc., Experimental Station, Wilmington, Delaware 19880.  
Received August 21, 1991

**Abstract:** A quantitative scale for the oxidizing strength of oxidative fluorinators has been developed for the first time. This scale is based on relative F<sup>+</sup> detachment energies, which were obtained by local density functional calculations, and is anchored to its F<sup>+</sup> zero point by an experimental value for KrF<sup>+</sup>. The oxidizing strength of 36 oxidizers was determined in this manner and shown to be consistent with all of the previously available qualitative experiments. An analysis of the trends in the calculated data reveals some expected but also some highly unexpected features. Thus, the oxidizer strength depends not only on the number of fluorine ligands and the oxidation state and electronegativity of the central atom but also on the presence of free valence electron pairs on the central atom and the geometry of the oxidizer. The heats of formation of these oxidizers were also determined from their F<sup>+</sup> detachment energy values.

## Introduction

The synthesis of fluorine-containing strong oxidizers generally requires powerful fluorinating agents. In this context, the question as to which agent is most powerful and which agent can oxidize a given substrate frequently arises. The ranking of these fluorinating agents according to their strength is very difficult. Direct electrochemical measurements of their oxidation potentials are not possible because the latter generally exceed the decomposition voltages of the available solvents. Therefore, no oxidizer strength scales exist at the present time, and the only data available are isolated observations<sup>1-4</sup> that some compounds can oxidize certain substrates while others cannot. Frequently, however, a lack of reaction is due to the choice of unfavorable reaction conditions or high activation energies and not necessarily to an insufficient oxidation potential, a thermodynamic measure.

Strong oxidizers can be separated into two main classes. The first one consists of one-electron oxidizers such as PtF<sub>6</sub> or UF<sub>6</sub>, and the second one of oxidative fluorinators such as KrF<sup>+</sup>, ClF<sub>6</sub><sup>+</sup>, or N<sub>2</sub>F<sup>+</sup>. The case of one-electron oxidizers has previously been analyzed by Bartlett and is best exemplified by his classic example of the reaction of PtF<sub>6</sub> with O<sub>2</sub> (eq 1).<sup>5</sup> The reaction enthalpy,



$\Delta H^\circ$ , of (1) can be derived from the Born-Haber cycle given in Figure 1, where IP, EA, and U<sub>L</sub> stand for the first ionization potential of O<sub>2</sub>, the electron affinity of PtF<sub>6</sub>, and the lattice energy of solid O<sub>2</sub><sup>+</sup>PtF<sub>6</sub><sup>-</sup>, respectively. Neglecting entropy changes,  $\Delta H^\circ$  must be negative for the reaction to occur spontaneously. Since the ionization potentials of the substrates are usually known and the lattice energies of the solid products can be estimated quite accurately, the occurrence or lack of spontaneous reaction with different substrates was used<sup>4</sup> to place upper and lower limits on the electron affinity of the oxidizing species. This method allows one to estimate rough electron affinity values which in turn can be taken as a measure for the oxidizing power of these one-electron oxidizers. Since these electron-transfer reactions do not involve significant activation energies, the "go-no go" reaction approach works rather well.

The case of oxidative fluorinators, such as KrF<sup>+</sup> or N<sub>2</sub>F<sup>+</sup>, is more complex and has not been analyzed previously. The oxidizer strengths of these species is not a simple function of the electron affinity or ionization potential of the atom or molecule to which the formal "F<sup>+</sup>" unit is attached. This was exemplified by a recent qualitative study<sup>1</sup> which showed that N<sub>2</sub>F<sup>+</sup> (IP<sub>N<sub>2</sub></sub> = 360.6 kcal

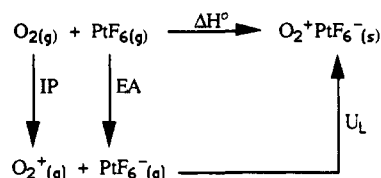


Figure 1. Born-Haber cycle for a typical one-electron oxidation reaction.

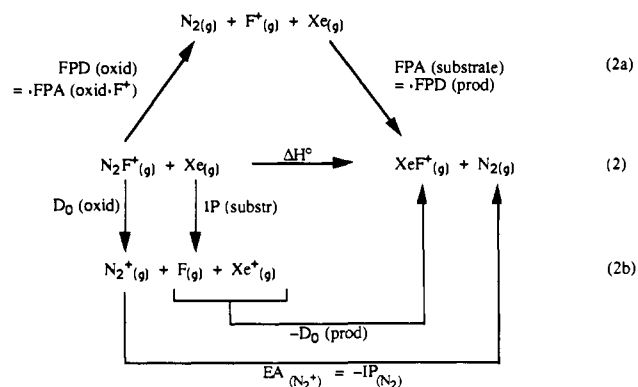


Figure 2. Two Born-Haber cycles which can be used for the description of a typical oxidative fluorination reaction, in this case the oxidative fluorination of Xe by N<sub>2</sub>F<sup>+</sup>.

mol<sup>-1</sup>)<sup>6</sup> is a weaker oxidative fluorinator than KrF<sup>+</sup> (IP<sub>Kr</sub> = 324.2 kcal mol<sup>-1</sup>).<sup>6</sup> Therefore, we have undertaken efforts to analyze this case and to define, if possible, a quantitative oxidizer strength scale.

## Results and Discussion

**Born-Haber Cycles for Oxidative Fluorination Reactions.** The case of oxidative fluorination reactions is more complex than that of one-electron oxidations. In addition to the transfer of a positive charge, an existing bond must be broken and a new one must be formed. Furthermore, the bond breaking can require a substantial

(1) Christe, K. O.; Wilson, R. D.; Wilson, W. W.; Bau, R.; Sukumar, S.; Dixon, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 3795.

(2) Christe, K. O.; Wilson, W. W.; Wilson, R. D. *Inorg. Chem.* **1984**, *23*, 2058.

(3) Sokolov, V. B.; Dobrychevskii, Yu. V.; Prusakov, V. N.; Ryzhkov, A. V.; Koroshev, S. S. *Dokl. Akad. Nauk SSSR* **1976**, *229*, 641.

(4) Bartlett, N. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 433.

(5) Bartlett, N.; Lohmann, D. H. *Proc. Chem. Soc.* **1962**, *277*; *J. Chem. Soc.* **1962**, 5253.

(6) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schuman, R. H.; Halow, I.; Bailey, S. M.; Churney, K. A.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, (Suppl. 2).

<sup>†</sup> Dedicated to Prof. Neil Bartlett on the occasion of his sixtieth birthday.

<sup>‡</sup> Du Pont Contribution No. 5889.

<sup>§</sup> Rocketdyne.

<sup>||</sup> Du Pont.

activation energy and, therefore, complicates experiments aimed at the determination of relative oxidizer strengths based on the observation or lack of observation of a reaction.

Consider the reaction between  $N_2F^+$  and Xe in HF solution<sup>1</sup> as a typical example of an oxidative fluorination reaction. Assuming that the solvation energies of  $N_2F^+$  and Xe are about the same as those of  $XeF^+$  and  $N_2$ , this reaction can be expressed by eq 2. Figure 2 shows two Born-Haber cycles, (2a) and (2b), which can be used to describe reaction 2.

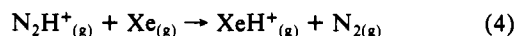
As in the case of the one-electron oxidations,  $\Delta H^\circ$  must be negative for a spontaneous reaction and, for the cycles 2a and 2b, is given by eq 3a and 3b, respectively, where FPA is the  $F^+$  affinity

$$\Delta H^\circ = \text{FPA}(\text{subst}) - \text{FPA}(\text{oxid} - F^+) \quad (3a)$$

$$\Delta H^\circ = \text{IP}(\text{substr}) - \text{IP}(\text{oxid} - F^+) + D_0(\text{oxid}) - D_0(\text{prod}) \quad (3b)$$

( $=\Delta H$  of the reaction  $A + F^+ \rightarrow AF^+$ ), FPD is the  $F^+$  detachment energy, IP is the first adiabatic ionization potential,  $D_0$  is the bond dissociation energy, and EA is the electron affinity. Until now, neither cycle 2a nor 2b had been used for the determination of  $\Delta H^\circ$  values since the  $F^+$  affinities and bond dissociation energies were generally unknown.

**Calculations.** If one considers reaction 2 as the transfer of  $F^+$  from one compound to another, it is very similar to the transfer of a proton from one base to another (reaction 4). Such pro-



ton-transfer reactions can be calculated quite accurately by molecular orbital methods for both relative values and absolute values.<sup>7</sup> The agreement with experiment for proton-transfer processes is usually excellent if one employs good geometries and if adequate basis sets with some consideration of the correlation energy are included in the calculations. Absolute values can be obtained with somewhat larger basis sets.

Such a theoretical model could also be employed for the calculation of relative FPAs. However, most of the compounds under consideration as strong oxidants contain atoms predominantly from the right-hand side of the periodic table, and contrary to  $H^+$ ,  $F^+$  has a significant number of electrons. Thus, some method is needed which, even for describing the geometries, includes correlation effects. Since there are a significant number of compounds, all of which need to have their geometries optimized, one also requires a computationally efficient method. Rather than using traditional Hartree-Fock methods (scaling as  $N^4$  with  $N$  as the number of basis functions) including correlation corrections (scaling as  $N^m$ ,  $m \geq 5$ ), we chose the local density functional (LDF) method (scaling as  $N^3$ ).<sup>8</sup>

The calculation of absolute proton affinities by theoretical methods is simplified because the dissociation of  $BH^+$  results in two closed-shell species, B and  $H^+$ , where B and  $BH^+$  have the same number of electron pairs. However, the calculation of absolute  $F^+$  affinities is complicated because (1) the generated  $F^+$  is not a closed-shell singlet but a ground-state triplet<sup>9</sup> and (2)

the number of electron pairs is different in B and  $BF^+$ . It is also well-established that the LDF method overestimates binding energies. Thus, instead of calculating absolute FPAs, we have calculated relative FPAs.

The LDF method is based on the Hohenberg-Kohn theorem,<sup>10</sup> which states that the total energy  $E_1$  is a functional of the charge density  $\rho$  as follows:

$$E_1[\rho] = T[\rho] + U[\rho] + E_{xc}[\rho] \quad (5)$$

where  $T$  is the kinetic energy of the noninteracting electrons of density  $\rho$ ,  $U$  is the classical Coulomb electrostatic energy, and  $E_{xc}$  includes all of the many-body contributions to the energy. The first two terms can be evaluated using straightforward techniques. The most important contributions to  $E_{xc}$  are the exchange energy and the correlation energy, and it is in the final term where the local density approximation is introduced. A good approximation for the final term is derived from the exchange-correlation energy of the uniform electron gas by following the assumption that the charge density varies slowly on the scale of exchange and correlation effects. The form of the exchange-correlation energy employed in our calculations is that of von Barth and Hedin.<sup>11</sup>

The calculations were done with the program DMol<sup>12</sup> on a CRAY-YMP computer system. DMol employs numerical functions for the atomic basis sets. These atomic basis sets are exact spherical solutions to the density functional equations. All of the calculations were done with a double numerical basis set augmented by  $d$  ( $l = 2$ ) polarization functions. Because exact numerical solutions are employed, the basis set is of higher quality than a normal molecular orbital basis set of the same size. Furthermore, basis set superposition errors should be minimized because of the quality of the basis set.

The various integrals required for the solution of eq 5 need to be evaluated on a grid due to our use of numerical basis functions.<sup>13</sup> The number of radial points is given by

$$N_R = (1.2)14(Z + 2)^{1/3} \quad (6)$$

where  $Z$  is the atomic number and the maximum distance for any function is 12 au. The angular integration points  $N_O$  are generated at the  $N_R$  radial points to form shells around each nucleus with  $N_O$  ranging from 14 to 302 depending on the density. Fitting functions for the spherical harmonics were all done with an angular momentum number  $\ell' = \ell + 1 = 3$ .

Geometries were optimized by using analytic gradient methods.<sup>14,15</sup> Because numerical methods are used, the error in atomic coordinates determined by the optimization is on the order of 0.001 Å, which gives bond lengths and angles with errors at least 1 order of magnitude smaller than the differences between calculated and experimental values. The spin state of each structure is a singlet except for those of  $O_2$  and  $F^+$ , which are triplets.

**Oxidizer Strength Scale.** Although a knowledge of the relative FPAs allows the prediction of whether a certain reaction is thermodynamically feasible and which oxidizer is stronger with respect to another one, it provides only a relative oxidizer strength scale. To obtain an absolute scale, one must identify the thermodynamic property governing the oxidizer strength, define a zero point for the scale, and then anchor the relative oxidizer strength values derived from the LDF calculations to the chosen zero point by an experimentally known number since LDF theory overes-

(7) Dixon, D. A.; Lias, S. G. In *Molecular Structures and Energies*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: Deerfield Beach, FL, 1987; Vol. 2, Chapter 7, p 269.

(8) (a) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989. (b) Salahub, D. R. In *Ab Initio Methods in Quantum Chemistry*; Lawley, K. P., Ed.; J. Wiley and Sons: New York, 1987; Vol. II. (c) Wimmer, E.; Freeman, A. J.; Fu, C. L.; Cao, P. L.; Chou, S. H.; Delley, B. In *Supercomputer Research in Chemistry and Chemical Engineering*; Jensen, K. F., Truhlar, D. G., Eds.; ACS Symposium Series 353; American Chemical Society: Washington, DC, 1987; p 49. (d) Jones, R. O.; Gunnarsson, O. *Rev. Mod. Phys.* **1989**, *61*, 689. (e) Dixon, D. A.; Andzelm, J.; Fitzgerald, G.; Wimmer, E.; Delley, B. *Science and Engineering on Supercomputers*; Pitcher, E. J., Ed.; Computational Mechanics Publications: Southampton, England, 1990; p 285. (f) Dixon, D. A.; Andzelm, J.; Fitzgerald, G.; Wimmer, E.; Jasien, P. In *Density Functional Methods in Chemistry*; Labanowski, J. K., Andzelm, J., Eds.; Springer-Verlag: New York, 1991; Chapter 3, p 33.

(9) Calculations of the  $F^+$  cation affinities of some simple organic bases have recently been reported. These ab initio molecular orbital calculations were done at the STO-3G(\*PS) level and the reported affinities are for an excited state of  $F^+(\text{S})$ : Alcamí, O.; Yáñez, M.; Abboud, J.-L. M. *J. Phys. Org. Chem.* **1991**, *4*, 177.

(10) Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 184.

(11) von Barth, U.; Hedin, L. *Physica C* **1972**, *5*, 1629.

(12) Delley, B. *J. Chem. Phys.* **1990**, *92*, 508. Dmol is available commercially from Biosym Technologies, San Diego, CA.

(13) This grid can be obtained by using the FINE parameter in DMol.

(14) For a discussion of Hartree-Fock methods, see: (a) Komornicki, A.; Ishida, K.; Morokuma, K.; Ditchfield, R.; Conrad, M. *Chem. Phys. Lett.* **1977**, *45*, 595. (b) Pulay, P. In *Applications of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; p 153. (c) Jorgensen, P.; Simons, J., Eds. *Geometrical Derivatives of Energy Surfaces and Molecular Properties*; NATO ASI Ser. C **1986**, *166*, 207.

(15) (a) Delley, B. In *Density Functional Methods in Chemistry*; Labanowski, J. K., Andzelm, J. W., Eds.; Springer-Verlag: New York, 1991; Chapter 11, p 101. (b) Fournier, R.; Andzelm, J.; Salahub, D. R. *J. Chem. Phys.* **1989**, *90*, 6371. (c) Versluis, I.; Ziegler, T. *J. Chem. Phys.* **1988**, *88*, 3322.

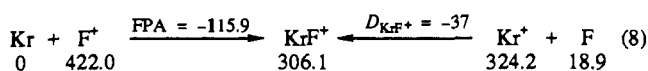
timates absolute binding energies.

According to the Born-Haber cycle 2a and eq 3a, the reaction enthalpy  $\Delta H^\circ$  equals the difference between the  $F^+$  affinities of the substrate and of the oxidizer minus  $F^+$ . Hence,  $F^+$  affinities are a useful criterion for an oxidizer strength scale. Since the  $F^+$  affinity (FPA) of a substrate equals the negative value of the  $F^+$  detachment energy (FPD) of the corresponding product, eq 3a can be rewritten as eq 7, and an oxidative fluorination reaction

$$\Delta H^\circ = \text{FPD}(\text{oxid}) - \text{FPD}(\text{prod}) \quad (7)$$

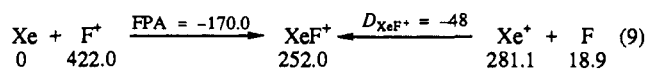
can be considered as the formal transfer of an  $F^+$  cation from an oxidizer to a substrate. Since the  $F^+$  detachment energy for  $F^+$  itself obviously is zero,  $F^+$  is the ideal zero point for an oxidizer strength scale based on  $F^+$  detachment energies. On this scale, then, increasing FPD values signify decreasing oxidizer strength.

The third objective, i.e., the anchoring of the relative FPD values to the  $F^+$  zero point, was accomplished by calculating the  $F^+$  affinity of Kr from experimental data. From the known heat of formation of  $KrF_2$ , the appearance potential of  $KrF^+$  from  $KrF_2$ , and the first adiabatic ionization potential of Kr, the bond energy and heat of formation of gaseous  $KrF^+$  have been estimated<sup>16</sup> to be 37 and 306.1 kcal mol<sup>-1</sup>, respectively, as shown by the right half of eq 8. [Numbers beneath the equations are  $\Delta H_f^\circ$  (kcal

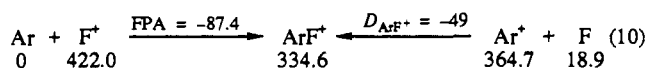


mol<sup>-1</sup>.) From the known heats of formation of gaseous  $KrF^+$  and  $F^+$ ,<sup>6</sup> the  $F^+$  affinity of Kr can then be estimated as -115.9 kcal mol<sup>-1</sup>, as shown by the left half of (8). The combination of this experimentally derived value with the  $F^+$  affinity differences obtained by our LDF calculations permits the construction of the absolute oxidizer strength scale given in Table I.

The quality of the values in Table I was cross-checked for  $XeF^+$ . Using the previously published experimental data,<sup>16</sup> the FPD of  $XeF^+$  was estimated (9) as 170.0 kcal mol<sup>-1</sup>, in fair agreement with our computed value of 164.8 kcal mol<sup>-1</sup> given in Table I.



An additional cross-check was made for the yet unknown  $ArF^+$  cation for which recent ab initio calculations<sup>17</sup> have yielded an Ar-F bond energy value of  $49 \pm 3$  kcal mol<sup>-1</sup>. Using this value, the  $F^+$  affinity of Ar can be estimated as -87.4 kcal mol<sup>-1</sup> (10) which is in good agreement with our FPD value of 84.3 kcal mol<sup>-1</sup> from Table I.



**Heats of Formation of the Oxidizers.** The knowledge of the  $F^+$  detachment energies of the oxidizers (see Table I) also provides a convenient source for their heats of formation  $\Delta H_f^\circ$ . The latter are given by eq 11, where  $\Delta H_f^\circ(\text{F}^+_{\text{g}})$  equals 422.0 kcal mol<sup>-1</sup>;

$$\Delta H_f^\circ(\text{XF}^+_{\text{g}}) = \Delta H_f^\circ(\text{X}_{\text{g}}) + \Delta H_f^\circ(\text{F}^+_{\text{g}}) - \text{FPD}(\text{XF}^+_{\text{g}}) \quad (11)$$

$\Delta H_f^\circ(\text{X}_{\text{g}})$ , the heat of formation of the parent molecule, is usually known, and the FPD values are taken from Table I. The resulting  $\Delta H_f^\circ(\text{XF}^+_{\text{g}})$  values have been included in Table I. Only few experimental estimates are available for these formation enthalpies. For example, the value of 204 kcal mol<sup>-1</sup> previously reported<sup>18</sup> for  $\Delta H_f^\circ(\text{NeF}^+_{\text{g}})$  is in fair agreement with our value of 210 kcal mol<sup>-1</sup> given in Table I.

**Characteristics of the Oxidizer Strength Scale.** The following comments can be made about the data given in Table I.

(16) Bartlett, N.; Sladky, F. In *Comprehensive Inorganic Chemistry*; Pergamon Press: Oxford, UK, 1973; Vol. 1, pp 213-330. The appearance potentials are from J. Berkowitz, unpublished work.

(17) Frenking, G.; Koch, W.; Deakne, C. A.; Liebman, J. F.; Bartlett, N. *J. Am. Chem. Soc.* **1989**, *111*, 31.

(18) Goetschel, C. J.; Campanile, V. A.; Curtis, R. M.; Loos, K. R.; Wagner, D. C.; Wilson, J. N. *Inorg. Chem.* **1972**, *11*, 1696.

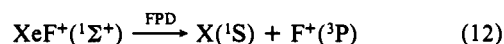
**Table I.** Absolute Oxidizer Strength Scale and Formation Enthalpies for Oxidative Fluorinators

oxidative fluorinator <sup>a</sup> XF <sup>+</sup>	F <sup>+</sup> detachment energy (kcal mol <sup>-1</sup> ) <sup>b</sup> FPD(XF <sub>g</sub> <sup>+</sup> )	formation enthalpy <sup>c</sup> (kcal mol <sup>-1</sup> )	
		$\Delta H_f^\circ(\text{XF}^+_{\text{g}})$	ref for $\Delta H_f^\circ(\text{X})$
(HeF <sup>+</sup> ) ( <sup>3</sup> π)	-1.6	423.6	6
(HeF <sup>+</sup> ) ( <sup>1</sup> Σ <sup>+</sup> )	(-16.2)	(438.2)	6
(F <sup>+</sup> )	0	422.0	6
(NeF <sup>+</sup> ) ( <sup>3</sup> π)	0.6	421.4	6
(NeF <sup>+</sup> ) ( <sup>1</sup> Σ <sup>+</sup> )	(-19.6)	(441.6)	6
(F <sub>3</sub> <sup>+</sup> )	60.0	362.0	6
(ArF <sup>+</sup> )	84.3	337.7	6
KrF <sup>+</sup>	115.9	306.1	6
(XeF <sub>7</sub> <sup>+</sup> )	116.7	222.2	15
(OF <sub>3</sub> <sup>+</sup> )	122.2	305.7	6
(BrF <sub>4</sub> O <sup>+</sup> )	131.1		
(O <sub>2</sub> F <sup>+</sup> ) <sup>f</sup>	133.8	288.2	6
(ClF <sub>3</sub> O <sup>+</sup> )	135.6	251.0	d
N <sub>2</sub> F <sup>+</sup>	139.3	282.7	6
(XeF <sub>5</sub> O <sup>+</sup> )	139.8	276.2	e
BrF <sub>6</sub> <sup>+</sup>	140.8	178.7	6
(XeF <sub>3</sub> O <sub>2</sub> <sup>+</sup> )	141.7	336.3	16
ClF <sub>6</sub> <sup>+</sup>	147.3	215.5	d
XeF <sub>3</sub> <sup>+</sup>	152.4	243.7	15
ClF <sub>4</sub> <sup>+</sup>	158.7	224.3	6
XeF <sub>5</sub> <sup>+</sup>	158.9	200.6	6
ClF <sub>2</sub> O <sub>2</sub> <sup>+</sup>	161.0	228.4	d
(IF <sub>4</sub> O <sup>+</sup> )	164.0		
XeF <sup>+</sup>	164.8	257.2	6
ClF <sub>2</sub> <sup>+</sup>	167.1	241.9	6
XeF <sub>3</sub> O <sup>+</sup>	173.1		
BrF <sub>4</sub> <sup>+</sup>	174.0	187.0	6
IF <sub>6</sub> <sup>+</sup>	175.0	40.4	6
NF <sub>2</sub> O <sup>+</sup>	175.3	230.8	6
Cl <sub>2</sub> F <sup>+</sup>	179.1	242.9	6
NF <sub>4</sub> <sup>+</sup>	180.1	210.5	6
(XeFO <sup>+</sup> )	182.4	290.1	16
BrF <sub>2</sub> <sup>+</sup>	182.4	217.2	6
ClF <sub>2</sub> O <sup>+</sup>	193.0		
XeFO <sub>2</sub> <sup>+</sup>	195.3		
BrF <sub>2</sub> O <sup>+</sup>	200.5		
IF <sub>4</sub> <sup>+</sup>	212.1	93.9	15
IF <sub>2</sub> <sup>+</sup>	213.5	185.7	6
(IF <sub>2</sub> O <sup>+</sup> )	230.0		

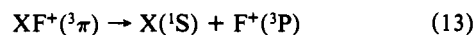
<sup>a</sup>The cations listed in parentheses have so far not been isolated in the form of stable salts. <sup>b</sup>All FPD values were computed for XF<sup>+</sup> and X being singlet ground states and F<sup>+</sup> being a triplet ground state, except for HeF<sup>+</sup> and NeF<sup>+</sup>, which have triplet ground states (see text) and O<sub>2</sub>F<sup>+</sup> (see footnote j). <sup>c</sup>Calculated by eq 7, using  $\Delta H_f^\circ(\text{X})$  values from refs 6 and 15c.d. <sup>d</sup>Barberi, P.; Carre, J.; Rigny, P. *J. Fluorine Chem.* **1976**, *7*, 511. <sup>e</sup>Gunn, S. R. *J. Am. Chem. Soc.* **1965**, *87*, 2290. <sup>f</sup>Calculated for the singlet state of O<sub>2</sub>F<sup>+</sup> going to the triplet state of O<sub>2</sub>.

(i)  $F^+$  detachment energies are a good measure for the oxidizing power of an oxidative fluorinator. The oxidizing power of a compound decreases with an increase in its  $F^+$  detachment energy.

(ii) A negative value for the  $F^+$  detachment energy of an XF<sup>+</sup> species signifies a species that is unstable with respect to decomposition to ground-state X(<sup>1</sup>S) and F(<sup>3</sup>P). The negative  $F^+$  detachment energy values for NeF<sup>+</sup> and HeF<sup>+</sup>, listed in parentheses in Table I, are due to the fact that for all of our calculations the following spin states were used (12).



Whereas for XeF<sup>+</sup>, KrF<sup>+</sup>, and ArF<sup>+</sup> a <sup>1</sup>Σ<sup>+</sup> state is the ground state; NeF<sup>+</sup> and HeF<sup>+</sup> have a <sup>3</sup>π ground state. Their <sup>1</sup>Σ<sup>+</sup> states are excited states which are calculated to lie 30.3 and 23.8 kcal mol<sup>-1</sup>, respectively, above their ground states.<sup>17</sup> If for NeF<sup>+</sup> and HeF<sup>+</sup> the FPDs are computed for their <sup>3</sup>π ground states (13)



slightly positive values of about 4.0 and 1.2 kcal mol<sup>-1</sup>, respectively, are obtained. This was shown by recent high-level ab initio

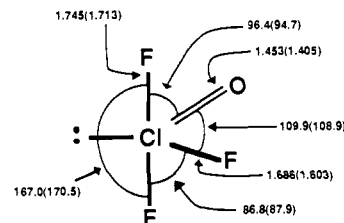
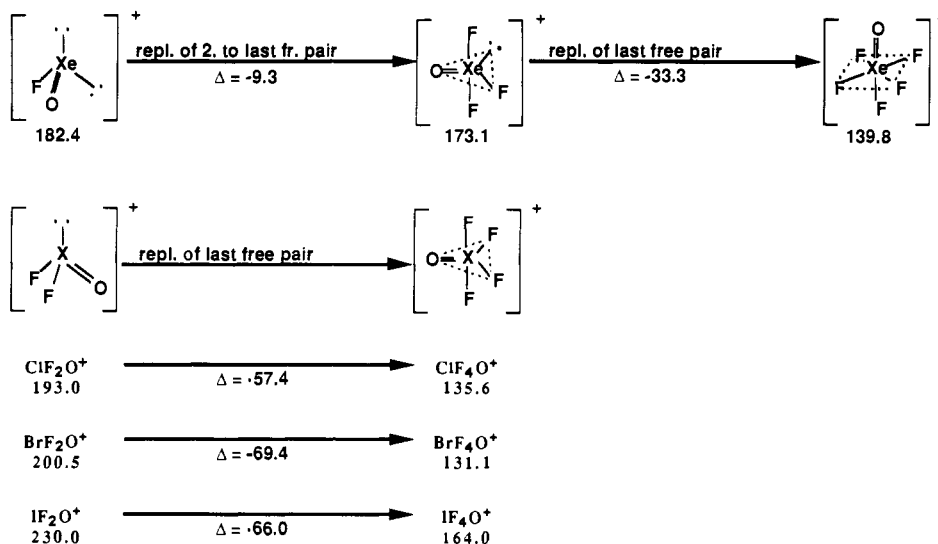


**Table III.** Relative Oxidizer Strengths (FPD Values) of the Binary Halogen Fluoride Cations as a Function of the Formal Oxidation State of the Central Atom

formal oxidn state of central atom	structure of cation	calcd FPD values (kcal/mol)		
+VII		ClF <sub>6</sub> <sup>+</sup> 147.3	BrF <sub>6</sub> <sup>+</sup> 141.7	IF <sub>6</sub> <sup>+</sup> 175.0
+V		ClF <sub>4</sub> <sup>+</sup> 158.7	BrF <sub>4</sub> <sup>+</sup> 174.0	IF <sub>4</sub> <sup>+</sup> 212.1
+III		ClF <sub>2</sub> <sup>+</sup> 167.1	BrF <sub>2</sub> <sup>+</sup> 182.4	IF <sub>2</sub> <sup>+</sup> 213.5

**Table IV.** Relative Oxidizer Strengths (FPD Values) of the Binary Xenon Fluoride Cations as a Function of the Formal Oxidation State of the Xenon Central Atom

formal oxidn state of Xe	structure of the cation	calcd FPD value (kcal/mol)
+VIII		116.7
+VI		158.9
+IV		152.4
+II		164.8

**Table V.** Relative Oxidizer Strengths (FPD Values) of Oxyfluorides Resulting from the Stepwise Replacement of Free Valence Electron Pairs by Two Fluorine Atoms (i.e., Oxidative Fluorination Reactions)**Figure 3.** Geometry of ClF<sub>3</sub>O (bond lengths in angstroms, angles in degrees) as calculated by the LDF method. The experimentally observed<sup>32</sup> values are given in parentheses.

larger (see Table III). For the xenon fluorides (see Table IV), a similar trend is observed. The FPD gap between XeF<sup>+</sup> and XeF<sub>5</sub><sup>+</sup> is only 5.9 kcal mol<sup>-1</sup> whereas that between XeF<sub>5</sub><sup>+</sup> and XeF<sub>7</sub><sup>+</sup> is 42.3 kcal mol<sup>-1</sup>.

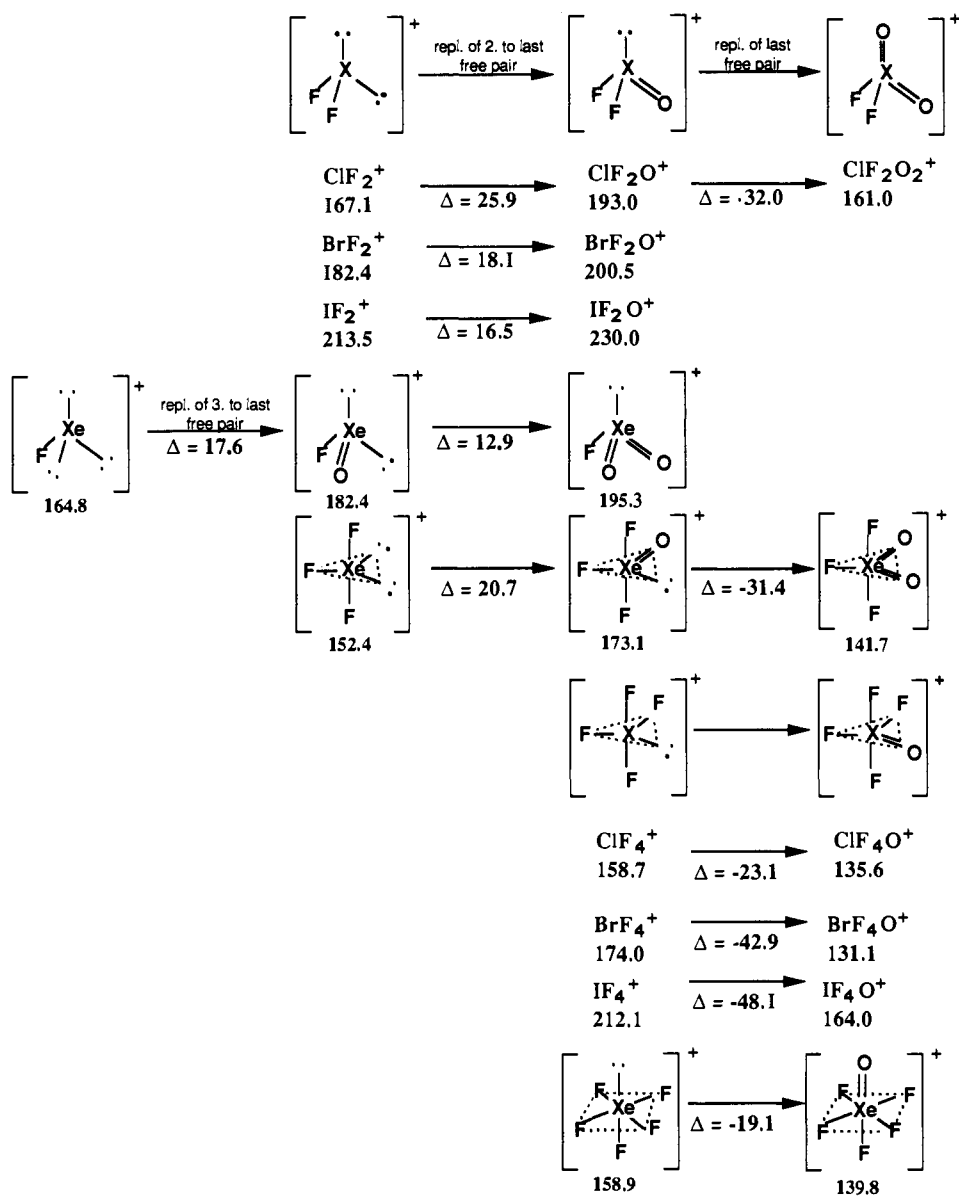
These features are best explained by the increased mobility of the free valence electron pair on the central atom with increasing atomic weight and by the replacement of the last free valence electron pair by two fluorine ligands, which causes a large decrease in the fluorine plus detachment (FPD) energy values. It is very plausible that the availability of a highly mobile free valence electron pair should counteract the removal of an electron-deficient F<sup>+</sup> cation from these species, thereby increasing the FPD values.

There appears to be a considerably weaker secondary effect, which is also apparent from the oxyfluoride cations (see below). Trigonal-bipyramidal species seem to exhibit slightly lower FPD values than the energetically more favored pseudotetrahedral or pseudooctahedral species. This causes the FPD value of XeF<sub>3</sub><sup>+</sup> to be slightly lower than those of XeF<sup>+</sup> and XeF<sub>5</sub><sup>+</sup> (see Table IV) and also accounts for the very small difference of 1.4 kcal mol<sup>-1</sup> between IF<sub>2</sub><sup>+</sup> and IF<sub>4</sub><sup>+</sup>.

The low FPD value of XeF<sub>7</sub><sup>+</sup>, which is almost identical to that of KrF<sup>+</sup> (see Table I), also explains the failure of our previous attempts<sup>29</sup> to prepare the yet unknown XeF<sub>7</sub><sup>+</sup> cation from XeF<sub>6</sub> and KrF<sup>+</sup>.

**II. Oxyfluorides.** The case of oxyfluorides is not quite as transparent as that of the binary fluorides. A priori, one might have predicted that the replacement of one free valence electron pair on a central atom by one doubly bonded oxygen ligand should increase the oxidizing power and decrease the FPD value of an oxidizer, albeit not by as much as that observed for the replacement of one free pair by two fluorine ligands. Inspection of Table I clearly shows that this is not the case. For example, the oxidizing strength of ClF<sub>2</sub>O<sup>+</sup> is 25.9 kcal mol<sup>-1</sup> lower than that of ClF<sub>2</sub><sup>+</sup> while that of ClF<sub>4</sub>O<sup>+</sup> is 23.1 kcal mol<sup>-1</sup> higher than that of ClF<sub>4</sub><sup>+</sup>.

Table VI. Relative Oxidizer Strengths (FPD Values) of Oxyfluorides Resulting from the Stepwise Replacement of Free Valence Electron Pairs by One Doubly Bonded Oxygen Atom (i.e., Oxidative Oxygenation Reactions)



To verify that these results were not caused by computational problems, the geometry of the  $\text{ClF}_3\text{O}$  molecule was computed and compared to that experimentally determined.<sup>32</sup> As can be seen from Figure 3, the agreement between the calculated and experimental geometry was good, particularly when one remembers that the bond lengths calculated by the LDF method are generally about 0.05 Å longer than the observed value for these types of compounds.<sup>33</sup> Similarly, the geometry calculated for  $\text{ClF}_4\text{O}^+$  is very similar to that previously determined<sup>34</sup> for isoelectronic  $\text{SF}_4\text{O}$  (see Figure 4). Therefore, the LDF method results are deemed reliable for this type of compounds.

In spite of the seeming lack of an obvious general trend to the FPD values of the oxyfluorides of Table I, a closer inspection reveals that the data are indeed self-consistent and exhibit systematic trends. These become obvious from an analysis of how the FPD values vary with the following three processes.

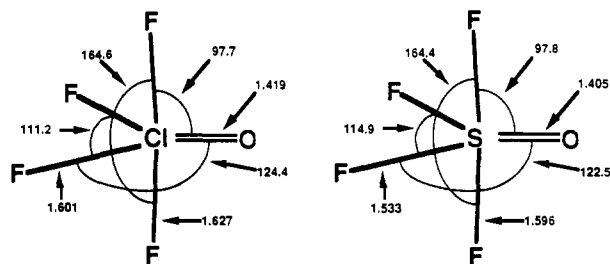


Figure 4. Calculated geometry of  $\text{ClF}_4\text{O}^+$  compared to that experimentally determined<sup>34</sup> for isoelectronic  $\text{SF}_4\text{O}$ .

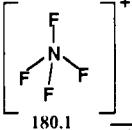
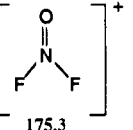
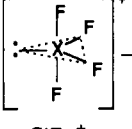
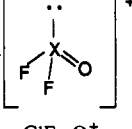
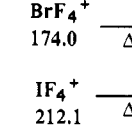
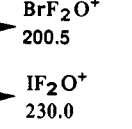
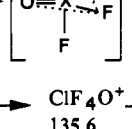
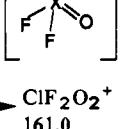
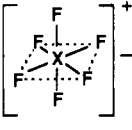
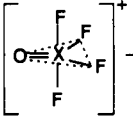
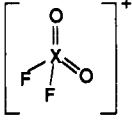
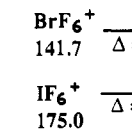
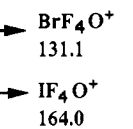
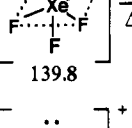
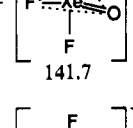
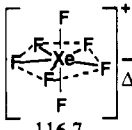
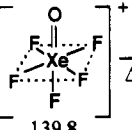
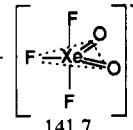
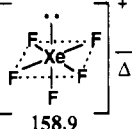
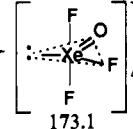
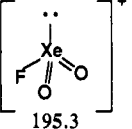
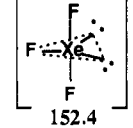
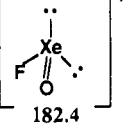
(i) **Stepwise Replacement of Free Valence Electron Pairs on the Central Atom by Fluorine Ligands (i.e., Oxidative Fluorination Reactions).** When a sterically active free valence electron pair is replaced by two fluorine ligands, the coordination number and the formal oxidation state of the central atom are increased by one and two units, respectively; i.e., we are dealing with an oxidative fluorination reaction. As can be seen from the examples given in Table V, and also from those given for oxidative oxygenation reactions (Table VI), the replacement of the last free valence electron pair results in a much larger increase in the

(32) Oberhammer, H.; Christe, K. O. *Inorg. Chem.* **1982**, *21*, 273.

(33) Christe, K. O.; Curtis, E. C.; Dixon, D. A.; Mercier, H. P.; Sanders, J. C. P.; Schrobilgen, G. J. *J. Am. Chem. Soc.* **1991**, *113*, 3351.

(34) (a) Gunderson, G.; Hedberg, K. J. *Chem. Phys.* **1969**, *51*, 2500. (b) Hargittai, I. *J. Mol. Struct.* **1979**, *56*, 301. (c) Oberhammer, H.; Boggs, J. E. *J. Mol. Struct.* **1979**, *56*, 107.

**Table VII.** Relative Oxidizer Strengths (FPD Values) of Oxyfluorides Resulting from the Stepwise Replacement of Two Fluorine Ligands by a Doubly Bonded Oxygen Ligand (i.e., Fluorine–Oxygen Exchange Reactions)

pentagonal bipyramid	octahedron	trigonal bipyramid	tetrahedron	trigonal plane
			 180.1	 175.3
			$\Delta = -4.8$	
		 158.7	 193.0	
		$\Delta = 34.3$		
		 174.0	 200.5	
		$\Delta = 26.5$		
		 212.1	 230.0	
		$\Delta = 17.9$		
		 147.3	 135.6	 161.0
		$\Delta = -11.7$		$\Delta = 25.4$
		 141.7	 131.1	
		$\Delta = -10.6$		
		 175.0	 164.0	
		$\Delta = -11.0$		
		 116.7	 139.8	 141.7
		$\Delta = 23.1$		$\Delta = 1.9$
		 158.9	 173.1	 195.3
		$\Delta = 14.2$		$\Delta = 22.2$
		 152.4	 182.4	
		$\Delta = 30.0$		

oxidizer strength of the product than the replacement of any of the other free pairs. As for the binary fluoride cations (see above), the FPD values increase for isotopic cations with increasing atomic weight of the central atom. Again, the only exception is Br(+VII), which is a slightly stronger oxidizer than Cl(+VII).<sup>31</sup>

(ii) **Stepwise Replacement of Free Valence Electron Pairs on the Central Atom by Oxygen Ligands (i.e., Oxidative Oxygenation Reactions).** Although, in oxidative oxygenation reactions, the replacement of a free valence electron pair by a doubly bonded oxygen ligand increases again the formal oxidation state of the central atom by two, its coordination number remains unchanged. As observed above for the oxidative fluorination reactions, the most salient feature is again the large decrease in the FPD value on replacement of the last free valence electron pair. For the replacement of any of the other pairs, the FPD values of all our examples actually increase; i.e., in these cases oxidative oxygen-

ation results in a weaker oxidizer. This is a highly remarkable and unexpected result. The only previous indication for the existence of such an effect was based on normal coordinate analyses for some of these ions, which showed that, for  $\text{XF}_n\text{O}_m^+$ -type compounds, frequently the X–F force constants decreased with oxidative oxygenation.<sup>35</sup> In these compounds, a weakening of the force constant implies an increase of the  $\text{X}^{(\delta+)} - \text{F}^{(\delta-)}$  polarity of the X–F bond which counteracts the F-plus dissociation (FPD), thereby increasing the FPD value and decreasing the oxidizer strength of the species.

(iii) **Stepwise Replacement of Two Fluorine Ligands by a Doubly Bonded Oxygen Ligand (i.e., Fluorine–Oxygen Exchange Reactions).** In fluorine–oxygen exchange reactions, two singly bonded

(35) Christe, K. O.; Schack, C. J. *Adv. Inorg. Chem. Radiochem.* 1976, 18, 331.

**Table VIII.** Comparison between Intuitively Predicted Qualitative and Calculated Oxidizer Strengths for Fluorides and Oxyfluorides of Chlorine and Xenon

predicted order		calculated order		
oxidation state	species	oxidation state	species	FPD value (kcal/mol)
+VII	ClF <sub>6</sub> <sup>+</sup>	+VII	ClF <sub>4</sub> O <sup>+</sup>	135.6
+VII	ClF <sub>4</sub> O <sup>+</sup>	+VII	ClF <sub>6</sub> <sup>+</sup>	147.3
+VII, +V	ClF <sub>2</sub> O <sub>2</sub> <sup>+</sup> , ClF <sub>4</sub> <sup>+</sup>	+V	ClF <sub>4</sub> <sup>+</sup>	158.7
+V	ClF <sub>2</sub> O <sub>2</sub> <sup>+</sup>	+VII	ClF <sub>2</sub> O <sub>2</sub> <sup>+</sup>	161.0
+III	ClF <sub>2</sub> <sup>+</sup>	+III	ClF <sub>2</sub> <sup>+</sup>	167.1
+I	Cl <sub>2</sub> F <sup>+</sup>	+I	Cl <sub>2</sub> F <sup>+</sup>	179.1
		+V	ClF <sub>2</sub> O <sup>+</sup>	193.0
+VIII	XeF <sub>7</sub> <sup>+</sup>	+VIII	XeF <sub>7</sub> <sup>+</sup>	116.7
+VIII	XeF <sub>3</sub> O <sup>+</sup>	+VIII	XeF <sub>3</sub> O <sup>+</sup>	139.8
+VIII, +VI	XeF <sub>3</sub> O <sub>2</sub> <sup>+</sup> , XeF <sub>5</sub> <sup>+</sup>	+VIII	XeF <sub>3</sub> O <sub>2</sub> <sup>+</sup>	141.7
+VI	XeF <sub>3</sub> O <sup>+</sup>	+IV	XeF <sub>5</sub> <sup>+</sup>	152.4
+VI, +IV	XeFO <sub>2</sub> <sup>+</sup> , XeF <sub>3</sub> <sup>+</sup>	+VI	XeF <sub>5</sub> <sup>+</sup>	158.9
+IV	XeFO <sup>+</sup>	+II	XeF <sup>+</sup>	164.8
+II	XeF <sup>+</sup>	+VI	XeF <sub>3</sub> O <sup>+</sup>	173.1
		+IV	XeFO <sup>+</sup>	182.4
		+VI	XeFO <sub>2</sub> <sup>+</sup>	195.3

fluorine ligands are replaced by one doubly bonded oxygen ligand. Therefore, the formal oxidation state of the central atom remains the same but its coordination number is decreased by one. Since the formal oxidation state does not change, the number of free valence electron pairs on the central atom also remains constant. Hence, a study of the trends of the FPD values in fluorine–oxygen exchange reactions is ideally suited for the elimination of the strong effect exercised by a change in the number of free valence electron pairs (see above) and for an analysis of the influence caused by a change in the coordination numbers, i.e., of steric effects. In the absence of any steric effects, the oxidizing strength should monotonically decrease (i.e., the FPD values increase) with the stepwise replacement of two fluorines by one oxygen. Inspection of Table VII, however, clearly shows that the FPD values do not change monotonically, and that pseudooctahedral and pseudotetrahedral species are considerably weaker oxidizers than pseudo-pentagonal-bipyramidal, pseudo-trigonal-bipyramidal, and pseudo-trigonal-planar species. This effect is most pronounced for the transitions from the HalF<sub>6</sub><sup>+</sup> to the HalF<sub>4</sub>O<sup>+</sup> cations. Instead of increasing FPD values, they exhibit a systematic decrease by about 11 kcal mol<sup>-1</sup>. The surprising implication that HalF<sub>4</sub>O<sup>+</sup> cations are significantly stronger oxidizers than the corresponding HalF<sub>6</sub><sup>+</sup> cations is in accord with our past experimental failures to synthesize these HalF<sub>4</sub>O<sup>+</sup> cations.

## Conclusions

Local density functional calculations are well-suited for the calculation of the geometries and relative energies of oxidative fluorinators. The oxidizing strength of oxidative fluorinators is determined by their F<sup>+</sup> detachment energies. A relative scale of FPD values can be obtained from the LDF calculations and can be converted to an absolute scale by the choice of a suitable zero point (FPD of F<sup>+</sup> ≡ 0) and an experimentally known FPD value (KrF<sup>+</sup> in this study).

An analysis of the oxidizer strengths, calculated in the above manner for 36 oxidative fluorinators, shows that the results are self-consistent and exhibit some expected, but also some highly unexpected features. Obviously, the oxidizing strength is governed to a large extent by the oxidation state and electronegativity of the central atom and the fact that the contribution of one doubly bonded oxygen is less than that of two singly bonded fluorine ligands. Among the less expected features are the following: (i) the presence of one or more free valence electron pairs on the central atom strongly decreases the oxidizing strength of a species, and (ii) the oxidizer strengths of pseudooctahedral and -tetrahedral species are depressed relative to those of pseudopentagonal or -trigonal-bipyramidal and -trigonal-planar ions. Thus, a simplistic picture is inadequate, that is, that the oxidizer strength should be governed exclusively by the oxidation state of the central atom and that, in case of similar values between a binary fluorine and oxyfluorides, the species with the larger number of fluorine ligands will be the stronger oxidizer. This is demonstrated by Table VIII, which shows a comparison between intuitive qualitative predictions and the quantitative results from our calculations for the fluorides and oxyfluorides of chlorine and xenon. For the chlorine compounds, the top placement of ClF<sub>4</sub>O<sup>+</sup> and last placement of ClF<sub>2</sub>O<sup>+</sup> are highly unexpected. Similarly, the last rank of XeFO<sub>2</sub><sup>+</sup> and the position of XeF<sub>5</sub><sup>+</sup> below XeF<sub>3</sub><sup>+</sup> and the high ranking of XeF<sup>+</sup> are a total surprise, but can be understood on the basis of the above analysis.

The availability of a quantitative oxidizer strength scale is expected to significantly contribute to our understanding of oxidizer chemistry and to the future syntheses of novel and known oxidative fluorinators. It also stresses the importance of employing high activation energy sources such as discharges or plasmas to generate intermediate F<sup>+</sup> cations, if novel oxidizers are desired which are more powerful than KrF<sup>+</sup>.

**Acknowledgment.** The work at Rocketdyne was financially supported by both the U.S. Army Research Office and the Air Force Phillips Laboratories. K. Dobbs (du Pont) is thanked for help in performing some of the calculations.

## A Protective Strategy in Carbene Complex Chemistry. Synthesis of Functionalized Fischer Carbene Complexes via Dianion Formation

Satoshi Aoki, Tsutomu Fujimura, and Eiichi Nakamura\*

*Contribution from the Department of Chemistry, Tokyo Institute of Technology, Meguro, Tokyo 152, Japan. Received September 12, 1991*

**Abstract:** Anionic derivatives of Fischer-type carbene complexes (A and B) are stable toward strong bases and nucleophiles, and their organic moieties R and R<sup>2</sup> can be elaborated under strongly basic conditions to provide access to heteroaromatic and aliphatic carbene complexes bearing organic functional groups. The concept of anionic protection has been illustrated by the reactions of dianions **9** and **14** and the preparation of carbene complexes possessing up to four chiral centers. Some attempts to effect ortho lithiation of aromatic carbene complexes are also described.

Despite the importance of Fischer carbene complexes for the development of novel organic transformations,<sup>1</sup> there are still a

very limited number of basic repertoires for the synthesis of complexes possessing elaborate organic functional groups.<sup>2</sup> This