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Density Functional Investigation of the Structure and Stability of SF_nCl, $n = 1-5$, and Their Anions SF_nCl^-

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The electronic and geometrical structures of chlorine-substituted sulfur fluorides SF_nCl ($n = 1-5$) as well as their singly charged negative anions have been studied by a computational method based on density functional theory. It was found that the stability of neutral chlorine-substituted sulfur fluorides is less than unsubstituted sulfur fluorides, SF_n, with respect to dissociation, and the adiabatic electron affinities (EA_{ad}) are on the average higher by ~0.5 eV. All the negative ions, SF_nCl^-, are stable with respect to dissociation and electron detachment, and anions with $n = 4$ and 5 are more stable than their neutral parents. The EA_{ad} values of SF_4Cl (4.8 eV) and SF_5Cl (4.1 eV) are high enough to classify the two species as superhalogens.

Introduction

Sulfur hexafluoride is the classical example of a hypervalent main group compound, and its interesting electronic structure has been studied extensively. The hexafluoride possesses in addition one of the largest cross sections for electron attachment. It has as a consequence found extensive use as an electron scavenger.[1d] Much attention has also been given to the sulfur fluorides of lower coordination number, SF_n ($n = 1-5$).

The only other well-characterized sulfur hexahalide is SF_5Cl. However, this chloro-substituted species has been studied to a much lesser degree than its parent SF_6 molecule. Virtually nothing is known about the series SF_nCl ($n = 1-4$) of mixed sulfur halides with a lower coordination number. We shall here present a systematic theoretical study on the entire series SF_nCl ($n = 1-5$). The emphasis will be on the structures of its members as well as their thermal stability toward dissociation of a single halogen atom. Attention will also be given to the vertical and adiabatic electron affinities of SF_nCl ($n = 1-5$) as well as the structures and thermal stabilities of the anionic species, SF_nCl^- ($n = 1-5$). We shall finally discuss how the replacement of a single fluorine atom by the less electronegative chlorine will influence the properties mentioned above.

The SF_5Cl molecule has been investigated by infrared and Raman spectroscopy.[1] The S–Cl bond length was determined from the rotational fine structure to be 2.0301 ± 0.0019[1a] and 2.0392 ± 0.0002 Å,[1c] respectively, in two independent studies. Investigations[2] based on electron diffraction techniques revealed that the ground state of SF_5Cl possesses C_{4v} symmetry with $R(S-Cl) = 2.047 \pm 0.003$ Å and an $\angle ClSF_{eq}$ valence angle of $90.7° \pm 0.2°$. The S–F bond lengths ($R(S-F_{eq}) = 1.566 \pm 0.003$ Å, $R(S-F_{ax}) = 1.588 \pm 0.009$ Å) are almost the same as in the neutral SF_6 molecule,[3] where $R(S-F) = 1.5622 \pm 0.0007$ Å. The photoelectron spectra for the SF_5Cl valence band[4] has been investigated theoretically[5] in an attempt to elucidate the d-orbital contribution to the hypervalent S–F bonds.

An early investigation[6] on bombardment of SF_5Cl with an electron beam did not detect any ions of the type SF_nCl^- ($n = 1-5$). A more recent work[7] succeeded in detecting a weak signal from SF_5Cl^-, but neither of the ions SF_nCl^- ($n = 1-4$) were observed. If was found[7] that the bombardment of SF_5Cl by electrons is dominated by dissociative attachment in which negative ions such as F^-, Cl^-, FCl^-, and SF_5^- are produced.

The present study is based on approximate density functional theory[8] (DFT). This approach has over the past decade emerged as a tangible and versatile computational method with applications in many subfields of chemistry.[9] It has recently been demonstrated[9] that DFT-based methods can provide bond energies, structures, and electron affinities of high accuracy. The method has previously been applied to similar studies on carbon halogenides[10] and their anions.

Computational Details

The calculations presented here were carried out with the LCAO-HFS program system developed by Baerends et al.[11] and vectorized by Ravenek.[12] Extensive use has been made of the numerical integration scheme developed by Becke.[13] Geometry optimizations were carried out according to the algorithm developed by Versluis and Ziegler[14] within the local density approximation (LDA)[15b] in Vosko's parametrization[16] from electron gas data and with modifications proposed by Stoll et al.[17] The molecular orbitals were expanded as a linear combination of Slater-type orbitals (STO). An uncontracted triple-ζ STO basis set[18] was augmented with two 3d polarization STOs of exponents 2.5 and 1.0 for C, F, and Cl. The same basis was employed for the neutral SF_nCl species and the anions SF_nCl^-.

The LDA energy expression was augmented by a gradient correction to the local LDA exchange. The correction is due to Becke[19] and given as

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$$E_X^{NL} = \sum_{\gamma}^{\alpha;\beta} -b \int \frac{[\rho_1^{\gamma}(\vec{r}_1)]^{4/3} X_\gamma^2}{1 + 6bX_\gamma \sinh^{-1} X_\gamma}\, d\vec{r}_1 \qquad (1)$$

where $b = 0.0042$ and X_γ is a dimensionless parameter defined as

$$X_\gamma = \frac{|\nabla \rho_1^{\gamma}(\vec{r}_1)|}{[\rho_1^{\gamma}(\vec{r}_1)]^{4/3}} \qquad (2)$$

Further, $\rho_1^{\gamma}(\vec{r}_1)$ is the density of electrons with spin up ($\gamma = \alpha$) or spin down ($\gamma = \beta$). The correction E_X^{NL} is introduced as a perturbation based on the LDA densities $\rho_1^{\gamma}(\vec{r}_1)$. We shall refer to the method in which E_X^{NL} is included as LDA/NL.

The adiabatic electron affinity (EA_{ad}) is defined as the difference in energy between the neutral molecule and its anion, where the energies are evaluated for the two species at the respective equilibrium geometries, i.e.

$$EA_{ad} = E_{tot}(M,R_e) - E_{tot}(M^-,R_e^-) \qquad (3)$$

The vertical electron affinity of the neutral molecule

$$EA_{vert} = E_{tot}(M,R_e) - E_{tot}(M^-,R_e) \qquad (4)$$

and the first ionization potential (FIP) of the anion

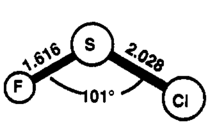
$$FIP = E_{tot}(M,R_e^-) - E_{tot}(M^-,R_e^-) \qquad (5)$$

are the total energy difference between M and M^- evaluated at, respectively, the neutral equilibrium geometry R_e and the equilibrium structure of the anion R_e^-. EA_{vert} and FIP were calculated within the LDA approximation using Slater's transition-state concept.[15a,20] Previous experience[10] has shown that nonlocal corrections are minor (~0.2 eV) for energy differences between species of identical geometries such as EA_{vert} and FIP. Nonlocal corrections are on the other hand crucial for the evaluation of EA_{ad} where changes in geometry must be taken into account, eq 3. This has been demonstrated in a previous study,[21] where EA_{ad} values were calculated by LDA and LDA/NL for a number of test molecules. This series of test calculations[21] revealed that LDA/NL affords estimates of EA_{ad} of the same accuracy as highly correlated ab initio methods.

The reliability of our approach may be assessed by comparing calculated EA values for S, F, and Cl with experimental data. On the LDA (LDA/NL) level of approximation the computed values are S 1.89 (2.01) eV, F 3.16 (3.44) eV, and Cl 3.17 (3.24) eV, whereas the corresponding experimental values[22] are given by 2.077 102 (1), 3.399 (9), and 3.617 (3) eV, respectively. Thus, both approaches are seen to reproduce the experimental data quite well, with LDA/NL representing the best fit. Atomic electron affinities are difficult to calculate by traditional ab initio methods where an elaborate treatment based on (extensive) configuration interaction is required in order to reproduce experimental values with the same accuracy as LDA/NL.

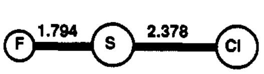
Results and Discussion

A full geometry optimization has been carried out on each of the species SFCl (**1a**), SF_2Cl (**1d**), and SF_3Cl (**1f**) as well as the anions $SFCl^-$ (**1b,c**), SF_2Cl^- (**1e**), and SF_3Cl^- (**1g**) within C_s symmetry constraints. The SFCl molecule has as expected an angular structure, **1a**, with ∠FSCl = 101°. The additional electron in $SFCl^-$ enters into an antibonding orbital primarily concentrated between chlorine and sulfur. The antibonding interaction is relieved by opening up the FSCl angle to nearly 172°, **1c**, whereby the orbital holding the additional electron becomes a π-type out-of-phase combination between p-components on chlorine and sulfur. The slightly bent structure, **1c**, represents the ground-state conformation for $SFCl^-$. However, the linear configuration, **1b**, is higher in energy by only 3 kJ mol^{-1}. The S–Cl bond is seen to be stretched (0.35 Å) more than the S–F bond (0.18 Å) in going from SFCl to $SFCl^-$. This is in line with the fact that the additional electron enters an antibonding orbital with the principal contributions from sulfur and chlorine.



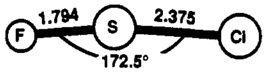
SFCl : $^1A'$

1a



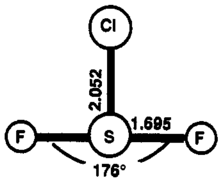
$SFCl^-$: $^2\Pi$

1b



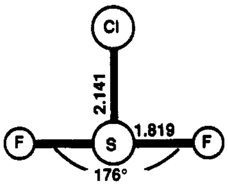
$SFCl^-$: $^2A'$

1c



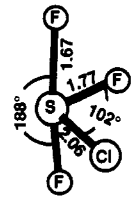
SF_2Cl : $^2A_1$

1d



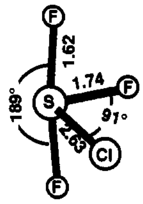
SF_2Cl^- : $^1A_1$

1e



SF_3Cl : $^1A'$

1f



SF_3Cl^- : $^2A'$

1g

The anion SF_2Cl^- is isoelectronic with IF_3 and has the same T-shaped structure, **1e**. The less electronegative halide is further seen to occupy the unique apical position in accordance with qualitative molecular orbital theory.[23a] The radical SF_2Cl has an electron count between the T-shaped IF_3 species and the trigonal NF_3 molecule. However, its optimized structure, **1d**, resembles closely that of the T-shaped anion SF_2Cl^-. The S–Cl and S–F bonds are elongated almost evenly as SF_2Cl is reduced to the anion SF_2Cl^-. This is so since the additional electron goes into a weakly antibonding π^*-type orbital with contributions from both S–F and S–Cl linkages.

The SF_3Cl molecule has according to the VSEPR theory of Gillespie[23b] five electron pairs around sulfur. Four of these are involved in the S–X bonds and one is nonbonding. The structure of SF_3Cl should as a consequence be that of a sawhorse with the nonbonding lone pair situated in the equatorial plane. The VSEPR theory would further predict that the S–Cl linkage should take up one of the equatorial sites since the electron density of the S–Cl bond pair is more diffuse than that of the S–F linkage. The optimized structure of SF_3Cl, **1f**, is seen to conform nicely to the prediction of the VSEPR theory. The additional electron in SF_3Cl^-, **1g**, enters into an antibonding orbital concentrated primarily on sulfur and chlorine. It is thus not surprising that the S–Cl bond of the anion, **1g**, is elongated substantially (by 0.6 Å!) compared to the same bond in the neutral molecule. One might consider the anion as an adduct $(SF_3\cdots Cl)^-$ in which the extra electron is shared by two units with nearly the same EAs, namely, 3.6 eV for Cl and ~3.0 eV[24] for SF_3.

We have studied three different conformations of the SF_4Cl^- anion. The first, **2d**, corresponds to a trigonal bipyramid of C_{3v} symmetry with the chlorine atom in an axial position. The second,

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Table I. Relative Energies for the Three Conformations of SF_4Cl and SF_4Cl^-, EA_{vert} of SF_4Cl, and FIP of SF_4Cl^- [a]

	SF_4Cl			SF_4Cl^-		
	C_s, $^2A'$	C_{4v}, $^2A_1$	C_{3v}, $^2A_1$	C_s, $^1A'$	C_{4v}, $^1A_1$	C_{3v}, $^1A_1$
LSDA	0.0	0.31	0.87	0.0	0.44	1.23
LSDA/NL	0.0	0.36	0.55	0.0	0.40	0.76
EA_{vert} [b]	3.00	2.83	2.68			
FIP [c]				4.91	5.47	4.42

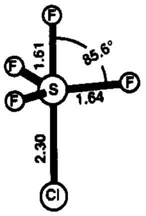
[a] EA_{vert} is the vertical EA of the radical. [b] FIP refers to the first ionization potential of the anion.

Table II. Adiabatic and Vertical EAs of Neutral SF_nCl, $n = 1$–5, and FIPs of Their Anions [a]

property	method	SFCl	SF_2Cl	SF_3Cl	SF_4Cl	SF_5Cl
EA_{ad}	LSDA	1.59	2.60	1.84	3.94	2.51
	LSDA/NL	2.36	3.24	2.94	4.77	4.09
EA_{vert}, [b]	LSDA	−0.33	2.49	0.73	3.00	0.73
FIP [c]	LSDA	3.81	3.16	3.40	4.91	4.52

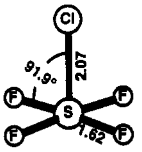
[a] All values in electronvolts. [b] Vertical electron affinity of neutral SF_nCl in its ground state configuration. [c] First ionization potential of SF_nCl^-.

2e, of C_{4v} symmetry represents a square pyramid with the chlorine in the apical position, whereas the third, **2f**, of C_s symmetry is a square pyramid with chlorine at a basal site. It follows from Table I that the square pyramidal structures, **2e** and **2f**, are more stable than the trigonal conformation, **2d**, and that chlorine prefers the basal site, **2f**, over the apical position, **2e**. The calculated relative stabilities for **2d–f** are in line with what one would expect from VSEPR theory.



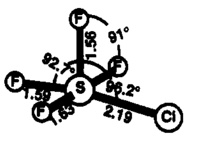
$SF_4Cl\ C_{3v}: {}^2A_1$

2a



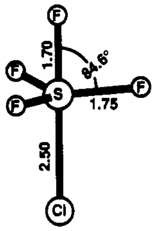
$SF_4Cl\ C_{s}: {}^2A'$

2b



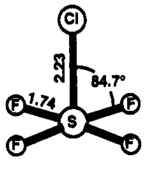
$SF_4Cl\ C_{s}: {}^2A'$

2c



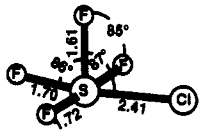
$SF_4Cl^-\ C_{3v}: {}^1A_1$

2d



$SF_4Cl^-\ C_{4v}: {}^1A_1$

2e

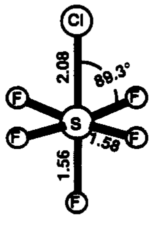


$SF_4Cl^-\ C_{s}: {}^1A'$

2f

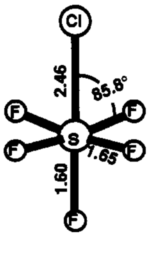
The SF_4Cl radical is intermediate in electron count between PF_5 with a trigonal bipyramidal geometry (TBP) and SF_4F^- with a square pyramidal geometry (SP). We have optimized a TBP structure, **2a**, as well as two SP geometries, **2b** and **2c**, for SF_4Cl. It follows from Table I that the SP conformations, **2b** and **2c**, are more stable than the TBP geometry, **2a**. The chlorine atom prefers further to occupy a basal, **2c**, rather than an apical site, **2b**. The S–Cl bond is seen to be stretched by 0.22 Å as an electron is added to SF_4Cl. The increases in the S–F distances are much smaller, **2**.

The ground-state geometry, **3a**, of the SF_5Cl molecule was assumed to be of C_{4v} symmetry, in correspondence with experimental data.[2] The anion SF_5Cl^- was also optimized within C_{4v} constraints, **3b**. The calculated geometrical parameters for SF_5Cl are in quite good accordance with the experimental data,[1,2] except for a difference of ~0.03 Å for the S–F_{ax} and S–Cl bond lengths. Experimental data are lacking for the anion, **3b**. Our calculations indicate a substantial elongation of 0.38 Å for the S–Cl bond length in going from the neutral molecule to the anion. Structural parameters for the SF_5 unit in SF_5Cl^- are placed between those[25] of the free SF_5, $R(S–F_{ax}) = 1.562$ Å, $R(S–F_{eq}) = 1.612$ Å, $\angle F_{ax}SF_{eq} = 90.8°$, and those of the anion SF_5^-, $R(S–F_{ax}) = 1.633$ Å, $R(S–F_{eq}) = 1.745$ Å, $\angle F_{ax}SF_{eq} = 84.7°$. The anion SF_5Cl^- may be described qualitatively as an adduct $(SF_5{}^{\bullet}Cl)^-$ in which an additional electron is shared by the SF_5 and Cl radicals, just as in the case of SF_3Cl^-. The longer S–Cl bond in SF_3Cl^- compared to SF_5Cl^- may be explained by SF_5 being more electronegative than SF_3.



$SF_5Cl\ C_{4v}: {}^1A_1$

3a



$SF_5Cl^-\ C_{4v}: {}^2A_1$

3b

The two molecules SF_2Cl (**1d**) and SF_4Cl (**2c**) are radicals with a single electron in a nonbonding or weakly antibonding orbital. They can as a consequence readily add an additional electron to the same orbital, thus forming the anions SF_2Cl^- (**1e**) and SF_4Cl^- (**2f**), respectively. It is for this reason not surprising that SF_2Cl and SF_4Cl have relatively high vertical (EA_{vert}) and adiabatic (EA_{ad}) electron affinities, Table II. The adiabatic corrections are further seen to be modest, Table II, as the nonbonding or weakly antibonding nature of the acceptor orbitals necessitate modest changes (increases) in the S–Cl and S–F bonds.

The three molecules in the series SFCl, SF_3Cl, and SF_5Cl all have a closed-shell ground state. The additional electron in the anions $SFCl^-$, SF_3Cl^-, and SF_5Cl^- enters a strongly antibonding orbital. The three molecules SFCl, SF_3Cl, and SF_5Cl have for this reason low vertical electron affinities, Table II, with EA_{vert} even being negative for SFCl. Adiabatic corrections are further seen to be substantial (~2–3 eV) due to the antibonding nature of the acceptor orbitals. The antibonding nature causes substantial elongations of the S–Cl bonds as the anions are formed; see **1c**, **1g**, and **3b** as compared to **1a**, **1f**, and **3a**, respectively. We note in addition an increase in EA_{vert} and EA_{ad} through either of two series: SFCl, SF_3Cl, and SF_5Cl and SF_2Cl and SF_4Cl. We ascribe this increase to a stabilization of the additional electron in the anion as it is delocalized over an increasing number of fluorine atoms.

The first ionization potential for the series of anions SF_nCl^- ($n = 1$–5) is seen to be high throughout the series, exceeding in all cases 3 eV, Table II. The FIP value represents, according to eq 5, the energy difference between SF_nCl and SF_nCl^- evaluated at the equilibrium geometry of the anion. We have in general that FIP > EA_{ad} > EA_{vert}. EA_{ad} is in the case of the SF_nCl series much closer to FIP than to EA_{vert}. Thus the FIP values are close upper bounds to EA_{ad} with $\Delta(\text{FIP} - EA_{ad})$ less than 0.4 eV for all the chlorine-substituted sulfur fluorides except for SFCl. The adiabatic correction $\Delta(EA_{ad} - EA_{vert})$ is on the other hand large and actually exceeds 3 eV for the last number of series, SF_5Cl.

Tables III and IV display theoretical fragmentation or dissociation energies for SF_nCl^{-m} ($m = 0, 1$). The theoretical values were calculated as the difference in total energy between SF_nCl^{-m} and the various fragments; i.e., they correspond to D_e. The zero-point corrections are usually quite small. It should thus be reasonable to compare our dissociation energies with experimental D_0 values. Table III contains dissociation energies for the frag-

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Table III. Dissociation Energies (eV) for the Neutral SF_nCl, Corresponding to Different Channels

channel	LSDA	LSDA/NL
$SFCl \rightarrow SF + Cl$	3.33	2.33
$\rightarrow S + FCl$	4.44	3.43
$\rightarrow SCl + F$	4.64	3.68
$SF_2Cl \rightarrow SF_2 + Cl$	1.97	1.06
$\rightarrow SF + FCl$	3.11	2.15
$\rightarrow SFCl + F$	3.59	2.66
$SF_3Cl \rightarrow SF_3 + Cl$	2.93	1.71
$\rightarrow SF_2 + FCl$	2.97	1.74
$\rightarrow SF_2Cl + F$	4.81	3.52
$SF_4Cl \rightarrow SF_4 + Cl$	0.95	−0.16
$\rightarrow SF_3 + FCl$	2.14	0.75
$\rightarrow SF_3Cl + F$	3.05	1.87
$SF_5Cl \rightarrow SF_5 + FCl$	1.93	0.07
$\rightarrow SF_5 + Cl$	3.04	1.31[a]
$\rightarrow SF_4Cl + F$	4.81	2.77
$\rightarrow S + 5F + Cl$	24.62	17.42[b]

[a] Experimental Estimation: <2.0,[6] 2.70 ± 0.15,[7] and 2.65 eV.[26] [b] Experimental value is 18.9 eV.[6]

Table IV. Dissociation Energies (eV) for the Low-Energy Decomposition Channels of SF_nCl^-

channel	LSDA	LSDA/NL
SFC^- $SF + Cl$	1.85	1.40
$\rightarrow SF^- + Cl$	3.14	2.51
$\rightarrow SCl + F^-$	3.08	2.59
$\rightarrow SCl^- + F$	4.21	3.63
SF_2Cl^- $SF_2 + Cl^-$	1.48	1.01
$\rightarrow SF_2^- + Cl$	3.39	2.33
$\rightarrow SFCl + F^-$	3.02	2.45
$\rightarrow SFCl^- + F$	4.58	3.54
SF_3Cl^- $SF_3 + Cl^-$	1.68	1.36
$\rightarrow SF_3^- + Cl$	2.41	1.60
$\rightarrow SF_2Cl + F^-$	3.48	3.01
$\rightarrow SF_2Cl^- + F$	4.05	3.22
SF_4Cl^- $SF_4 + Cl^-$	1.79	1.37
$\rightarrow SF_4^- + Cl$	3.49	2.08
$\rightarrow SF_3Cl + F^-$	3.79	3.19
$\rightarrow SF_3Cl^- + F$	5.12	3.70
SF_5Cl^- $SF_5^- + Cl$	1.73	0.62
$\rightarrow SF_4Cl^- + F$	3.39	2.09
$\rightarrow SF_5 + Cl^-$	2.38	2.11
$\rightarrow SF_4Cl + F^-$	4.21	4.03

Table V. Comparison of Adiabatic EAs (eV) and Bond Dissociation Energies (eV) for the SF_n and SF_nCl, n = 2–6, Series[a]

property	SF_2	SF_3	SF_4	SF_5	SF_6
EA_{ad}(calcd)	1.97	2.73	2.56	4.79	3.44
EA_{ad}(exp)		2.95 ± 0.05[b] 3.07 ± 0.2[c]	2.35 ± 0.1[d]	3.8 ± 0.15[e]	1.0 ± 0.2[f]
$D(SF_{n-1}-F)$					
D_e(calc)	3.93	2.86	3.71	1.55	3.50
$D_0°$(exp)[d]	3.98	2.74	3.65	2.30	3.95

property	SFCl	SF_2Cl	SF_3Cl	SF_4Cl	SF_5Cl
EA_{ad}(calc)	2.36	3.24	2.94	4.77	4.09
$D_e(SF_{n-1}-Cl)$	2.33	1.06	1.71	−0.16	1.31
$D_e(SF_{n-2}Cl-F)$	3.68	2.66	3.52	1.87	2.77

[a] Reference 25. [b] Reference 27. [c] Reference 2. [d] Reference 28. [e] Reference 29a. [f] Reference 29b,c.

mentation channels of lower energy. The dissociation energies were calculated at the LDA and LDA/NL levels of theory. The LDA/NL values should be considered as the more accurate estimates.

The channel of lowest energy coresponds for most of the SF_nCl species to detachment of the chlorine atom. The only exception is SF_5Cl, where the dissociation channel of lowest energy is represented by the decay of SF_5Cl into SF_4 and FCl. Experimental values are available for the S–Cl dissociation energy of SF_5Cl.[6,7,26] There is in addition an accurate determination of the atomization energy for SF_5Cl[6] of 18.9 eV, which compares reasonable well with our LDA/NL value of 17.4 eV. A comparison between the theoretical and experimental values indicates that the LSDA/NL level of theory on the average underestimates S–F and S–Cl bond dissociation energies by ~0.3 eV (7 kcal), if we accept the average error to be equal to (18.9 − 17.4)/6 eV. With this assumption the LSDA level of theory should overestimate the dissociation energies by 0.9 eV (21 kcal), Table III. Of course, these estimates for the accuracy of the theoretical approaches are very approximate and may rather serve as indications.

As seen from Table III, all SF_nCl species are only moderately stable with respect to dissociation. In particular, the SF_4Cl radical is near the threshold with respect to rupture of the S–Cl bond. On the LDA/NL level it is even predicted to be unstable by 3.7 kcal/mol. However, this prediction might have to be revised when we keep in mind that the LDA/NL method appears to underestimate bond dissociation energies by ~7 kcal/mol. The same conclusion is true for the SF_5Cl molecule, where the energy of the topmost channel, estimated to be 0.07 eV on the LSDA/NL level of theory, appears also to be understimated. In either case, these molecules are indeed known to be unstable and decompose thermally[6] at 200 °C.

The analogous results from calculations on the dissociation energies of the anion SF_nCl^- are presented in Table IV. It follows from the data in this table that all the anions are stable. Moreover, the anions in this series are in general more stable with respect to dissociation than their neutral precursors. For all the anions, the topmost dissociation channel corresponds to detachment of Cl^-. The first dissociation energy of the SF_5Cl^- anion is further calculated to be smaller than the EA_{ad} of its neutral parents, SF_nCl. This might explain the predominant dissociative attachment of electrons by SF_5Cl^- observed experimentally.

It might be of interest to compare EA_{ad} and D_0 values for the SF_nCl species with experimental[27] and theoretical[25] estimates of the same properties in the much better investigated SF_n series (n = 2–6). The pertinent data are collected in Table V. Theoretical values for SF_n were obtained[25] from calculations analogous to those described here with the employment of the same basis sets for S and F.

The parallel series of closed-shell systems, SF_n and $SF_{n-1}Cl$ (n = 2, 4, 6), have in general stronger calculated sulfur–halogen bonds than the two series of radicals with n = 3, 5. This trend, which is borne out experimentally, stems simply from the fact that the radicals have less than two electrons in each bonding orbital. The calculated first sulfur–halogen bond dissociation energy exhibits in addition, for n even and n odd, a gradual increase toward larger n.

The calculated adiabatic electron affinities are finally seen to increase through the series of radicals as well as closed-shell molecules toward larger values of n, as the added electron can delocalize over more fluorine atoms. Theory reproduces the known experimental EA_{ad} data for the sulfur fluoride series quite well except for SF_6 and SF_5. We fell that the EA_{ad} values for SF_5 and SF_6 should be higher and present a detailed discussion of this point elsewhere.[25]

Conclusions

Density functional calculations have allowed us to determine the ground-state geometries for the monochloro-substituted sulfur fluorides SF_nCl (n = 1–5) and their anions. Total energies of the optimized configurations have further been used to determine bond dissociation energies and adiabatic electron affinities. The adiabatic electron affinity was found to increase through the series of radicals (n even) as well as closed-shell molecules (n odd) toward larger values of n, as the added electron can delocalize over more

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fluorine atoms. The topmost dissociation channel of the SF_5Cl molecule corresponds to detachment of the FCl interhalogen, and not to dissociation of a chlorine atom, as it is the case for the rest of the series. The anions in the end of series, SF_4Cl^- and SF_5Cl^-, are more stable than their neutral precursors with respect to dissociation. All the members of the SF_nCl series possess relatively high EA_{ad} values, and it is suggested that the commonly accepted EA_{ad} value of 1.0 ± 0.2 eV for SF_6 might be underestimated.

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Diequatorial and Axial-Equatorial Orientations of Eight-Membered Rings in Monocyclic Pentaoxyphosphoranes Containing Trifluoroethoxy Groups[1]

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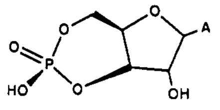
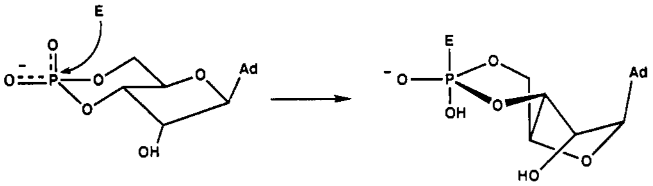
Reaction of $(CF_3CH_2O)_3P$ with diols yielded new monocyclic pentaoxyphosphoranes with eight-membered ring systems containing methylene or sulfur bridges. Trigonal-bipyramid (TBP) geometries were shown to be present by X-ray analysis for $CH_2(C_6H_4O)_2P(OCH_2CF_3)_3$ (**2**) and $S(Me_2C_6H_2O)_2P(OCH_2CF_3)_3$ (**3**) with the ring in **2** located in axial-equatorial (a-e) positions and the ring in **3** in diequatorial (e-e) sites. These structures are compared with the first pentaoxyphosphorane derivative to exhibit a diequatorial ring in a TBP, $CH_2[Me(t\text{-}Bu)C_6H_2O]_2P(OCH_2CF_3)_3$ (**1**), recently prepared in our laboratory. A pseudooctahedral structure was revealed by X-ray analysis for $S[(t\text{-}Bu)_2C_6H_2O]_2P(OCH_2CF_3)_3$ (**4**). ^1H, ^{31}P, and ^{19}F solution NMR data indicated rapid intramolecular ligand exchange for **2** and **3** at room temperature. In contrast, NMR data on **1** and **4**, which contained *tert*-butyl groups, did not indicate exchange behavior. Here, retention of the basic solid-state TBP in solution was consistent with the observed spectra. Comparison of solid-state ^{31}P NMR spectra with solution ^{31}P NMR data of **3** and **4** suggested retention of their basic solid-state geometries in solution. Comparisons with related pentaoxyphosphoranes having six- and seven-membered rings suggest that seven- and eight-membered rings are more easily accommodated in diequatorial positions compared to positioning saturated six-membered rings in this location of a TBP. Oxyphoshorane **2** crystallizes in the triclinic space group $P\bar{1}$ with a = 9.712 (2) Å, b = 11.039 (3) Å, c = 12.521 (2) Å, α = 97.48 (2)°, β = 111.77 (1)°, γ = 110.56 (2)°, and Z = 2. Derivative **3** crystallizes in the triclinic space group $P\bar{1}$ with a = 9.245 (2) Å, b = 12.464 (2) Å, c = 12.891 (2) Å, α = 76.77 (1)°, β = 74.69 (2)°, γ = 70.60 (1)°, and Z = 2. Oxyphosphorane **4** crystallizes in the triclinic space group $P\bar{1}$ with a = 11.202 (2) Å, b = 11.307 (4) Å, c = 16.372 (8) Å, α = 99.66 (3)°, β = 94.39 (3)°, γ = 103.42 (2)°, and Z = 2. The final conventional unweighted residuals are 0.050 (**2**), 0.075 (**3**), and 0.076 (**4**).

Introduction

Considerable interest has developed recently in establishing whether it is possible to isolate pentaoxyphosphoranes with six-membered ring systems in diequatorial sites (e-e) as well as in axial-equatorial sites (a-e) of a trigonal-bipyramid (TBP) geometry.[2] This interest stems from the role of these pentacoordinated phosphorus compounds as intermediates or activated states postulated to exist in reaction mechanisms,[3-6] particularly in enzymatic reactions involving c-AMP.[7-11] Various mechanisms have been advanced suggesting axial-equatorial placement of the six-membered ring in the hydrolysis of c-AMP catalyzed by c-AMP phosphodiesterase,[9] whereas in the activation of protein kinases by c-AMP, diequatorial placement of the cyclophosphate ring has been proposed[9,12] to result from attack by a functional group of the enzyme yielding a covalent complex.



c-AMP



However, despite a variety of studies, no unambiguous structural characterization of a pentaoxyphosphorane with a diequatorial six-membered ring system has been found. Broeders et al.[13] have reported the presence of such a ring orientation in equilibrium with an a-e isomer deduced from ^1H NMR data on the cyclic phosphorane A.

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