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Theoretical study of the thermochemistry and the kinetics of the SF_xCl (x = 0–5) series

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ABSTRACT

A systematic thermodynamic and kinetic study of the entire SF_xCl (x = 0–5) series has been carried out. High-level quantum chemical composite methods have been employed to derive enthalpy of formation values from calculated atomization and isodesmic energies. The resulting values for the SCl, SFCl, $SF_2Cl(C_1)$, $SF_3Cl(C_s)$, $SF_4Cl(C_s)$ and SF_5Cl molecules are 28.0, −36.0, −64.2, −134.3, −158.2 and −237.1 kcal mol^{-1}. A comparison with previous experimental and theoretical values is presented. Statistical adiabatic channel model/classical trajectory, SACM/CT, calculations of selected complex-forming and recombination reactions of F and Cl atoms with radicals of the series have been performed between 200 and 500 K. The reported rate coefficients span over the normal range of about 6×10^{-12} and 5×10^{-11} cm^3 molecule^{-1} s^{-1} expected for this type of barrierless reactions.

1. Introduction

Many compounds containing sulfur-halogen bonds are relevant in environmental chemistry [1–3] and semiconductor technology [4]. However, a limited set of indirect experimental or estimated data related to the thermochemistry of these compounds is available in the literature, and some of them are inexact. The thermochemical properties of the compounds bearing S–F bonds are the best established. In particular, studies of the SF_x (x = 0–6) and S_2F_x (x = 0–10) series have been critically reviewed by Herron [5,6] and, more recently, enthalpies of formation values have been predicted by using high-level quantum-chemical methods [7,8]. By contrast, the themochemistry of the members of the SF_xCl (x = 0–5) series has not been investigated in detail. The simplest sulfo-chlorinated compound, the SCl radical, has been involved in the reaction mechanism of ionic atmospheres and is also present in volcanic emissions [9]. The accepted enthalpy of formation value for this species, as derived from the ClS–Cl bond dissociation energy, is $\Delta H_{f,298}^{\circ} = 37.4 \pm 4.0$ kcal mol^{-1} [10]. This value is significantly larger than recent theoretical estimates of 29.1 [11] and 32 kcal mol^{-1} [12]. The larger member of the SF_xCl (x = 1–5) series, SF_5Cl, is normally employed in liquid crystal (LCD) technologies [4]. The recommended NIST-JANAF value of $\Delta H_{f,298}^{\circ} = -248.3 \pm 2.5$ kcal mol^{-1} [10] is considerably smaller than the recent value of −231.8 kcal mol^{-1} obtained from the SF_5Cl total atomization energy and from the energetics of the $SF_5Cl + HF \rightarrow SF_6 + HCl$ working reaction, −238.5 kcal mol^{-1}, both computed at the G3 *ab initio* level. The reported values for the other members of the series are (in kcal mol^{-1}) −33.8 (SFCl), −62.0 (SF_2Cl), −139.9 (SF_3Cl), −147.3 (SF_3Cl) and −155.3 (SF_4Cl) [11]. For the rest of the series, no experimental data are available for comparison.

The scarcity of direct experimental thermochemical data and the abovementioned discrepancies between the recommended and the theoretically estimated values, claim for a new study of the enthalpy of formation of the members of the SF_xCl series. For this, DFT and accurate *ab initio* composite methods which provide mean errors within the chemical accuracy of about 1 kcal mol^{-1} were employed. On the other hand, there is a complete lack of kinetic data for reactions of the molecular species forming the SF_xCl series. Therefore, computed bimolecular rate coefficients for selected reactions of F and Cl atoms with several radicals of the series are reported.

2. Theoretical and computational methods

Enthalpies of formation were calculated from total atomization energies and from isodesmic reaction schemes. The first approach requires accurate atomic and molecular energies and, therefore, constitutes a stringent test of the quantum methods employed. In the second one, the enthalpy of formation for a given compound is derived by coupling the theoretically computed enthalpy change of a balanced isodesmic reaction with well-known enthalpies of formation for the other reaction species. In such reactions (normally hypothetical), the reactants and products contain the

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same number of bonds of a given type, i.e. the numbers of bonds broken and formed are conserved [13,14]. Therefore, errors in the molecular energies that arise from the truncation of the number of configurations employed for treating correlation energies, and those due to the incompleteness of the basis set used, cancel to a large extension. Under these conditions, the error in the enthalpy of formation of the studied molecule is largely due to the errors in the enthalpies of formation of the other molecules. Therefore, the obtained enthalpies of formation can be often more accurate than those derived from atomization energies [15].

The well-known B3LYP hybrid functional combined with the 6-311+G(d) and 6-311+G(3df) basis set and different *ab initio* composite methods as implemented in the Gaussian 09 software package [16] were employed in this work. In particular the G3MP2B3, G3B3 [17], G4MP2 [18], G4 [19], CBS-QB3 [20], W1U and W1BD [21–23] model chemistries have been here used. Systematic errors arisen in the Gaussian-3 methods have been accounted for by subtracting a bond additivity correction term (BAC), $E_{\mathrm{BAC\ correction}}$ from the G3MP2B3 and G3B3 enthalpies of formation computed from atomization energies [24]. This correction takes into account errors due to atomic, molecular and pairwise bond effects.

Electronic energy barriers for the conversion between different conformers and arisen in kinetic studies were computed with the hybrid meta exchange-correlation functional M06-2X combined with the 6-311+G(3df) basis set [25]. This is a high-nonlocality functional (with double the amount of nonlocal exchange) recommended for main-group kinetics. All transition states, as confirmed by normal-mode analysis, present only one imaginary frequency.

Rate coefficients for selected reactions of radicals of the SF_xCl series with F and Cl atoms were estimated using the statistical adiabatic channel model/classical trajectory treatment developed for the capture of atoms by linear rotors on standard valence potentials [26].

3. Results and discussion

3.1. Molecular structures and harmonic vibrational frequencies for the SF_xCl compounds

Molecular geometries were fully optimized employing analytical gradient methods using the B3LYP functional and the *ab initio* MP2 formulations combined with the 6-311+G(3df) basis set. Determined MP2/6-311+G(3df) geometries are depicted in Fig. 1, while structural values along with available experimental data are respectively listed in Table 1. The values derived for the S–Cl bond distances at the B3LYP/6-311+G(3df) level are identical to those reported in Ref. [11] and have been omitted here for the sake of simplicity. The computed S–Cl and S–F bond distances for the SCl, SFCl and SF_5Cl molecules differ in only 0.002–0.004 and 0.004–0.013 Å from the experimental values. The angles are exactly reproduced by the calculations. A somewhat poorer agreement is obtained at the B3LYP level [11].

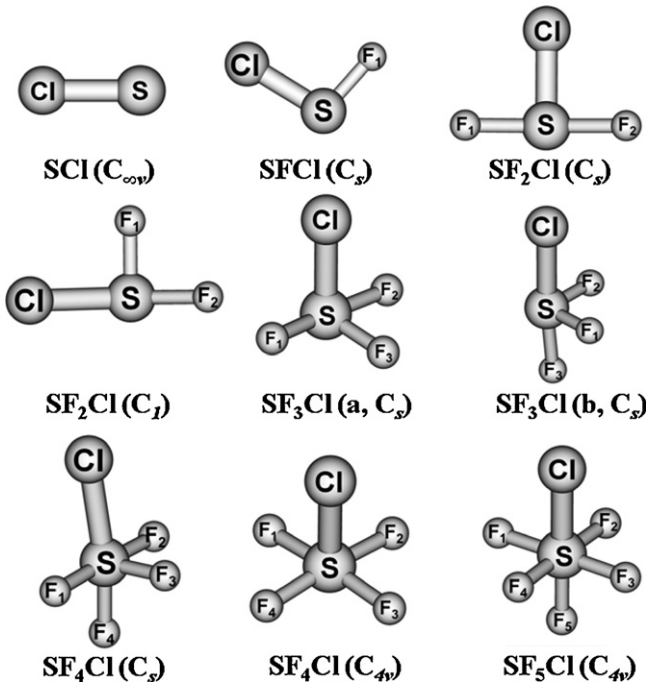

Fig. 1. Molecular conformations determined for the SF_xCl (x = 0–5) molecules at the MP2/6-311+G(3df) level.

Two stable structures have been found for each of the SF_2Cl, SF_3Cl and SF_4Cl molecules. The M06-2X/6-311+G(3df) electronic barriers at 0 K are shown in Fig. 2. The stability of the SF_2Cl (C_1) and SF_2Cl (C_s) molecules is identical and they are separated by a barrier of 17.7 kcal mol^{-1}. Also similar energy values were computed for the two SF_3Cl molecules. However, they are separated for a barrier high of about 5 kcal mol^{-1} larger than the corresponding to the precedent member of the series. Moreover, a larger barrier of 30.1 kcal mol^{-1} has been found for the conversion of SF_4Cl (C_s) into the less stable SF_4Cl (C_{4v}) species. These high barriers indicate that

Table 1
Structural parameters for the compounds of the SF_xCl (x = 0–5) series (bond lengths in Å, angles in°) calculated at the MP2/6-311+G(3df) level.

Parameter	SCl	SFCl	SF_2Cl (C_s)	SF_2Cl (C_1)	SF_3Cl (a, C_s)	SF_3Cl (b, C_s)	SF_4Cl (C_s)	SF_4Cl (C_{4v})	SF_5Cl
r(S–Cl)	1.973 (1.975)[a]	1.992 (1.994)[b]	1.985	2.115	1.996	2.161	2.090	2.005	2.043 (2.047)[c]
r(S–F_1)		1.616 (1.606)[b]	1.690	1.579	1.671	1.554	1.612	1.612	1.575 (1.588)[c]
r(S–F_2)			1.690	1.665	1.671	1.554	1.612	1.612	1.575
r(S–F_3)					1.566	1.655	1.550	1.612	1.575
r(S–F_4)							1.593	1.612	1.575
r(S–F_5)									1.570 (1.566)[c]
∠(ClSF_1)		100.7 (100.7)[b]	90.1	90.3	89.1	89.1	91.1	92.7	90.7 (90.7)[c]
∠(ClSF_2)			90.0	153.7	89.1	89.1	91.1	92.7	90.7
∠(ClSF_3)					103.8	175.3	94.4	92.7	90.7
∠(ClSF_4)							172.5	92.7	90.7
∠(ClSF_5)									180.0
∠(F_1SF_2)			164.8	88.5	172.9	101.5	177.5	89.9	90.0 (90.0)[c]
∠(F_1SF_3)					86.9	87.4	90.6	174.6	178.6
∠(F_1SF_4)							88.8	89.9	90.0
∠(F_1SF_5)									89.3

[a] Ref. [27].
[b] Ref. [28].
[c] Ref. [29].

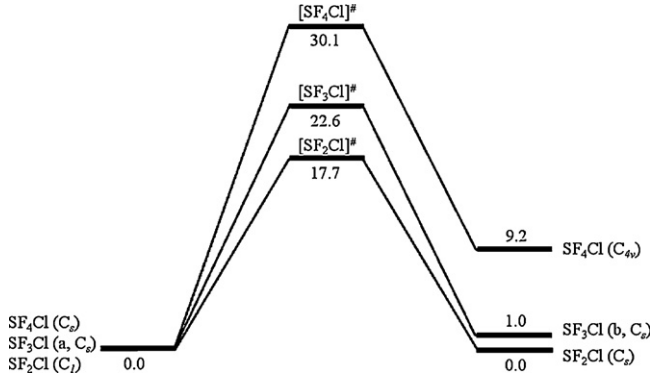

Fig. 2. Electronic barriers (in kcal mol^{-1}) for the conversion between the isomers of the SF_2Cl, SF_3Cl and SF_4Cl species (see Fig. 1) computed at the M06-2X/6-311+G(3df) level at 0 K.

Table 2
Harmonic vibrational frequencies (in cm^{-1}) and approximate assignments for SFCl, SF_3Cl and SF_5Cl calculated at the MP2/6-311+G(3df) level. The atoms are numbered as in Fig. 1.

Assignment	This work	Experimental
SFCl		
Bend	276	275.5[a]
SCl stretch	568	547.5[a]
SF stretch	787	779.5[a]
$SF_3Cl(a, C_s)$		
Cl–S–F_3 bend	190	
Cl–S–$F_{1,2}$ bend	326	
S–F_{1-2} op-deform.	332	
S–F_{1-2} ip-deform.	433	
F_3–S–$F_{1,2}$ bend	493	
S–F_{1-2} sym. stretch	514	506[b]
SCl stretch	626	606[b]
S–F_{1-2} asym. stretch	699	668[b]
S–F_3 stretch	845	841[b]
SF_5Cl		
Cl–S–$F_{2,4,5}$ op-deform.	273	271[c]
Cl–S–$F_{1,3,5}$ op-deform.	273	271[c]
S–F_{1-4} op-deform.	345	397[c]
S–Cl stretch	415	402[c]
S–$F_{1,3}$ ip-deform.	446	441[c]
S–$F_{2,4}$ ip-deform.	446	441[c]
S–F_{1-4} ip-deform.	506	505[c]
S–F_{1-3} wag.	584	579[c]
S–F_{2-4} wag.	584	579[c]
S–F_{1-4} op-deform.	609	602[c]
S–F_{1-4} asym. stretch	631	625[c]
S–F_{1-4} sym. stretch	716	707[c]
S–F_5 stretch	862	855[c]
S–$F_{1,3}$ def. stretch	923	909[c]
S–$F_{2,4}$ def. stretch	923	909[c]

[a] Ref. [28].
[b] Ref. [31].
[c] Ref. [32].

the interconversion between pairs of isomers is highly hindered, and in normal conditions, are expected to be non-operative.

At the calculated structures, the harmonic vibrational frequencies were then derived *via* analytical second derivative methods. At the employed levels of theory, the frequency scaled factors are expected to be close to unity [30]. Mode assignment was accomplished with the help of the animations of the normal modes corresponding to the fundamental vibrational frequencies. Some of the modes are strongly mixed and thus, only an approximate assignment is given. The computed frequency for the SCl diatomic at the B3LYP, MP2 and CCSD levels combined with the 6-311+G(3df) basis set are 562, 591 and 578 cm^{-1}. All these values are larger than that estimated in Ref. [10] with the Badger's rule to be 536 cm^{-1}. Calculated vibrational frequencies for the SCl, SF_3Cl and SF_5Cl molecules and available experimental values are presented in Table 2. A very good agreement between the MP2/6-311+G(3df) frequencies and the experimental ones is apparent. The average deviations for the SFCl, SF_3Cl (a, C_s) and SF_5Cl molecules are only 10, 16 and 11 cm^{-1}. These deviations are smaller than those derived with the functionals B3LYP/6-311+G(3df) (21, 29 and 25 cm^{-1} [11]) and M06-2X/6-311+G(3df) (26, 40 and 18 cm^{-1}). It looks interesting to compare the MP2/6-311+G(3df) vibrational frequencies calculated for the SF_3Cl(b, C_s) molecule of 523, 654, 860, 863 cm^{-1} with the experimental values of 506, 606, 668 and 841 cm^{-1} [31]. In this case the agreement is poorer than the obtained for the SF_3Cl (a, C_s) molecule, especially that corresponding to the S–F_{1-2} asym. stretch mode (see Fig. 1 and Table 2) for which a large difference of 192 cm^{-1} results. This fact suggests that the SF_3Cl(a, C_s) molecule is probably the observed in the low temperature experiments of Minkwitz et al. [31].

3.2. Enthalpies of formation for the SF_xCl compounds determined from total atomization energies

As abovementioned, we have used two methods to estimate the enthalpies of formation of SCl, SFCl, SF_2Cl, SF_3Cl, SF_4Cl and SF_5Cl molecules. The first method was used to derive the enthalpies of formation at 0 K by subtracting the computed total atomization energies from the experimental enthalpies of formation of the sulfur (65.66 ± 0.06 kcal mol^{-1}), fluorine (18.47 ± 0.07 kcal mol^{-1}) and chlorine atoms (28.59 ± 0.001 kcal mol^{-1}) [20]. These values were then transformed to 298 K, $\Delta H_{f,298}^{\circ}$, using estimated thermal contributions obtained from the calculated vibrational frequencies and $H_{298.15}^{\circ}-H_0^{\circ}$ values for sulfur, fluorine and chlorine atoms of 1.05, 1.05, 1.10 kcal mol^{-1} [33]. The results derived at the various levels of theory are listed in Table 3. As expected, the importance of including high d- and f-polarization functions in sulfur and fluorine containing compounds is evident from the B3LYP calculations [8]. The estimated value of 36.0 kcal mol^{-1} for SCl at the B3LYP/6-31G(d) level agrees

Table 3
Enthalpies of formation at 298 K (in kcal mol^{-1}) for the molecules of the SF_xCl (x = 0–5) series calculated from atomization energies.

Level of theory	SCl	SFCl	SF_2Cl (C_1)	SF_3Cl (a, C_s)	SF_4Cl (a, C_s)	SF_5Cl
B3LYP/6-31G(d)	36.0	−20.4	−53.6	−107.5	−135.0	−195.4
B3LYP/6-311+G(3df)	29.4	−31.1	−64.1	−125.8	−150.0	−213.3
G3MP2B3	28.3	−33.7	−61.4	−129.0	−150.1	−227.9
G3B3	29.7	−32.8	−60.4	−128.9	−150.8	−229.3
BAC-G3MP2B3	27.7	−34.3	−63.2	−133.2	−156.3	−238.5
BAC-G3B3	29.0	−35.0	−63.7	−133.8	−157.2	−238.5
G4MP2	27.0	−36.7	−66.8	−134.9	−161.6	−236.5
G4	28.4	−35.6	−64.7	−134.0	−159.8	−236.2
CBS-QB3	27.1	−36.5	−65.7	−133.3	−159.2	−236.2
W1U	28.6	−35.9				
W1BD	28.6	−35.9				
	37.4 ± 4.0[a]					−248.3 ± 2.5[a]

[a] Ref. [10].

Table 4
Bond additivity corrections (in kcal mol^{-1}) for the G3B3 and G3MP2B3 (in parentheses) model chemistries.

Correction	SCl	SFCl	SF_2Cl (C_1)	SF_3Cl (a, C_s)	SF_4Cl (C_s)	SF_5Cl
$E_{BAC\text{-}atom}$	−0.518 (−2.118)	−0.495 (−2.198)	−0.472 (−2.278)	−0.449 (−2.358)	−0.426 (−2.438)	−0.403 (−2.518)
$E_{BAC\text{-}molecule}$	−0.318 (−0.286)	−0.636 (−0.572)	−0.636 (−0.572)	−0.954 (−0.858)	−0.954 (−0.858)	−1.273 (−1.144)
$E_{BAC\text{-}bond}$	1.539 (3.003)	3.331 (3.327)	4.411 (4.607)	6.310 (7.382)	7.790 (9.542)	10.876 (14.260)
$E_{BAC\text{-}correction}$	0.703(0.599)	2.200 (0.557)	3.303 (1.757)	4.907 (4.166)	6.410 (6.246)	9.200 (10.598)

with the recommended NIST-JANAF value of 37.4 ± 4.0 kcal mol^{-1} [10]. However, the value computed at the better level B3LYP/6-311+G(3df) and the values obtained with the *ab initio* methods (including the very accurate W1 results; mean error of 0.4 kcal mol^{-1} for compounds with second-row elements [21–23]) are almost 8 kcal mol^{-1} smaller. The differences between the results increase with the molecular complexity of the species. As expected, basis set effects are very large for SF_5Cl at the B3LYP level. In addition, as Table 3 shows, the differences between the G3 and the BAC corrected G3 enthalpies, BAC-G3B3, increase also with the size of the molecule. In fact, the BAC correction increases the SF_5Cl stability in about 10 kcal mol^{-1}. The individual terms in the total $E_{BAC\ correction}$ are listed in Table 4. The term $E_{BAC\ bond}$ depends on the type and the number of bonded atoms and represents the most important contribution to $E_{BAC\ correction}$. The reliability of these corrections is supported by the present G4, CBS-QB3 and W1 results and by the determined isodesmic enthalpies of formation (*vide infra*).

Table 5 shows the $\Delta H_{f,298}^{\circ}$ values computed by averaging the BAC-G3MP2, BAC-G3B3, G4MP2, G4, CBS-QB3, W1U y W1BD results, together with the G3 values reported by Van Doren et al. [11]. It can be seen that the present $\Delta H_{f,298}^{\circ}$ values are systematically smaller than those derived in Ref. [11], being the difference 5.5 kcal mol^{-1} for the largest member of the series.

3.3. Enthalpies of formation for the SF_xCl compounds determined from isodesmic reactions

To estimate accurate enthalpies of formation from isodesmic reactions for a given compound, well-established thermochemical data for the species different to one of the interests are required. The employed reactions are given in Table 6. With exception of SCl + H_2 → HCl + HS, all the reactions are isodesmic and, due to the fact that spin multiplicity does not change, isogyric. The enthalpies of formation for the molecules involved (in kcal mol^{-1}) are the following: SCl_2 = −4.2 ± 0.8 [10], SF_6 = −291.7, SF_5 = −202.3, SF_4 = −183.7, SF_3 = −105.6, SF_2 = −70.6 and SF = 0.7 [8].

A comparison of Tables 3 and 6 shows that the large difference observed between the enthalpies of formation computed from atomization energies along the whole SF_xCl series, for instance, between the B3LYP/6-311+G(3df) and G4 levels, is strongly reduced from about 0.6–23 to 0.4–2 kcal mol^{-1} by using the working reactions of Table 6. This improvement is mostly ascribed to the abovementioned compensation effects. On the other hand, it can be observed that for each pair of isodesmic reactions, the reaction enthalpy changes, $\Delta H_{r,298}$, computed at all levels of theory, vary from about 2 to 28 kcal mol^{-1}, while the $\Delta H_{f,298}^{\circ}$ values are within 0.7 ± 0.9 kcal mol^{-1} with a maximum deviation of 3.0 kcal mol^{-1}. A small $\Delta H_{r,298}$ value indicates a small deviation from

Table 5
Best values for the enthalpies of formation (in kcal mol^{-1}) of the SF_xCl (x = 0–5) series (see Section 3.2).

Molecule	Atomization		Isodesmic		Best values
	Van Doren et al.[a]	This work	Van Doren et al.[a]	This work	
SCl	29.1	28.1 ± 0.8		27.9 ± 1.1	28.0 ± 1.1
SFCl	−33.8	−35.7 ± 0.8		−36.2 ± 0.3	−36.0 ± 0.8
SF_2Cl (C_1)	−62.0	−64.8 ± 1.5		−63.5 ± 0.5	−64.2 ± 1.5
SF_3Cl (a, C_s)	−130.9	−133.8 ± 0.7		−134.7 ± 0.8	−134.3 ± 0.8
SF_4Cl (C_s)	−155.3	−158.8 ± 2.1		−157.6 ± 1.3	−158.2 ± 2.1
SF_5Cl	−231.8	−237.2 ± 1.2	−238.5	−237.0 ± 0.9	−237.1 ± 1.2

[a] Ref. [11].

Table 6
Isodesmic schemes, reaction enthalpies and enthalpies of formation (in kcal mol^{-1}) for the SF_xCl (x = 0–5) series.

Isodesmic reaction	B3LYP/6-311+G(3df)		G3MP2B3		G3B3		G4MP2		G4	
	$\Delta H_{r,298}$	$\Delta H^{\circ}_{f,298}$	$\Delta H_{r,298}$	$\Delta H^{\circ}_{f,298}$	$\Delta H_{r,298}$	$\Delta H^{\circ}_{f,298}$	$\Delta H_{r,298}$	$\Delta H^{\circ}_{f,298}$	$\Delta H_{r,298}$	$\Delta H^{\circ}_{f,298}$
Cl										
$2SCl + SF_2 \rightarrow 2SF + SCl_2$	12.4	27.7	11.0	28.4	11.2	28.3	11.6	28.1	11.7	28.1
$SCl + H_2 \rightarrow HCl + HS$	−13.0	25.1	−16.6	28.7	−17.2	29.3	−15.0	27.1	−15.7	27.8
SFCl										
$SFCl + SF \rightarrow SF_2 + SCl$	−6.8	−36.1	−6.8	−36.1	−6.6	−36.2	−7.1	−35.7	−7.0	−35.9
$2SFCl \rightarrow SF_2 + SCl_2$	−1.2	−36.8	−2.5	−36.1	−2.2	−36.3	−2.6	−36.1	−2.3	−36.2
SF_2Cl (C_s)										
$SF_2Cl + SF \rightarrow SF_3 + SCl$	−14.4	−63.5	−14.5	−63.4	−13.9	−64.0	−15.3	−62.6	−14.7	−63.2
$2SF_2Cl + SF_2 \rightarrow 2SF_3 + SCl_2$	−16.4	−64.2	−17.9	−63.4	−16.6	−64.1	−19.0	−62.9	−17.6	−63.6
SF_3Cl (a, C_s)										
$SF_3Cl + SF \rightarrow SF_4 + SCl$	−20.7	−135.3	−21.3	−134.7	−20.5	−135.4	−22.6	−133.4	−21.8	−134.2
$2SF_3Cl + SF_2 \rightarrow 2SF_4 + SCl_2$	−28.9	−136.0	−31.5	−134.7	−29.9	−135.5	−33.6	−133.7	−31.9	−134.5
SF_4Cl (C_s)										
$SF_4Cl + SF \rightarrow SF_5 + SCl$	−15.6	−159.0	−18.6	−159.0	−17.4	−157.2	−18.4	−156.2	−17.5	−157.2
$2SF_4Cl + SF_2 \rightarrow 2SF_5 + SCl_2$	−18.9	−159.7	−26.2	−156.0	−23.7	−157.2	−25.3	−156.5	−23.3	−157.5
SF_5Cl										
$SF_5Cl + SF \rightarrow SF_6 + SCl$	−26.6	−237.4	−26.9	−237.1	−26.1	−237.9	−28.5	−235.6	−27.5	−236.5
$2SF_5Cl + SF_2 \rightarrow 2SF_6 + SCl_2$	−40.8	−238.1	−42.8	−237.1	−41.0	−238.0	−45.3	−235.9	−43.3	−236.8

the additivity of bond energies. However, independently of the magnitude of $\Delta H_{r,298}$, the small scatter observed can be certainly ascribed to the abovementioned cancellation effects in isodesmic and isogyric schemes.

Table 5 shows the average isodesmic $\Delta H_{f,298}^{\circ}$ values predicted for the studied molecules. They have been derived from all the presented results. It is evident the very nice agreement found between the $\Delta H_{f,298}^{\circ}$ obtained from both, the atomization and the isodesmic schemes. Therefore, the present best values listed in Table 6 where obtained averaging both sets of results. As noted, the present value for SCl supports the reported by Van Doren et al. [11] and differs markedly from the recommended in Ref. [10] of 37.4 ± 4.0 kcal mol^{-1}. On the other extreme of the series, the present enthalpy of formation of -237.1 kcal mol^{-1} for SF_5Cl is considerably larger than the listed in the NIST-JANAF Thermochemical Tables of -248.3 kcal mol^{-1} [10]. This last value was estimated from a reevaluated enthalpy of formation of -252.9 kcal mol^{-1} based on the experimental heat of hydrolysis of SF_5Cl in aqueous caustic conditions [34] and a reevaluated heat of vaporization of 4.6 kcal mol^{-1} [32]. The very good agreement obtained from different theoretical levels and reaction schemes here employed support the present value of -237.1 kcal mol^{-1}. Taking into account the practical importance of this compound, a direct experimental determination of the enthalpy of formation is highly desirable. As mentioned, experimental enthalpy values for the other members of the SF_xCl series are not available for comparison.

Table 7 lists the bond dissociation enthalpies calculated employing the best results of Table 5 and values computed directly from G3, M06-2X/6-311+G(3df) and G4 energies. The last two methods lead to very good results when compared with the best values. A somewhat large dispersion is obtained at the G3 level of theory. It can be appreciated that all S–F bond strengths are larger than those corresponding to the S–Cl bonds. This fact suggests that fast bimolecular reactions between F and Cl atoms and some radicals of the SF_xCl series could be important in the modeling of some industrial processes [1–4].

3.4. Rate coefficients for the reactions of F and Cl atoms with different radicals of the SF_xCl series

Bimolecular reactions proceed *via* either a direct pathway or involve a complex-forming process. Well known examples of the second type involve, for instance, the $O + OH \rightarrow HO_2^* \rightarrow H + O_2$ and $OH + CO \rightarrow HOCO^* \rightarrow H + CO_2$ reactions [35–37]. The set of reactions

$$\begin{array}{l} F + SF_xCl \underset{k_{-c}}{\overset{k_c}{\rightleftarrows}} SF_{x+1}Cl^* \xrightarrow{k(E)} SF_{x+1} + Cl \\ \qquad\qquad\qquad\quad \downarrow k_d[M] \\ \qquad\qquad\qquad\quad SF_{x+1}Cl \end{array} \qquad (1)$$

presented here (where $x = 0$–4) probably proceed initially through configurations corresponding to ground-state vibrationally excited bound complexes $SF_{x+1}Cl^*$ (capture rate coefficient k_c) which afterwards allow energy randomization. Once formed, these intermediates can either be collisionally stabilized by the bath gas M present in the system (rate coefficient k_d) to form thermalized $SF_{x+1}Cl$ species or generate SF_{x+1} and Cl products (specific rate coefficient $k(E)$). The specific rate coefficient for the back redissociation to reagents is denoted by k_{-c}.

According to M06-2X/6-311+G(3df) calculations, the initial step for the reactions of F atoms with the SCl, SF_2Cl and SF_4Cl radicals are barrierless association processes. By contrast, although formally the reactions of the F atoms with the stable molecules SFCl and SF_3Cl are quite similar to those abovementioned, they exhibit small electronic barriers in the entrance channels and, in consequence, are expected to have considerably smaller rate coefficients. Schematic potential energy diagrams (critical energies at 0 K, E_0) for the first set of reactions calculated at the M06-2X/6-311+G(3df) level are illustrated in Fig. 3. In addition, computed transition states for the elimination of ClF and F_2 molecules from the different energized adducts are shown.

As Fig. 3 shows, large calculated exotermicities ranging from about 15 to 33 kcal mol^{-1} are expected for these processes. This fact strongly suggests that the energy-dependent specific rate coefficients $k(E)$ for the pathways leading to SF_{x+1} + Cl products are large. Due to the fact that the fate of the energized intermediates depends on the interplay established between reactive and collisional processes, calculations of $k(E)$ and k_d were carried out to quantify the systems. $k(E)$ can be conveniently estimated by using the inverse Laplace transform expression $k(E) = A_\infty \rho(E - E_\infty)/\rho(E)$, where E, A_∞, $E_\infty \approx E_0 + kT$ and ρ are, respectively, the total energy of the dissociating molecule, the temperature-independent Arrhenius pre-exponential factor, the activation energy for the limiting-high pressure rate constant and the vibrational density of states at the indicated energies [38]. This is a useful and reasonably accurate approximation, suitable in the absence of detailed knowledge of the transition state [39]. The above $k(E)$ expression is converted to $k(E) = A_\infty[(E - E_\infty + a(E - E_\infty)E_Z)/(E + a(E)E_Z)]^{s-1}$ by using the Whitten–Rabinovitch approximation for the density of states [40]. Here, $a(E - E_\infty)$ and $a(E)$ are correction factors (close to the unity) to the zero-point vibrational energy E_Z of the dissociating molecule and s is the number of oscillators. $k(E)$ calculations for the barrierless reactions $SF_2Cl^* \rightarrow SF_2 + Cl$, $SF_3Cl^* \rightarrow SF_3 + Cl$ and $SF_5Cl^* \rightarrow SF_5 + Cl$ were performed using the energies given in Fig. 3 and the vibrational frequencies of Table 2. For these simple bond fission reactions a typical value for A_∞ of 10^{15} s^{-1} was assumed. In this way, microcanonical rate coefficients values of $k(E) = 4 \times 10^{13}$, 5×10^{11} and 5×10^{9} s^{-1} were derived for the

Table 7
Bond dissociation enthalpies (in kcal mol^{-1}) at 298 K for the members of the SF_xCl ($x = 0$–5) series.

Reactions	M06-2X/6-311+G(3df)	G3	G4	Best values
$SFCl \rightarrow SCl + F$	82.6	81.8	83.0	82.9
$SFCl \rightarrow SF + Cl$	67.3	63.5	65.4	65.7
$SF_2Cl \rightarrow SFCl + F$	47.3	47.1	48.0	47.1
$SF_2Cl \rightarrow SF_2 + Cl$	25.1	20.4	23.5	22.6
SF_3Cl (a, C_s) $\rightarrow SF_2Cl + F$	87.0	87.7	88.2	89.0
SF_3Cl (a, C_s) $\rightarrow SF_3 + Cl$	57.1	54.2	56.1	57.7
SF_4Cl (C_s) $\rightarrow SF_3Cl + F$	44.2	43.1	44.7	42.8
SF_4Cl (C_s) $\rightarrow SF_4 + Cl$	6.7	0.3	5.4	3.5
$SF_5Cl \rightarrow SF_4Cl + F$	95.3	95.6	95.3	97.8
$SF_5Cl \rightarrow SF_5 + Cl$	61.7	58.4	60.3	63.8

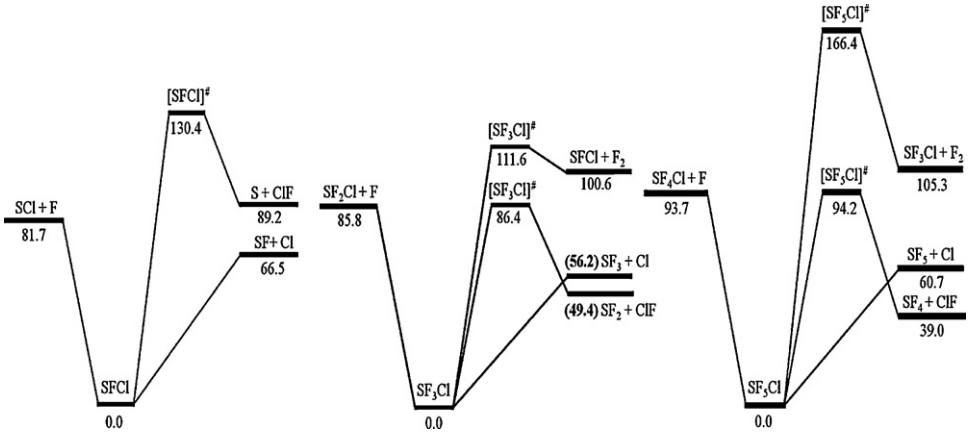

Fig. 3. Schematic diagram for the potential energy surface (in kcal mol^{-1}) for the reactions of F atoms with SCl, SF_2Cl and SF_4Cl calculated at the M06-2X/6-311+G(3df) level at 0 K.

decomposition of the prompt formed SF_2Cl^*, SF_3Cl^* and SF_5Cl^* energized adducts.

On the other hand, the collisional deactivation rate coefficient was calculated as $k_d \approx \beta_c Z_{LJ}$. For instance, at 100 mbar total pressure (M = Ar) and using typical values of 0.2 and 3×10^{-10} cm^3 molecule^{-1} s^{-1} for the collisional efficiency β_c and for the Lennard–Jones collisional frequency Z_{LJ} at 300 K [41], a collisional rate of $k_d[Ar] \approx 2 \times 10^8$ s^{-1} can be estimated. These results indicate that, under the conditions considered, the dissociation rate predominates over the stabilization rate ($k(E) \gg k_d[Ar]$) and, thus, the reactive process is the dominant fate of the energized intermediate ($SFCl^*$, SF_2Cl^* or SF_3Cl^*). However, clearly the stabilization of the two last species can be operative at larger pressures. In fact, the overall rate coefficient for the mechanism (1) can be formally expressed as $k \approx k_c[k_d[M] + k(E)]/[k_d[M] + k(E) + k_{-c}]$. In this way, at sufficiently high pressures ($k_d[M] \gg k(E) + k_{-c}$) the reaction is association controlled and k approaches the recombination high pressure rate coefficient $k \approx k_c = k_\infty$. By contrast, at very low pressures ($k_d[M] \ll k(E) + k_{-c}$), the global rate coefficient is given by $k \approx k_\infty[k(E)]/[k(E) + k_{-c}]$. Due to the fact that the available energy for the back reaction is very small in most cases, the microscopic rate coefficient k_{-c} is much smaller than $k(E)$ and, therefore, the redissociation factor $[k(E)]/[k(E) + k_{-c}]$ approaches to one [36] and $k \approx k_\infty$. For high pressures, the $SF_{x+1}Cl$ molecules are stabilized, while the products SF_{x+1} and Cl are formed in the second case.

On the other hand, no direct Cl abstraction by the F atoms has been observed in the $F + SF_xCl \rightarrow [SF_{x+1}Cl]^\# \rightarrow SF_x + ClF$ reactions. In fact, all calculations lead to deformed tetrahedral structures for the transition states. In particular, for the $F + SF_2Cl \rightarrow [SF_3Cl]^\# \rightarrow SF_2 + ClF$ reaction, the three-center configuration of the transition state formed by the reacting F atom and the S and Cl atoms of SF_2Cl present, at the M06-2X/6-311+G(3df) level, bond distances of S-F = 2.411, S–Cl = 2.249 and F–Cl = 1.948 Å and a small FSCl angle of 49.3°. The detailed reaction path of this process was determined by integrating the corresponding intrinsic reaction coordinate (IRC method) [16]. This calculation clearly shows that the $[SF_3Cl]^\#$ transition state connects the SF_3Cl adduct with the SF_2 and ClF products. Therefore, these reactions can be interpreted employing a mechanism similar to (1).

For the more favorable elimination reactions $F + SF_2Cl \rightarrow [SF_3Cl]^\# \rightarrow SF_2 + ClF$ and $F + SF_4Cl \rightarrow [SF_5Cl]^\# \rightarrow SF_4 + ClF$, the null or, within the error of the calculations, very low available energy of the transition complexes (see Fig. 3) indicates that the specific rate coefficients $k(E)$ for the decomposition of the tight-complexes $[SF_3Cl]^\#$ and $[SF_5Cl]^\#$ are surely expected to be very much smaller than those corresponding to the $SF_{x+1}Cl^* \rightarrow SF_{x+1} + Cl$ (n = 0, 2 and 4) elemental steps. As a consequence, the participation of the ClF elimination reactions of Fig. 3 is certainly unimportant.

The $F + SF_xCl$ (x = 0, 2 and 4) barrierless reactions involve potential energy surfaces with a smooth transition between an atom and a rotor (at large elongations) and some vibrational motions (at the transition state region). In the framework of the statistical adiabatic channel model, SACM, specific for type of reactions, the recombination high pressure rate coefficients can be expressed as $k_\infty = f_{rigid} k_\infty^{PST}$ [42]. Here, k_∞^{PST} is the phase space theory rate coefficient which exclusively depends on the isotropic radial potential and establishes the upper bound for k_∞. f_{rigid} is the called rigidity factor which accounts for dynamical constrains arisen from the anisotropy of the potential energy surface. The most recent version for f_{rigid} developed for the association reactions of atoms with linear molecules, SACM/CT, was here employed [26]. As for other systems, we approach the present polyatomic radicals by quasi-linear rotors [42,43]. In the absence of accurate *ab initio* potentials, Morse potentials were used for the isotropic potentials, while, as in earlier SACM [42] and in the SACM/CT formulations [26], we assume a standard value of $\alpha/\beta = 0.5 \pm 0.1$ for the ratio between the average looseness parameter α of the anisotropic potentials and the Morse parameter of the dissociating bond β. These simplified potentials have been found appropriate to reproduce very well a large number of important recombination and dissociation rate coefficients [42].

Table 8
Calculated rate coefficients k_∞^{PST} and k (in cm^3 molecule^{-1} s^{-1}) and f_{rigid} values for the reactions F + SCl → SF + Cl, F + SF_2Cl → SF_3 + Cl and F + SF_4Cl → SF_5 + Cl.

T (K)	F + SCl			F + SF_2Cl			F + SF_4Cl		
	k_∞^{PST}	f_{rigid}	k	k_∞^{PST}	f_{rigid}	k	k_∞^{PST}	f_{rigid}	k
200	5.34×10^{-11}	0.647	3.47×10^{-11}	4.84×10^{-11}	0.539	2.61×10^{-11}	3.76×10^{-11}	0.176	6.60×10^{-12}
300	5.42×10^{-11}	0.647	3.51×10^{-11}	5.33×10^{-11}	0.537	2.86×10^{-11}	4.12×10^{-11}	0.175	7.20×10^{-12}
400	5.32×10^{-11}	0.644	3.43×10^{-11}	5.63×10^{-11}	0.535	3.01×10^{-11}	4.35×10^{-11}	0.174	7.56×10^{-12}
500	5.20×10^{-11}	0.642	3.34×10^{-11}	5.86×10^{-11}	0.533	3.12×10^{-11}	4.51×10^{-11}	0.173	7.81×10^{-12}

Table 9
Calculated rate coefficients k_∞^{PST} and k (in cm^3 $molecule^{-1}$ s^{-1}) and f_{rigid} values for the reactions Cl + SF → SFCl, Cl + SF_3 → SF_3Cl and Cl + SF_5 → SF_5Cl.

T (K)	Cl + SF			Cl + SF_3			Cl + SF_5		
	k_∞^{PST}	f_{rigid}	k_∞	k_∞^{PST}	f_{rigid}	k_∞	k_∞^{PST}	f_{rigid}	k_∞
200	4.78×10^{-11}	0.900	4.30×10^{-11}	4.29×10^{-11}	0.670	2.87×10^{-11}	7.05×10^{-11}	0.101	7.10×10^{-12}
300	5.02×10^{-11}	0.896	4.50×10^{-11}	4.90×10^{-11}	0.668	3.27×10^{-11}	7.98×10^{-11}	0.101	8.02×10^{-12}
400	5.06×10^{-11}	0.893	4.52×10^{-11}	5.33×10^{-11}	0.665	3.46×10^{-11}	8.61×10^{-11}	0.100	8.64×10^{-12}
500	5.04×10^{-11}	0.890	4.48×10^{-11}	5.65×10^{-11}	0.663	3.75×10^{-11}	9.06×10^{-11}	0.100	9.08×10^{-12}

The SACM/CT model is well documented, such that details of the calculations are omitted for simplicity [26]. Moreover, detailed theoretical studies for the association reactions of FC(O)O radicals with F [44] and Cl [45] atoms can be found elsewhere. The required molecular parameters were extracted (vibrational frequencies and energetics) or calculated (rotational constants) from the data listed in Tables 1 and 2. The computed k_∞^{PST}, f_{rigid} and k values for the bimolecular reactions F + SCl → SF + Cl, F + SF_2Cl → SF_3 + Cl and F + SF_4Cl → SF_5 + Cl are listed in Table 8. The calculated f_{rigid} factors are in the normal range of values expected for reactions of atom + polyatomic radicals and exhibit small temperature dependencies [26,44,45]. The reduction observed in f_{rigid} with the mayor radical complexity is determined by the interplay established along the reaction coordinate, between the increase of the rovibrational adiabatic energy of the transitional channels and the decrease of the electronic potential energy [26,46]. For the F + SCl reaction, the bending is the only transitional mode, while for F + SF_2Cl there are two transitional modes: the Cl–S–F_3 and the F_3–S–$F_{1,2}$ bends (see Table 2). Finally, for the F + SF_4Cl process the evolution of the degenerated S–F_{1-3} and S–F_{2-4} waging modes determines the reaction kinetics. In general, reactions of large radicals with small rotational constants and high transitional modes values exhibit the smaller rate coefficients [47].

Table 9 shows the results of a high-pressure limit kinetic analysis of the association reactions Cl + SF → SFCl; Cl + SF_3 → SF_3Cl and Cl + SF_5 → SF_5Cl. Features similar to those observed for the above discussed F atom reactions are here apparent. The rate coefficients derived for the Cl atom reactions are somewhat larger that those calculated for the F atom reactions. In addition, the k_∞ value derived for Cl + SF_5 → SF_5Cl is similar to the estimated for the related process F + SF_5 → SF_6 [48]. The results found suggest that the studied Cl atom reactions could be, in principle, employed to prepare efficiently the SFCl, SF_3Cl and SF_5Cl molecules. All the resulting rate coefficients fall within the range of the experimental values found for other association reactions of F atoms with $FS(O_2)O$ [49], FCO [50], FC(O)O [44] and $FC(O)O_2$ [51] radicals and of Cl atoms with $FS(O_2)O$ [45] and FC(O)O [52] radicals.

4. Conclusions

DFT and high-level *ab initio* composite models have been employed to determine accurate standard enthalpies of formation and bond dissociation enthalpies at 298 K for all members of the SF_xCl (x = 0–5) series. The computed $\Delta H_{f,298}^\circ$ best values for SCl, SFCl, $SF_2Cl(C_1)$, $SF_3Cl(C_s)$, $SF_4Cl(C_s)$ and SF_5Cl are 28.0, −36.0, −64.2, −134.3, −158.2, −237.1 kcal mol^{-1}. The SACM/CT analysis performed for bimolecular reactions of F and Cl atoms with selected radicals of the studied series indicate that all these are fast processes and could be employed to generate quantitatively other fluorine-contained molecules and radicals.

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