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Gaseous Trihalogen Cations. Formation, Structure and Reactivity of Cl_3^+ and Cl_2F^+ Ions from a Joint ab Initio and FT-ICR Study

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Gaseous Cl_3^+ ions were obtained by two convenient routes, namely Cl^+ transfer to chlorine from Cl_2H^+ or $Cl_2^{\cdot+}$ ions, whereas Cl_2F^+ was prepared upon fluorination of chlorine by XeF^+. The structure and the stability of the trihalogen cations were investigated by reactive probing, utilizing FTICR mass spectrometry to survey their reactivity, in particular Cl^+ transfer processes toward selected nucleophiles. The structure, relative stability, and dissociation enthalpies of Cl_3^+ and Cl_2F^+ were investigated by computational methods based on density functional theory up to the CCSD(T)/cc-pVQZ//B3LYP/6-311++G(3df, 3pd) level. The results show that an A_1 singlet of C_{2v} symmetry is the global minimum on the Cl_3^+ potential energy surface. Consistent with earlier results, the asymmetric bent $[Cl{-}Cl{-}F]^+$, also an A_1 singlet, is more stable by 44.3 kcal mol^{-1} at 298 K than the symmetric isomer of $[Cl{-}F{-}Cl]^+$ connectivity. By combining theoretically computed dissociation enthalpies with available thermochemical data the heats of formation of Cl_3^+ and Cl_2F^+ cations, in their ground state, can be estimated to be 251.5 ± 5 and 245.0 ± 5 kcal mol^{-1} at 298 K. Comparison of the Cl^+ and F^+ binding energies to simple halogenated molecules shows an excellent linear correlation, which is not the case when the comparison is extended to the proton affinities. The different factors that influence the stability of protonated and halogenated adducts are briefly discussed.

Introduction

Decades of experimental and theoretical work have yielded a rich harvest of information on homo- and hetero-trihalogen cations, in particular Cl_3^+ and Cl_2F^+, whose interest stems, inter alia, from their role in electrophilic halogenation.[1−6] The structure of Cl_2F^+ has been the focus of a lively controversy fueled by conflicting evidence on the relative stability of the $[Cl{-}Cl{-}F]^+$ and $[Cl{-}F{-}Cl]^+$ isomers.[7−14] The Cl_3^+ and Cl_2F^+ cations have been characterized in the solid state by the spectroscopic study of their AsF_6^- salts, but are unstable in solution, even in superacid media.[7,8] In striking contrast with the wealth of information gathered in condensed phases, very little is known on gaseous trihalogen cations, except for the detection of Cl_3^+ as a secondary, unreactive product reported in a study on the reactions of rare gas ions with Cl_2.[15]

As a continuation of a previous study on hydrohalonium ions,[16] we have investigated the formation, structure, stability, and reactivity of gaseous Cl_3^+ and Cl_2F^+ ions by FTICR mass spectrometry and theoretical methods. An additional motivation for this study is the potential value of its thermochemical results to the evaluation of the Cl^+ affinity of simple molecules containing halogen atoms, and its correlation with other relevant quantities, such as F^+ affinity, ionization potential (IP), and proton affinity (PA).

Experimental Section

FTICR mass spectrometry. All the gases and the other chemicals utilized in the FTICR experiments were research-grade products from commercial sources with a stated purity in excess of 99.99 mol % and were used without further purification. HCN and HN_3 were obtained from the reaction of stearic acid with KCN and NaN_3. All the experiments were performed using a Bruker Spectrospin Apex 47e instrument, equipped with an external chemical ionization (CI) source, a pulsed valve, a cylindrical 'infinity' cell,[17] and a Bayard−Alpert ionization gauge, whose readings were corrected for its different sensitivity to the gases used.[18] The ions generated in the external ion source were transferred into the ICR cell and isolated by the standard procedure based on the "soft" ejection of all the unwanted ions, care being taken to prevent appreciable excitation of the selected species. When required, the ions were thermalized by collision with Ar introduced for a short time (20 ms) via the pulsed valve to a peak pressure of ca. 10^{-5} Torr. The ions were then allowed to react with the neutral reagent continuously admitted into the cell in order to reach stationary pressures ranging from 1×10^{-8} to 4×10^{-7} Torr. The pseudo-unimolecular rate constants were derived from the slope of the plot of the experimental intensities vs the reaction time. The bimolecular rate constants were then calculated taking into account the number density of the neutral molecules, deduced from the pressure in the cell. Finally, the collisional efficiencies were evaluated by dividing the bimolecular rate constants by the collision rate constants k_{coll}, estimated using the ADO theory, or the trajectory algorithm.[19]

Computational Details. Density functional theory, using the hybrid[20] B3LYP[21] functional, was used to localize the stationary

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points of the investigated systems and to evaluate vibrational frequencies. Single point energy calculations at the optimized geometries were performed using the coupled-cluster single and double excitation method[22] with a perturbational estimate of the triple excitations according to the CCSD(T) approach.[23] Zero point energy (ZPE) corrections evaluated at B3LYP level were added to the CCSD(T) energies. The 0 K total energies of the species of interest were corrected to 298 K by adding translational, rotational, and vibrational contributions. The absolute entropies were calculated by using standard statistical−mechanistic procedures from scaled harmonic frequencies and moments of inertia relative to B3LYP/6-311++G(3df,3pd) optimized geometries. All the B3LYP calculations were performed using the 6-311G++(3df) basis set,[24] whereas the CCSD(T) calculations were done using both the 6-311G++-(3df,3pd) basis set and the cc-pVQZ correlation-consistent polarized valence set developed by Dunning and co-workers,[25] the choice of the latter sets being suggested by the results of previous calculations of the PA of Cl_2 and ClF.[16] For the excited states of Cl_3^+, Cl−Cl−F$^+$, and Cl−F−Cl$^+$, the CCSD(T) calculations were performed using only the smaller basis set. All calculations were carried out utilizing Gaussian 94. [26]

Experimental Results

Cl_3^+. The ion was generated in the external CI source of the FTICR spectrometer, operated at pressures up to 10^{-5} Torr, by two alternative reactions, whose product was unambiguously identified by accurate mass measurements.

The first route utilizes Cl_2H^+, conveniently obtained by CH_4/CI of Cl_2 and recently characterized as an effective gaseous chlorinating agent[16]

$$Cl_2H^+ + Cl_2 \rightarrow Cl_3^+ + HCl \qquad (1)$$

This formation pathway of Cl_3^+, first observed as a side reaction in the study of the prototropic equilibrium involving Cl_2 and HCl,[16] was firmly established by allowing the Cl_2H^+ ion, prepared in the external source and isolated by selective-ejection techniques, to react with chlorine in the resonance cell. Reaction 1 is relatively fast, its rate coefficient being $2.6 \pm 0.3 \times 10^{-10}$ cm^3 s^{-1} molecule^{-1} at 298 K, which corresponds to a collisional efficiency of ca. 30%.[16]

Cl_3^+ ions are formed as well in the CI of neat chlorine according to the process

$$Cl_2^{+\bullet} + Cl_2 \rightarrow Cl_3^+ + Cl \qquad (2)$$

furthered by $Cl_2^{+\bullet}$, the most abundant primary ion. Consistent with the endothermic character of the process suggested by previous observations,[27] FTICR experiments showed that $Cl_2^{+\bullet}$ ions produced in the external source, isolated and thermalized, react with Cl_2 at a very low rate, pointing to the presence of a sizable barrier to reaction 2. Its endothermic character was verified by utilizing a technique whereby the translational energy of the reagent ions is increased by the application of a radio frequency signal at the appropriate cyclotron frequency. The translationally excited ions are then allowed to interact with the neutral reagent for a chosen period of time, followed by detection of the charged products.[28] In the case of interest, application of the above technique showed that the rate of reaction 2 *increases* with the kinetic energy of $Cl_2^{+\bullet}$ ions, consistent with the trend typical of endothermic processes. Accordingly, we conclude that reaction 2 is moderately endothermic for ground-state reagents, and its occurrence in the CI source must be traced to those $Cl_2^{+\bullet}$ ions that are formed with excess internal energy in the primary electron-impact ionization.

TABLE 1: Cl^+ Transfer Reactions from Cl_3^+ and Cl_2F^+ to Gaseous Nucleophiles[a]

nucleophile	Cl_3^+	Cl_2F^+
H_2	no	very slow
HCl	no	slow
Xe	no	slow
Cl_2		fast
CH_4	fast	
CO	fast	fast
CH_3CN	fast	fast
HCN		fast
C_2H_2		fast
HN_3		fast
C_2H_4		no
NH_3	fast	
NO	charge transfer	
NF_3		no
N_2O		no
N_2	no	
O_2	no	
C_6H_6		charge transfer

[a] The efficiencies of reactions are classified on the basis of their coefficients as follows: fast ($k > 10^{-11}$ cm^3 s^{-1} molecule^{-1}), slow ($10^{-11} > k < 10^{-10}$ cm^3 s^{-1} molecule^{-1}), very slow ($k < 10^{-11}$ cm^3 molecule^{-1}).

The reactivity of Cl_3^+ toward selected nucleophiles, Nu, was surveyed by monitoring the occurrence of the Cl^+-transfer reactions

$$Cl_3^+ + Nu \rightarrow NuCl^+ + Cl_2 \qquad (3)$$

and measuring their rate coefficients. To this end, Cl_3^+ ions, generated in the ion source by reaction 1 or 2, were isolated and transferred into the resonance cell containing the nucleophile. Reaction 3 does not occur when the nucleophile is characterized by a Cl^+ affinity lower than that of Cl_2, or by a low ionization potential, which allows predominant charge-exchange.

Cl_2F^+. In the condensed phase, Cl_2F^+ has been obtained from the coordination of Cl^+ to ClF.[7,8] We followed a different synthetic route, based on the oxidative fluorination process

$$XeF^+ + Cl_2 \rightarrow Cl_2F^+ + Xe \qquad (4)$$

corresponding to a formal F^+ transfer from Xe to Cl_2. As recently reported,[29] XeF^+ is the most abundant ion in the CI spectra of XeF_2, and the XeF_2/CI of Cl_2 yields Cl_2F^+ ions, whose isotopomers were unambiguously identified by accurate mass measurements. A recently computed scale of the oxidizing strength of some fluorinators[30] predicts reaction 4 to be energetically favored owing to the higher F^+ affinity of chlorine than of xenon. Actually, reaction 4 does occur, albeit at a slow rate, its measured rate constant amounting to $3.5 \pm 0.5 \times 10^{-11}$ cm^3 s^{-1} molecule^{-1},[31] whereas the reverse process, i.e., the reaction with xenon of Cl_2F^+ ions prepared in the external source was never observed, the only process occurring being instead the Cl^+-transfer

$$Cl_2F^+ + Xe \rightarrow XeCl^+ + ClF \qquad (5)$$

This observation is consistent with the general reactivity of Cl_2F^+, that behaves as a Cl^+ donor to various nucleophiles (Table 1).

Cl^+ Ion-Transfer Reactions. The study of the Cl^+ exchange processes

$$NuCl^+ + Nu_1 \rightarrow Nu_1\,Cl^+ + Nu \tag{6}$$

was extended to several nucleophiles in the attempt to evaluate their relative Cl^+ ion affinities. A quantitative study is hampered by several factors that prevent accurate measurement of the required thermochemical quantities, namely the Cl^+ binding energies (BE) to the neutral ligands. Application of the most reliable approach, the FTICR equilibrium-method, is prevented by the excessive spacing of the BE of the nucleophiles investigated. This prevents as well the evaluation of the K_6 equilibrium constant according to the kinetic method, from the k_6/k_{-6} ratio of the rate coefficients for the forward and the reverse Cl^+ transfer processes. Even the less accurate "bracketing" approach is adversely affected by the incursion of side reactions, in particular charge exchange. Since, however, the "bracketing" technique appeared the only viable approach, FTICR experiments were undertaken whereby $NuCl^+$ ions, generated in the external source, collisionally thermalized and mass-selected, were allowed to react with the other nucleophile, Nu_1. Occurrence of reaction 6, or of the reverse process in a mirror experiment involving the reaction of Nu_1Cl^+ ions with neutral Nu molecules, provides a criterion to establish which nucleophile has the higher Cl^+ BE. Systematic application of the "bracketing" technique led to the qualitative results summarized in Table 2.

TABLE 2: Cl^+ Transfer Reactions from $NuCl^+$ Ions to Nu_1 Nucleophiles[a]

	H_2	HCl	Xe	Cl_2	CH_4	CO	CH_3CN	NH_3
Cl_2F^+	slow	yes	yes	yes		yes		
H_2Cl^+				no		no		
Cl_2H^+	yes		yes	yes	yes	yes		
$XeCl^+$	no	yes						
Cl_3^+	no	no	no		yes	yes	yes	yes
CH_4Cl^+				no		no	no	
$COCl^+$				no	no		yes	yes
CH_3CNCl^+					no	no		yes
NH_3Cl^+				no		no	no	

[a] The efficiences of reactions are classified on the basis of their coefficients as follows: fast ($k > 10^{-11}$ cm^3 s^{-1} molecule^{-1}), slow ($10^{-11} > k < 10^{-10}$ cm^3 s^{-1} molecule^{-1}), very slow ($k < 10^{-11}$ cm^3 s^{-1} molecule^{-1}).

Theoretical Results

Table 3 reports the bond lengths, vibrational frequencies and energies for the Cl_2, Cl_2^+, ClF, ClF^+ diatomics. For comparison also the experimental bond lengths and frequencies are reported.[32] The optimized bond distances agree with the experimental values within 0.02 Å. As to the vibrational frequencies the agreement with experiment is also reasonable and slightly better than that obtained with the MP2/6-31G(d) calculations.[14] The frequencies computed for Cl_2 and Cl_2^+ are comparable to those recently obtained at CCSD(T) level.[33] Table 4 reports vibrational frequencies and energies of Cl_3^+, $[Cl-Cl-F]^+$, and $[Cl-F-Cl]^+$ in their ground and first excited states, whose geometrical parameters are illustrated in Figure 1. The vibrational frequencies of Cl_3^+ and Cl_2F^+ in their ground state compare well with the experimental values,[7,8] and with those recently computed for Cl_3^+ at the CCSD(T) level.[33] Table 5 shows the $\Delta H°_{298}$ changes of the dissociation reactions of Cl_3^+ and Cl_2F^+ into X_2^+, X^+, XY^+, and Y^+ ($X = Cl$, $Y = F$), whereas Table 6 shows the $\Delta H°_{298}$ changes of several Cl^+ transfer reactions calculated both at the B3LYP and the CCSD(T) levels.

Discussion

Structure of Cl_3^+ and Cl_2F^+ Ions. The theoretical results show that the global minimum on the Cl_3^+ energy surface is the singlet **I** of C_{2v} symmetry shown in Figure 1, whose geometry is in reasonable agreement with those from earlier theoretical studies,[10−12,33] the differences being ascribed essentially to the different methodology employed. The lowest excited triplet state, $^3A''$, has the asymmetric structure **III**, located 30 kcal mol^{-1} above the ground state, whereas the symmetric $^3B_1$ state **II** is almost degenerate with the lowest $^3A''$ state, being higher by less than 3 kcal mol^{-1} at the CCS(D)T/6-311++G(3df) level. The much smaller previously reported[11] singlet−triplet energy difference, only 2.5 kcal mol^{-1}, is likely arise from the neglect of the correlation effects.

Conflicting reports on the structure of Cl_2F^+ arose out of early spectroscopic evidence[7] assigning the Cl_2F^+ ion a symmetric bent C_{2v} structure, unique in having the most electronegative atom as the central one. A later study reversed the above conclusion, providing evidence for the higher stability of the asymmetric C_s structure,[8] also supported by high-level theoretical calculations.[14] The chlorinating ability of Cl_2F^+ apparent from Tables 1 and 2 is not particularly informative from the structural standpoint, since both the $[Cl-Cl-F]^+$ and $[Cl-F-Cl]^+$ isomers are expected to undergo Cl^+ transfer. Nevertheless, the specific reaction pathway (4) followed to generate Cl_2F^+ is expected to form ions retaining the Cl−Cl bond present in the Cl_2 precursor. Therefore the ion assayed in our mass spectrometric experiments is most likely the asymmetric $[Cl-Cl-F]^+$ isomer, its chlorinating ability reflecting the Cl^+ ion affinity of the chlorine atom of ClF. Our theoretical results independently confirm that the stability of the asymmetric $[Cl-Cl-F]^+$ ion exceeds that of the $[Cl-F-Cl]^+$ isomer by as much as 44.3 kcal mol^{-1}. This difference computed at the CCSD(T)/cc-pVQZ level compares well with the value of 43.0 kcal mol^{-1} previously reported by Frenking et al. [14] Like Cl_3^+, also $[Cl-Cl-F]^+$ and $[Cl-F-Cl]^+$ display singlet ground states, denoted as **IV** and **VI**, respectively, in Figure 1. For $[Cl-Cl-F]^+$, the first excited state **V** is located 35.2 kcal mol^{-1} above the ground state **IV**, whereas the $^3A''$ state of $[Cl-F-Cl]^+$ characterized by the asymmetric structure **VIII**, is only 9.6 kcal mol^{-1} above the ground state **VI**. A second $^3B_1$ triplet state, **VII**, is located 21.3 kcal mol^{-1} above the ground state.

Thermochemical Results. Inspection of Table 2 shows that Cl^+ transfer from Cl_3^+ to HCl, namely the reverse of reaction 1, does not occur. This suggests that reaction 1 is appreciably exothermic and hence the Cl^+ BE of Cl_2 exceeds that of HCl, estimated to be 71.6 ± 2 kcal mol^{-1} from the heat of formation of Cl_2H^+.[16] On the basis of the endothermic character of reaction 2 and available thermochemical data,[34] the experimental heat of formation of Cl_3^+ can roughly be located in the 246 to 256 kcal mol^{-1} range. The heat of formation of Cl_3^+ can theoretically be derived from the computed endothermicity of reaction 8 reported in Table 5, corresponding to the binding energy of Cl^+ to Cl_2. Here and throughout the paper, the halonium ion affinities are referred to the halogen cations in their ground state. The value computed at the CCSD(T) level of theory, using the cc-pVQZ basis set, is 73.2 kcal mol^{-1}. This is not fully consistent with the experimental evidence pointing to a difference between the Cl^+ affinities of Cl_2 and HCl larger than 0.6 kcal mol^{-1}, although the estimated 2 kcal mol^{-1} uncertainty must be considered. Moreover, problems such as spin contamination are known to affect the accuracy of theoretical calculations concerning processes involving multiplicity changes, as those reported in Table 5. A more reliable theoretical value, unaffected by these problems, is the computed $\Delta H°_{298}$ change of reaction 1 reported in Table 6, that directly gives the difference between the Cl^+

TABLE 3: Optimized Geometries at the B3LYP/6-311++G(3df) Level, Energies and Frequencies of Cl_2, Cl_2^+, FCl, and FCl^+ [a,b]

	Cl_2 ($^1\Sigma_g^+$)	Cl_2^+ ($^2\Pi_g$)	FCl ($^1\Sigma^+$)	FC^+ ($^2\Pi$)
r_e	2.010 (1.988)	1.908 (1.892)	1.642 (1.628)	1.544 (1.526)
ν	541 (560)	637 (646)	785 (786)	931 (870.912)
E_{B3LYP}	−920.424713	−920.006588	−560.026738	−559.563374
ZPE[c]	0.001232	0.001450	0.001787	0.002121
$E_{CCSD(T)/6-311++G(3df)}$	−919.409495	−918.991918	−559.372395	−558.912092
$E_{CCSD(T)/cc-pVQZ}$	−919.475689	−919.053737	−559.437859	−558.974462

[a] Bond lengths in Å, angles in degrees, total energies in hartree, vibrational frequencies in cm^{-1}. [b] Experimental values in parentheses.[32] [c] Zero point energies.

TABLE 4: Energies and Frequencies of Cl_3^+, Cl−Cl−F^+ and Cl−F−Cl^+ at the B3LYP/6-311++G(3df) Level[a]

	Cl_3^+			Cl−Cl−F^+		Cl−F−Cl^+		
	$^1A_1$	$^3B_1$	$^3A''$	$^1A'$	$^3A''$	$^1A_1$	$^3B_1$	$^3A''$
bending	195 (0.7)	168 (0.1)	62 (0.2)	263 (4.9)	211 (2.8)	209 (0.5)	160 (2.4)	57 (0.7)
symmetric stretch	484 (0.6)	353 (0)	110[b] (2.1)	540[b] (19.9)	327[b] (13.5)	538 (7.0)	372 (2.4)	125[c] (2.4)
asymmetric stretch	481 (34.9)	142 (9.7)	571[b] (37.2)	760[c] (66.0)	568[c] (88.2)	461 (6.5)	1.506 (16989.3)	809[c] (93.3)
E_{B3LYP}	−1380.237450	−1378.201812	−1378.201745	1018.829892	−1018.789086	−1018.756848	−1018.740315	−1018.770751
ZPE[d]	0.002642	0.001508	0.001694	0.003562	0.002520	0.002750	0.004644	0.002257
$E_{CCSD(T)/6-311++G(3df)}$	−1380.716728	−1378.664176	−1378.668800	1018.669313	−1018.613137	−1018.601271	−1018.567262	−1018.585932
$E_{CCSD(T)/cc-pVQZ}$	−1378.813087			1018.766586		1018.695997		

[a] IR intensities (km/mol) in parentheses; total energies in hartree; vibrational frequencies in cm^{-1}. [b] Cl−Cl stretching mode. [c] Cl−F stretching mode. [d] Zero point energy.

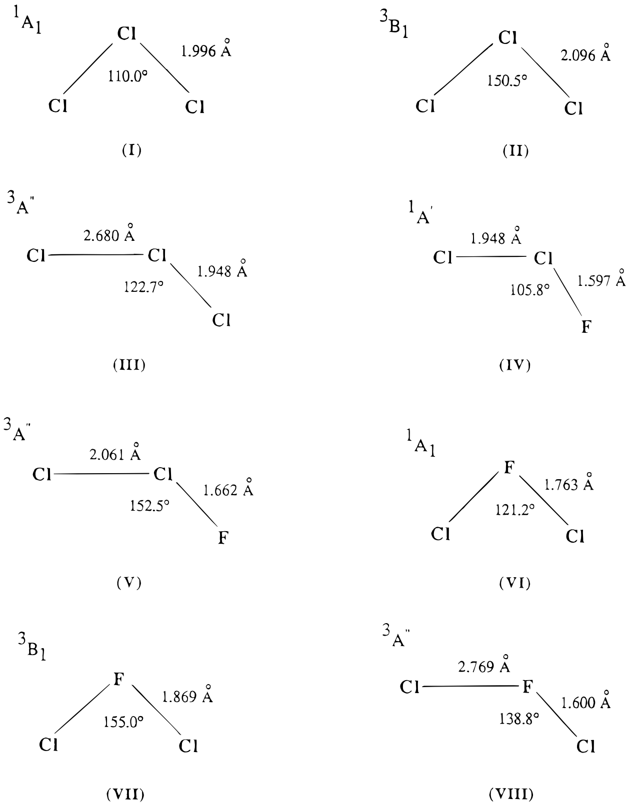

Figure 1. Optimized geometries of the investigated species. Bond lengths in Å, angles in degrees.

TABLE 5: Dissociation Enthalpies (kcal mol^{-1}) at 298 K of Cl_3^+ and Cl−Cl−F^+

	B3LYP 6-311++G(3df)	CCSD(T) 6-311++G(3df)	CCSD(T) cc-pVQZ
(7) $Cl_3^+ \rightarrow Cl_2^+ + Cl$	39.1	39.0	41.3
(8) $Cl_3^+ \rightarrow Cl_2 + Cl^+$	78.0	70.1	73.2
(9) $Cl_2F^+ \rightarrow Cl_2^+ + F^+$	38.1	36.9	38.7
(10) $Cl_2F^+ \rightarrow ClF^+ + Cl$	185.2	172.7	172.8
(11) $Cl_2F^+ \rightarrow ClF^+ + Cl$	61.4	59.2	61.8
(12) $Cl_2F^+ \rightarrow ClF + Cl^+$	71.9	63.5	67.7

TABLE 6: Enthalpy Changes (kcal mol^{-1}) at 298 K of Selected Reactions

	B3LYP 6-311++G-(3df)	CCSD(T) 6-311++G-(3df)	CCSD(T) cc-pVQZ
(1) $Cl_2H^+ + Cl_2 \rightarrow Cl_3^+ + HCl$	−6.5	−5.6	−4.9
(2) $Cl_2^+ + Cl_2 \rightarrow Cl_3^+ + Cl$	16.1	14.1	14.6
(13) $Cl_2F^+ + Cl_2 \rightarrow Cl_3^+ + ClF$	−6.1	−6.6	−5.6
(14) $Cl_2F^+ + HCl \rightarrow Cl_2H^+ + ClF$	0.4	−1.0	−0.6

BE of HCl and of Cl_2. In this way, consistent with the experimental evidence, reaction 1 is computed to be exothermic, by 4.9 kcal mol^{-1} at the CCS(D)T/cc-pVQZ level. Utilizing the experimental Cl^+ affinity of HCl and the theoretically computed $\Delta H°$ (1) change (Table 6), one can assign a value of 76.5 ± 3 kcal mol^{-1} to the Cl^+ BE of Cl_2, and hence a heat of formation of Cl_3^+ can be derived of 251.5 kcal mol^{-1}, that falls within the experimentally defined range (vide supra), and that, given the many sources of error, is conservatively estimated with an uncertainty range of ±5 kcal mol^{-1}. This value combined with available thermochemical data,[34] allows the endothermicity of reaction 2 to be estimated to amount to 15.5 ± 5 kcal mol^{-1}, in good agreement with the directly computed value of 14.6 kcal mol^{-1} reported in Table 6.

As to Cl_2F^+, experimental evidence points to a Cl^+ affinity of ClF very close to that of HCl. The occurrence of the Cl^+ ion transfer reaction,

$$Cl_2F^+ + Cl_2 \rightarrow Cl_3^+ + ClF \qquad (13)$$

a side reaction of the fluorination process (4), suggests that Cl_2 has a higher Cl^+ affinity than ClF. Furthermore, the occurrence of Cl^+ transfer from Cl_2F^+ to HCl (see Table 2) indicates that the Cl^+ BE to Cl_2 exceeds by an approximately equal extent those of ClF and HCl. Consistent with the experimental evidence, reactions 1 and 13 are computed at the CCSD(T)/cc-pVQZ level to have nearly the same exothermicity, and hence the Cl^+ transfer from Cl_2F^+ to HCl appears but slightly exothermic. Combining the experimental Cl^+ affinity of HCl as the anchor value with available thermochemical data,[34] one can obtain a Cl^+ BE of the chlorine atom of ClF of 71.0 ± 3 kcal mol^{-1} and a heat of formation of $[Cl-Cl-F]^+$ of 245 ± 5 kcal mol^{-1}.

Halonium Ion Affinity and PA Trends. From Table 2, the Cl^+ BE of the nucleophiles investigated increase in the order

$$\mathrm{ClF} \leq \mathrm{HCl} \leq \mathrm{Xe} < \mathrm{Cl_2} < \mathrm{CO} < \mathrm{CH_3CN} < \mathrm{NH_3}$$

More quantitative data concerning very simple halogenated molecules, i.e., HF, ClF, HCl, and Cl_2, are reported in Table 7, that summarizes their PA, IP, and Cl^+ and F^+ BE, derived from the heats of formation of the corresponding adducts. Despite their uncertainty range, especially large when the heat of formation is obtained combining experimental and theoretical data, the estimated Cl^+ and F^+ BE are sufficiently spaced to allow meaningful comparison. The following trends emerge from the data of Table 7:

$$\begin{array}{rl} \mathrm{PA} & \mathrm{HF} < \mathrm{ClF} < \mathrm{Cl_2} < \mathrm{HCl} \\ \mathrm{Cl^+\ BE} & \mathrm{HF} < \mathrm{ClF} \leq \mathrm{HCl} < \mathrm{Cl_2} \\ \mathrm{F^+\ BE} & \mathrm{HF} < \mathrm{HCl} \leq \mathrm{ClF} < \mathrm{Cl_2} \end{array}$$

It is apparent that, whereas Cl^+ and F^+ BE display a good linear correlation ($r = 0.9974$), this is not the case when they are related to PA. As an example, both X^+ cations, (X = Cl, F) have nearly the same BE to ClF and HCl, despite the significantly larger PA of the latter (Table 7). It is also apparent that the PA and the (X^+) BE follow opposite trends in passing from HCl to Cl_2. These findings point to the operation of different factors affecting the strength of the bonds formed by H^+ and X^+ cations with halogenated ligands. From the limited set of available data the (X^+) BE appears to reflect the ability of the ligand *molecule* as a whole to accommodate the positive charge upon addition of the X^+ cation. This emerges, inter alia, from the fairly linear dependence of the F^+ and Cl^+ BE on the IP of the ligands, characterized by correlation coefficients of 0.978 and 0.980, respectively, and accounts for the increase of the X^+ BE with the number of Cl atoms, since they are the most electron-rich and polarizable ones in the molecules of interest. The PA trend appears instead to reflect the electron-donor ability of the specific *atom* that undergoes protonation, a property that depends on its intrinsic electronegativity and the effects of the substituents. Thus, Cl_2 is more basic than ClF because the electron density of the Cl atom undergoing protonation is lowered to a much larger extent by the F than by the Cl substituent. In the same way, the electron-withdrawing effect of a more electronegative substituent such as Cl with respect to H accounts for the lower electron-donating ability of the chlorine atom in Cl_2 than in HCl, and hence for the larger PA of the latter ligand. These considerations can be epitomized utilizing the hard and soft acids and bases (HSAB) concept, in that it can be expected that a hard acid such as H^+ binds more effectively to the relatively hard bases as HCl and ClF than to the relatively softer Cl_2 base, characterized by a higher size and polarizability and more readily oxidable. The same considerations hold for the large and polarizable atom of xenon, whose Cl^+ affinity in the qualitative scale results higher than expected from its low PA. Finally, the same arguments may help in explaining the higher stability of $[Cl-Cl-F]^+$ than that of the $[Cl-F-Cl]^+$ isomer, in that the soft Cl^+ cation is expected to preferentially bind to the Cl atom, the softer basic center of the FCl molecule.

It should be noted that neither the chlorination of H_2 nor that of CH_4 have been taken into account in the construction of the above scales. As a matter of fact, the reactive probing of the structure of H_2Cl^+ and CH_4Cl^+ products has shown that neither of them displays a chlorinating ability, behaving instead as pure Brønsted acids even toward molecules of high Cl^+ affinity, suggestive of the $[H-Cl-H]^+$ and $[H-Cl-CH_3]^+$ connectivity.[35] As a consequence, these products cannot be regarded as adducts where Cl^+ is bound to a single nucleophilic center. This and the likely occurrence of an activation barrier for the two reactions justify their neglect.

TABLE 7: Thermochemical Properties of Simple Halogenated Molecules

	PA[a] (kcal mol^{-1})	(Cl^+) BE (kcal mol^{-1})	(F^+) BE (kcal mol^{-1})	IP[a] (eV)
HF	115.7	25.2[d]	68.9[b]	16.04
ClF	121.0[d]	71.0 ± 3[e]	166.8[c]	12.65
HCl	133.1	71.6[d]	165.9[d]	12.75
Cl_2	131.4[d]	76.5 ± 3[e]	175.7 ± 3[e]	11.48

[a] (PA = proton affinity, IP = ionization potential; otherwise stated the thermochemical data are from ref 34. [b] Ref 36. [c] Ref 30. [d] Ref 16. [e] This work.

Conclusions

Two convenient routes have been utilized for the preparation of gaseous Cl_3^+ and Cl_2F^+ ions, whose structure and reactivity have been investigated with a combination of mass spectrometric and density functional methods. The heats of formation of Cl_3^+ and Cl_2F^+ in their ground state, obtained by combining the theoretical results reported in Table 6 with the experimentally estimated Cl^+ affinity of HCl, are estimated to be 251.5 ± 5 and 245.0 ± 5 kcal mol^{-1}, respectively, corresponding to Cl^+ BE to Cl_2 and ClF, of 76.5 ± 3 and 71.0 ± 3 kcal mol^{-1}, respectively. Comparison of the F^+ and Cl^+ affinity of simple halogenated molecules with their PA shows that the factors affecting the halogen cations BE and the proton BE to the ligands are different. Based on the limited set of available data, it can tentatively be suggested that the PA depends on the electron-donating ability of the specific atom undergoing protonation, which in turn reflects its intrinsic electronegativity and the effects of the substituents. The Cl^+ and F^+ BE appear instead to depend on the ability of the ligand molecule to accommodate the positive charge imparted by the addition of the cation. In this case, the stability of the charged adduct is enhanced by the size of the ligand and its polarizability.

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