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Elemental Chlorine and Chlorine Fluoride: Theoretical and Experimental Proton Affinity and the Gas Phase Chemistry of Cl_2H^+ and $FClH^+$ Ions

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The chemistry of the title cations was investigated in the gas phase by Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry and by theoretical methods. Cl_2H^+ (**1**) was obtained from the protonation of Cl_2 by gaseous Brønsted acids and the chlorination of HCl by Cl_2F^+ and $XeCl^+$. The proton affinity (PA) of Cl_2 measured by the FT-ICR equilibrium method is 131.4 ± 1 kcal mol^{-1} at 298 K, which compares with the 132.0 kcal mol^{-1} value computed at the CCSD(T) level of theory. **1** has the Cl−Cl−H connectivity, as indicated by its 2-fold reactivity as a Brønsted acid and a chlorinating agent, and confirmed by the theoretical results. The $FClH^+$ cation was obtained from the fluorination of HCl by XeF^+ and its most stable protomer (**2**) has the F−Cl−H connectivity, as shown by its behavior as a pure Brønsted acid and by the theoretical results that identify **2** as the global minimum, whereas protomer **3**, having the H−F−Cl connectivity, is computed to be less stable by 5.0 kcal mol^{-1} at the CCSD(T) level of theory, respectively. For lack of sufficiently accurate experimental data, the best estimate of the PA of ClF is 121.0 kcal mol^{-1}, computed at the CCSD(T) level of theory and referred to protonation of the Cl atom.

Introduction

Polyhalogen cations have been the subject of extensive study in solution and in the solid phase, owing to their fundamental interest and to the role played in a variety of electrophilic reactions of cationic complexes formed by halogen molecules with strong acids.[1−3] By contrast, little is known on gaseous polyhalogen cations. A case in point is Cl_2H^+, the most simple homopolychlorine cation, whose only experimental study, reported in a short communication by Hop and Holmes,[4] concerns its formation from the corresponding anion by charge-reversal mass spectrometry. Even more surprising, in view of the importance of elemental chlorine to fundamental and applied research, to the best of our knowledge, no experimental measurements of the gas-phase basicity (GB) and proton affinity (PA) of Cl_2 have been reported, the only available data being those obtained by Li et al. utilizing a theoretical method.[5] It should be noted that GB and PA are very fundamental thermochemical properties that control proton-transfer equilibria and affect the ability of the Cl_2 molecule to form proton-bound complexes. Finally, Cl_2H^+ is the prototypal electrophile among polychlorine cations and the balance between its Brønsted acid/Lewis acid reactivity toward typical bases/nucleophiles is of considerable fundamental interest.

Here we report a joint mass spectrometric and theoretical study on the formation, the structure, and the reactivity of gaseous Cl_2H^+ (**1**), aimed, in addition, at the comparative evaluation of the GB and PA of Cl_2 by experimental and theoretical techniques.

The study was extended to the most simple heteropolyhalogen cation, protonated chlorine fluoride, which can conceivably exist in two isomeric forms, $FClH^+$ (**2**) and $ClFH^+$ (**3**). No experimental gas-phase studies of these ions and their generation by protonation of ClF or other processes have been reported so far. The structure and the relative stability of **2** and **3** have been investigated in a theoretical study[6] in connection with the experimental controversy about the structure of a strictly related cation, Cl_2F^+, in condensed media.[7−9]

Experimental Section

FT-ICR Mass Spectrometry. The experiments were performed using a Bruker Spectrospin Apex 47e instrument, equipped with an external ion source, a cylindrical "infinity" cell,[10] a computer-operated pulsed valve, and a Bayard-Alpert ionization gauge, whose readings were corrected for the sensitivity to the neutral gas used,[11] and periodically calibrated measuring the rate of ion−molecule reactions, of known rate constants, e.g. $CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$.

Kinetic Experiments. The ions were generated in the external CI source and then transferred into the resonance cell and, when required, thermalized by collision with Ar, introduced by opening the pulsed valve for 10−20 ms. Following an appropriate delay time, the ions of interest were isolated by removing all other ions by a "soft" ejection technique (single shots). The neutral reagents were continuously introduced into the cell through leak valves, resulting in total pressures ranging from 10^{-8} to 10^{-7} Torr. In the kinetic experiments, the intensities of the reagent ion and those of all ions formed were normalized to the sum of the intensities and plotted vs the reaction time.

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TABLE 1: Experimental GB and PA (kcal mol^{-1}, 298 K) of Cl_2 and ClF

method	base	H^+ transfer to B	K_1	$\Delta G°_1$	GB	PA
			Cl_2			
B[a]		from Cl_2H^+				
	N_2	no transfer			>110[b]	>118[b]
	CF_4	very slow transfer			>120	>126
	N_2O	fast transfer			<132	<137
E[c]	CO_2		ca. 29	ca. -2	ca. 125	ca. 131
	HCl		ca. 0.035	ca. $+2$	ca. 125	ca. 131
K[d]	CO_2		25.6 ± 3	-1.94 ± 0.2	125.2 ± 0.2[e]	131.4 ± 0.4[e]
	HCl		0.066 ± 0.01	1.62 ± 0.2	125.1 ± 0.2	131.3 ± 0.4
			ClF			
		from $ClFH^+$				
B	Ar	no transfer			>83	>88
	O_2	no transfer			>95	>101
	Kr	no transfer			<96	>102
	N_2	transfer			<110	<118
	CO_2	fast transfer			<123	<129

[a] B = "bracketing" technique. [b] The GB and PA of reference bases are taken from ref 17. [c] FT-ICR equilibrium method. [d] FT-ICR equilibrium method measuring K_1 from the k_1/k_{-1} ratio. [e] The error bars quoted refer to the measurement of the GB and PA of Cl_2 *relative* to those of the references bases. For a discussion of the uncertainty of *absolute* GB and PA values, see text.

The pseudo-unimolecular rate constants, obtained by fitting the data to an exponential function by a least-squares treatment, allowed calculation of the bimolecular rate constants using the number density of the neutral molecules, deduced in turn from the pressure in the cell. Finally, the collisional efficiency of the reaction was evaluated by dividing the bimolecular rate constant by the ion−molecule collision rate constant k_c, calculated utilizing the average dipole orientation (ADO) theory[12] or the Su and Chesnavich trajectory algorithm,[13] which gave very close values in the cases of interest.

Materials and Reagents. Chlorine (99.99%) and all other gases utilized in the FT-ICR experiments were research-grade products obtained from commercial sources and used without further purification. XeF_2 (99.99%) and all other chemicals were also research-grade products from Aldrich Chemical Inc.

Experimental Results

Formation of Cl_2H^+ (1). Systematic FT-ICR experiments showed that **1** can be obtained from two different general reactions, namely protonation of molecular chlorine

$$BH^+ + Cl_2 \rightleftarrows \underset{\mathbf{1}}{Cl_2H^+} + B \qquad (1)$$

and chlorination of hydrochloric acid

$$YCl^+ + HCl \rightleftarrows \underset{\mathbf{1}}{Cl_2H^+} + Y \qquad (2)$$

The charged products from the two routes are indistinguishable by all structural tests performed, including GB and PA measurements and reactivity patterns with selected nucleophiles (vide infra). As discussed in a subsequent section, the efficiency of (1) depends on $\Delta(GB) = GB(Cl_2) - GB(B)$. When Δ(GB) is large, e.g. for $B = H_2$ or N_2, the collisional efficiency approaches unity. Consistent with a general trend,[14] when Δ(GB) does not exceed 2 kcal mol^{-1} the collisional efficiency decreases, e.g. to ca. 0.64 for $B = CO_2$. When Δ(GB) is negative by less than ca. 2 kcal mol^{-1} proton transfer to Cl_2 still occurs, but with a low collisional efficiency, e.g. down to ca. 0.03 for B = HCl, and of course process 1 is not observed at all when it is appreciably endoergic.

Passing to the alternative route (2), only two chlorinating agents have proved effective, namely Cl_2F^+, obtained from the fluorination of Cl_2 by XeF^+, and $XeCl^+$, prepared by chlorination of Xe by Cl_2F^+.[15]

GB and PA of Cl_2. The experimental measurement of the basicity of Cl_2 is adversely affected by the limited number of suitable reference bases and by the high reactivity of Cl_2 toward its conjugate acid (vide infra). Among the available approaches, recently reviewed by Witt and Grützmacher,[16] the FT-ICR "bracketing" method was utilized for a preliminary survey. The results show that the basicity of Cl_2 is intermediate between those of CF_4 and N_2O, which defines a PA interval from 126 to 137 kcal mol^{-1} (Table 1), according to the most recent NIST database.[17]

Next, the FT-ICR equilibrium method, involving the evaluation of the $\Delta G°_1$ change of the proton-transfer reaction 1 was tried. Among the few available reference bases of known and appropriate GB, the results of the bracketing experiments have suggested the choice of CO_2 and HCl. The PA and GB of CO_2 amount to 129.2 and 123.3 kcal mol^{-1} at 298 K, the reference temperature used throughout this work.[17] Incidentally, the NIST PA value agrees quite well with that reported in the earlier scale of Szulejko and McMahon, 129.4 kcal mol^{-1},[18] and the NIST GB of CO_2 corresponds almost exactly to that calculated from its PA according to the accurate method described by East et al.[19]

The other reference base utilized was HCl, whose GB and PA are 126.7 and 133.1 kcal mol^{-1}, respectively.[17] Irrespective of the base chosen, accurate evaluation of prototropic equilibria (1) is adversely affected by the incursion of the secondary process

$$Cl_2H^+ + Cl_2 \rightarrow Cl_3^+ + HCl \qquad (3)$$

whose charged product rapidly becomes the predominant ion, as shown by the typical kinetic plot of Figure 1. In spite of the interference from reaction 3, the intensities of the Cl_2H^+ and BH^+ ions have been found to reach a fairly constant ratio that persists for a period of time sufficiently long to allow the equilibrium constant K_1 to be assessed especially in the experiments performed at the highest $[B]/[Cl_2]$ ratios.

The results show that the GB of Cl_2 is almost exactly halfway between those of CO_2 and HCl, which leads to a value of 125 ± 3 kcal mol^{-1}. Given the limited accuracy of these measurements, it is legitimate to take $\Delta G°_1 \sim \Delta H°_1$ and hence the PA of Cl_2 can be estimated to be 131 ± 3 kcal mol^{-1} .

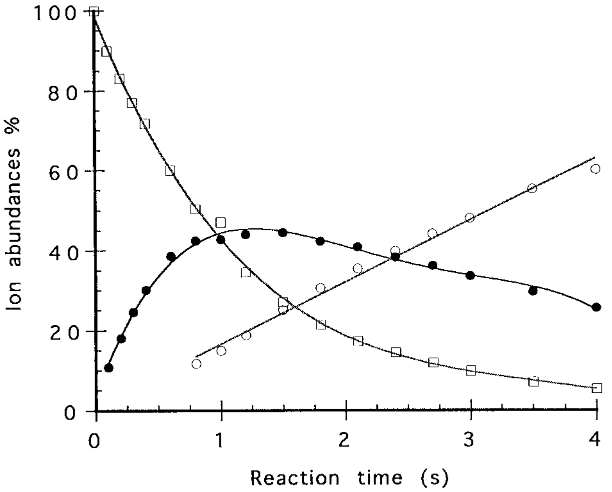


Figure 1. Kinetic plot of ion intensity vs time for the reaction of CO_2H^+ ions in a 21.7:1 mixture of CO_2 and Cl_2: (□) = CO_2H^+, $m/z = 45$, (●) = Cl_2H^+, $m/z = 71$ and 73, (○) = Cl_3+, $m/z = 105$, 107, and 109.

More accurate results were obtained utilizing the kinetic approach to equilibrium evaluation, based on the measurement of the forward and reverse rate coefficients of reaction 1, whose ratio gives the equilibrium constant, $K_1 = k_1/k_{-1}$. In these experiments, Cl_2H^+ or BH^+ ions as described in the Experimental Section, mass-selected and thermalized have been allowed to react at 298 K with the neutral species, B or Cl_2. In the evaluation of k_1 (forward reaction), formation of Cl_3^+ is still possible, but process 3 is just a consecutive reaction of the initially formed Cl_2H^+ ions, and its occurrence cannot affect the rate of BH^+ deprotonation, and hence the evaluation of k_1. In the study of the reverse reaction, no Cl_2 is present in the cell, and hence the secondary process (3) cannot occur at all.

The kinetic approach to K_1 evaluation has proved highly reproducible and is expected to be accurate, the only significant source of errors being associated with the measurement of the pressure of the neutral reagents. From the known GB of the reference base and the $\Delta G°_1$ change calculated from K_1, one can compute the GB, and hence[19] the PA of Cl_2.

Inspection of Table 1 shows that the results of the two sets of experiments utilizing CO_2 and HCl as the reference base are in excellent agreement and fall within the range defined by less accurate methods. Our best experimental estimates of the GB and PA of Cl_2 are 125.2 and 131.4 kcal mol^{-1}, respectively, each with a standard deviation of the order of ±0.2 kcal mol^{-1} and an overall experimental error estimated below 0.2 kcal mol^{-1} in the case of GB and 0.4 kcal mol^{-1} in the case of PA. This of course refers to the measurements of the GB and PA of Cl_2 *relative* to those of the reference bases utilized. In passing to *absolute* values, other sources of errors need to be considered, such as the uncertainty attached to the absolute standard to which the basicity scale utilized is anchored, the unavoidable propagation of errors along a ladder spanning a wide basicity range, etc.[20] A recent analysis based on the comparison between experimentally and theoretically derived basicity data suggests an overall uncertainty range of ca. 2 kcal mol^{-1} for experimental absolute GB and PA values.[21] Accordingly, our best experimental estimates of the GB and PA of Cl_2 are 125.1 ± 1.0 and 131.4 ± 1 kcal mol^{-1} respectively.

GB and PA of ClF. Owing to the highly corrosive and extremely reactive nature of chlorine fluoride, introducing the gas into the resonance cell of the FT-ICR spectrometer and measuring its pressure with any degree of accuracy has proved impracticable. As a consequence, the basicity of ClF has been estimated by the bracketing technique evaluating the rate of deprotonation of $FClH^+$ ions, by reference bases. The results, reported in Table 1, allow the GB and the PA of ClF to be assigned the approximate values of 103 and 110 kcal mol^{-1}, respectively, the uncertainty range being in both cases as large as ±8 kcal.

Reactivity of Cl_2H^+ (1). To prevent occurrence of predominant charge exchange, the study has been restricted to molecules of sufficiently large IP, i.e., exceeding 12 eV. The results show that **1** reacts as a Brønsted acid according to the process

$$Cl_2H^+ + B \rightarrow BH^+ + Cl_2 \qquad (1r)$$

i.e. the reverse of reaction 1, and/or as a chlorinating agent, according to the general equation

$$Cl_2H^+ + B \rightarrow BCl^+ + HCl \qquad (4)$$

The proton-transfer reactions and the dependence of their rates on the energetics of the process have been examined in a preceding section. Here the salient features of the most interesting Cl^+-transfer reactions will briefly be examined. One such reaction, the Cl^+ transfer to Cl_2 yielding Cl_3^+, has already been mentioned. From the results of a kinetic study, process 3 appears to be relatively fast, being characterized by a rate coefficient of 2.6×10^{-10} cm^3 s^{-1} $molecule^{-1}$, corresponding to a k_3/k_{ADO} collisional efficiency of ca. 30%. The estimated error bar attached to k_3, and to the other rate coefficients reported in this work, is ca. ±10%, unless otherwise stated. The results show that the Cl^+ affinity of Cl_2 *exceeds* that of HCl, which stands in contrast with the *higher* basicity of hydrochloric acid than of chlorine (Table 1). In this connection, it is interesting to note that when allowed to react with HCl, Cl_2H^+ behaves exclusively as a Brønsted acid, and the conceivable thermoneutral Cl^+ transfer

$$Cl_2H^+ + HCl \rightarrow HCl + Cl_2H^+ \qquad (5)$$

does not occur, as indicated by the lack of ^{37}Cl enrichment in mass-selected $^{35}Cl_2H^+$ ions allowed to interact with HCl of natural isotopic composition. Passing to the chlorination of xenon

$$Cl_2H^+ + Xe \rightleftarrows XeCl^+ + HCl \qquad (6)$$

it appears that the Cl^+ affinities of hydrogen chloride and xenon are very close, in that Cl^+ transfer can be observed in both directions allowing Cl_2H^+, or $XeCl^+$, ions to react with Xe, or HCl, respectively. Chlorination of methane

$$Cl_2H^+ + CH_4 \rightarrow CH_3ClH^+ + HCl \qquad (7)$$

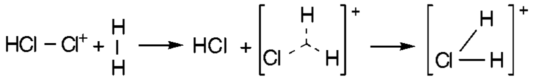
yields methyl chloride protonated on the halogen atom, as indicated by its reactivity pattern toward bases/nucleophiles, which characterizes the ion as a Brønsted acid, devoid of chlorinating properties and indistinguishable from the CH_3ClH^+ ion produced upon direct protonation of methyl chloride.

Chlorination of hydrogen

$$Cl_2H^+ + H_2 \rightarrow ClH_2^+ + HCl \qquad (8)$$

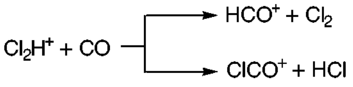
is a particularly interesting reaction and hence it has been investigated in some details. The kinetic analysis has shown that the process is moderately fast, its rate coefficient being (6.3 ± 0.5) × 10^{-11} cm^3 s^{-1} $molecule^{-1}$ and the k_8/k_{ADO} collisional efficiency ca. 6.5%.

The ion from reaction 8 has the same H−Cl−H connectivity as that formed upon protonation of HCl, consistent with its lack of chlorinating properties in reactions with bases/nucleophiles such as CO, characterized by a high Cl^+ affinity and readily chlorinated by Cl_2H^+. Furthermore, the ClH_2^+ ions from reaction 8 and from protonation of HCl undergo H^+ transfer to a given base, e.g. Cl_2, at the same rate, within experimental errors. Further mechanistic insight was obtained by replacing H_2 with D_2. The rate coefficient drops to (3.9 ± 0.2) × 10^{-11} cm^3 s^{-1} $molecule^{-1}$, and accordingly the k_{H_2}/k_{D_2} kinetic isotope effect is estimated to be 1.6 ± 0.2. Remarkably, only ClD_2^+ formation has been observed, which stands in contrast with the predominant formation of FHD^+ from the strictly related reaction of F_2H^+ with D_2.[22] Such a discrepancy shows that, whereas both reactions involve a formal transfer of the halogen cation to hydrogen, only the process promoted by Cl_2H^+ proceeds via a true Cl^+ transfer, the mechanism of the apparently similar reaction promoted by F_2H^+ being more complex.[22] The experimental evidence from this study suggests that reaction 8, a formal Cl^+ insertion into the H−H bond, possibly involves the preliminary formation of a 2-electrons, 3-centers bonded species that rapidly evolves into protonated hydrochloric acid



A similar route can reasonably be suggested to account for the formation of CH_3ClH^+ from reaction 7.

Carbon monoxide is the only reagent among those examined in this study whose protonation and chlorination by Cl_2H^+ occur at comparable rates, 4.9 × 10^{-10} and 3.7 × 10^{-10} cm^3 s^{-1} $molecule^{-1}$, respectively. The branching ratio of the competing processes



$$Cl_2H^+ + CO \rightarrow HCO^+ + Cl_2 \quad (9)$$

$$Cl_2H^+ + CO \rightarrow ClCO^+ + HCl \quad (10)$$

is therefore ca. 1.3.

Finally, the predominant reaction of **1** with H_2O is proton transfer, whereas the charged product from the chlorination reaction

$$Cl_2H^+ + H_2O \rightarrow H_2OCl^+ + HCl \qquad (11)$$

probably also fast, undergoes deprotonation by water, yielding H_3O^+, which prevents accurate kinetic analysis.

As a final remark, we note that the reactivity pattern of Cl_2H^+ is consistent with the $(Cl-Cl-H)^+$ connectivity, which is hardly surprising when the ion is generated by direct protonation of the Cl_2 molecule, containing a preformed Cl−Cl bond. Formation of Cl_2H^+ by chlorination of HCl could conceivably yield the $(Cl-H-Cl)^+$ isomer, whose reactivity pattern could be different, e.g. the ion could be a chlorination agent devoid of protonating properties. Actually, no differences between the reactivity of the Cl_2H^+ populations from reactions 1 and 2 have been noted, which speaks against the role of the hypothetical $(Cl-H-Cl)^+$ isomer, consistent with the evidence for its spontaneous rearrangement into $(Cl-Cl-H)^+$ provided by earlier charge-reversal experiments.[4]

Reactivity of $FClH^+$. The reactions of $FClH^+$ toward selected bases/nucleophiles, including Kr, Ar, O_2, N_2, and CO_2, were investigated by FT-ICR mass spectrometry. The choice of the neutral reagent is limited by the occurrence of fast charge-exchange processes when compounds of high basicity/nucleophilicity are used, which makes the experiments scarcely informative. As illustrated in Table 1, the only reaction channel of $FClH^+$ other than charge exchange is proton transfer, a behavior more consistent with the H−Cl−F, connectivity typical of isomer **2**. Indeed one would expect that isomer **3**, characterized by the H−F−Cl connectivity, should react as well as a chlorinating agent, as the $(Cl-Cl-H)^+$ ion **1** does. This structural evidence is undoubtedly circumstantial in that the inefficiency of the Cl^+-transfer process could reflect operation of a purely kinetic bias in favor of H^+ transfer, and/or the insufficient Cl^+ affinity of the few bases/nucleophiles investigated. However, if one considers that formation of $FClH^+$ involves fluorination by XeF^+ of hydrochloric acid, a molecule containing a preformed H−Cl bond, it seems reasonable to conclude that the experimental evidence favors, although not conclusively, the assignment of structure **2** to the $FClH^+$ ion.

Theoretical Results

Methods. Density functional theory, using the hybrid[23] B3LYP functional,[24] has been used to localize the stationary points of the investigated systems and to evaluate the vibrational frequencies. Single-point energy calculations at the optimized geometries were performed using the coupled-cluster single and double excitation method[25] with a perturbational estimate of the triple excitations [CCSD(T)] approach.[26] Zero-point energy 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,3dp) optimized geometries. Several basis sets have been used in calibration calculations performed on the PA of HCl; in particular we have used the 6-31G(d), the 6-311+G(3df, 2p), and the 6-311++G(3df,3pd) basis sets[27] and the correlation-consistent polarized valence sets developed by Dunning and co-workers[28] cc-pVTZ, AUG-cc-pVTZ, cc-pVQZ, AUG-cc-PVQZ, and cc-pV5Z. These results show that for the B3LYP calculations the 6-311++G(3df, 3pd) basis set is sufficiently extended, whereas for the CCSD(T) calculations a more extended basis set is required. The cc-pVQZ seems to be the best choice for the CCSD(T) calculations of this work. For comparison purposes, CCSD(T) calculations have been performed also with the smaller 6-311++G(3df, 3pd) basis. Due to the high singlet−triplet energy difference, CCSD(T) calculations on the excited triplet states have been performed only with the latter basis. The agreement between B3LYP and CCSD(T) results for large basis sets and the small differences between CCSD and CCSD(T) results suggest also that the treatment of correlation effects is satisfactory. All calculations were performed using Gaussian 94.[29]

Geometries. Table 2 shows the optimized geometries, the energies, and the vibrational frequencies of the diatomic species HCl, Cl_2, and ClF and of the protonated species Cl_2H^+, $FClH^+$, and $ClFH^+$, whereas Table 3 shows the same parameters of H_2Cl^+ for both the singlet ground state and the triplet $^3B_1$ state. The structures of the investigated species, together with the optimized geometrical parameters, are reported in Figure 2.

For the protonation of Cl_2 we considered as starting geometries both a $[ClClH]^+$ structure with the proton interacting only with one chlorine atom and a $[ClHCl]^+$ structure with the proton

TABLE 2: Optimized Geometries, at the B3LYP/6-311++G(3df,3dp) Level, Energies, and Frequencies of Cl_2, ClF, HCl, Cl_2H^+, $FClH^+$, and $ClFH^{+a}$

	Cl_2	ClF	HCl
r_e	2.010	1.642	1.281
ω_e	540.9	784.6	2951.0
E_{B3LYP}	−920.424713	−560.026738	−460.839043
ZPE^a	0.001232	0.001787	0.006723
$E_{\mathrm{CCSD(T)/6-311++G\ (3df,\ 3pd)}}$	−919.409495	−559.372395	−460.330659
$E_{\mathrm{CCSD(T)/cc-pVQZ}}$	−919.475689	−559.437859	−460.362125

	Cl_2H^+			
	$^1A'$	$^3A''$	$FClH^+$ (II)	$ClFH^+$ (III)
r(XY)	2.014	2.583	1.588	1.782
r(YH)	1.314	1.302	1.323	0.963
$\angle$(XYH)	99.7	94.8	97.7	111.8
a'	501.5	227.9	816.4	584.9
a'	869.5	460.3	1017.8	942.2
a'	2680.7	2790.9	2617.2	3504.3
E_{B3LYP}	−920.641892	−920.603193	−560.225289	−560.215831
ZPE^a	0.009230	0.007926	0.010141	0.011462
$E_{\mathrm{CCSD(T)/6-311++G\ (3df,\ 3pd)}}$	−919.629430	−919.581143	−559.573552	−559.566775
$E_{\mathrm{CCSD(T)/cc-pVQZ}}$	−919.692187		−559.637209	−559.630578

[a] Bond lengths in Å, angles in deg, total energies in hartrees, and vibrational frequencies in cm^{-1}. [b] Zero-point energy.

TABLE 3: Optimized Geometries, at the B3LYP/6-311++G(3df,3pd) Level, Energies, and Frequencies of H_2Cl^{+a}

	$^1A_1$	$^3B_1$
r(HCl)	1.312	2.157
r(HH)	1.928	0.804
$\angle$(HClH)	94.6	21.5
a_1	1216.3	646.8
b_2	2700.1	208.3i
a_1	2716.0	3587.8
E_{B3LYP}	−461.059643	−460.897597
ZPE^a	0.015109	0.009648
$E_{\mathrm{CCSD(T)/6-311++G\ (3df,\ 3pd)}}$	−460.553697	−460.381266
$E_{\mathrm{CCSD(T)/cc-pVQZ}}$	−460.582682	

[a] CCSD(T) energies computed with the cc-pVQZ basis set. Bond lengths in Å, angles in deg, total energies in hartrees, and vibrational frequencies in cm^{-1}. [b] Zero-point energy.

inserted in the Cl−Cl bonding. However, also this structure converges to the $^1A'$ $[ClClH]^+$ geometry which corresponds to the global minimum. Also, the structure of the first excited triplet state has been optimized. However, the $^3A''$ state is 24.3 kcal mol^{-1} at B3LYP level and 30.3 kcal mol^{-1} at the CCSD(T) level above the singlet ground state. The singlet−triplet energy difference for Cl_2H^+ was first reported by Li et al.[5] However, with the inclusion of correlation effects this energy difference becomes much more pronounced than previously calculated.

For protonated chlorine fluoride both $[ClFH]^+$ and $[FClH]^+$ are minima, the latter one being the global minimum, whereas the $[FHCl]^+$ structure converges to the $[FClH]^+$ one. The only previous theoretical analysis of the [H, F, Cl]$^+$ system is an ab initio study performed in 1979 in the framework of the restricted Hartree−Fock theory utilizing the 4-31G basis set.[6] Its results differ from ours in that the stability order of protomers $FClH^+$ and $ClFH^+$ is reversed, the latter ion being found to be more stable than the former one by ca. 36 kcal mol^{-1}.

In the case of HCl we investigated the protonation of both the chlorine and the hydrogen atom. However, only on the triplet surface were we able to localize a stationary point where the H−H bonding is present. Anyway, this point does not correspond to a local minimum since it does have an imaginary frequency and it is more than 100 kcal mol^{-1} above the singlet ground state.

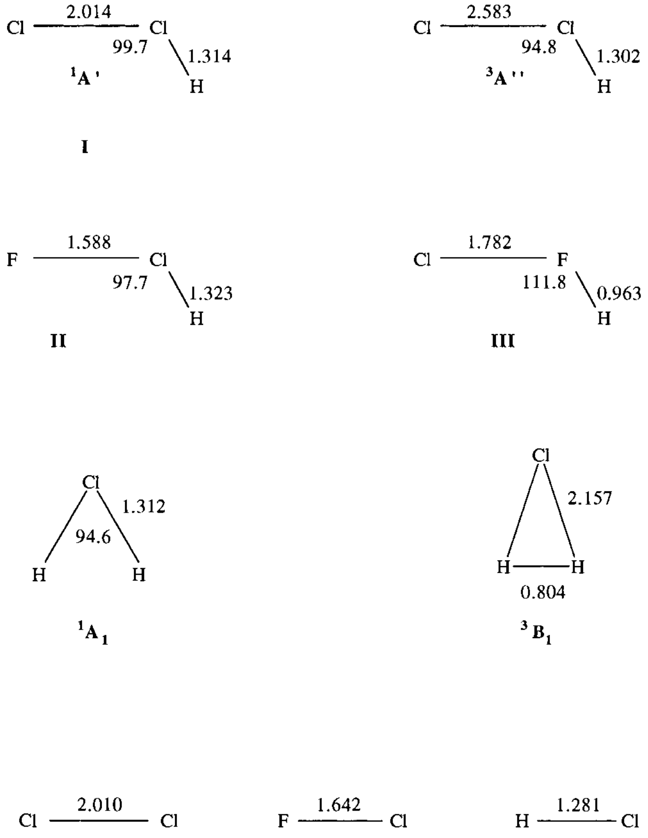


Figure 2. Geometry of relevant species optimized at the B3LYP/6-311++G(3df,3pd) level of theory. Bond lengths in Å, angles in deg, labels as in Table 2.

The optimized geometries of H_2Cl^+ and Cl_2H^+ have been previously reported by Li et al. at UHF/6-31G* level.[5] The agreement with the values reported in this work is reasonably good, the differences being traced essentially to the different methodologies employed.

Proton Affinity. Table 4 shows the PA at 0 and 298 K and the GB at 298 K of HCl, Cl_2 and ClF. For the last species we considered the attack of the proton on both the fluorine and the chlorine atoms. For comparison, both the B3LYP and CCSD(T) results are reported.

TABLE 4: Calculated PA (kcal mol^{-1}) at 0 and 298 K and GB (kcal mol^{-1}) at 298 K of HCl, Cl_2, and FCl[a]

	PA_0		PA_{298}		GB_{298}	
	B3LYP	CCSD(T)	B3LYP	CCSD(T)	B3LYP	CCSD(T)
$HClH^+ \rightarrow HCl + H^+$	133.2	133.1	134.3	134.3	127.6	127.6
$Cl_2H^+ \rightarrow Cl_2 + H^+$	131.3	130.8	132.4	132.0	126.3	125.8
$FClH^+ \rightarrow FCl + H^+$	119.4	119.8	120.5	121.0	113.9	114.4
$ClFH^+ \rightarrow ClF + H^+$	112.6	114.9	113.7	116.0	107.1	109.4

[a] Total energies at the CCSD(T)/cc-pVQZ level evaluated at the optimized B3LYP/6-311++G (3df,3pd) geometries; zero-point energies, thermal corrections and absolute entropies evaluated with the B3LYP/3-611++G (3df,3dp) frequencies.

TABLE 5: PA (kcal mol^{-1}, 298 K) of HCl and Cl_2 from Different Methods

molecule	PA	method	ref
HCl	(131.0)[a]	UHF/6-31G*	5
	134.2	G2	19
	133.5	G1	30
	134.5	G2	30
	131.8−137.1	D F T	31
	(138.5)	MP4SDTQ(FT)	32
	132.9−133.5	various methods	33
	132.9	CBS-Q	34
	134.3	B3LYP	this work
	134.3	CCSD(T)	this work
	134.8	expt	36
	136.5	expt	35
	133.1	expt	17
	133.0	expt	37
Cl_2	(125.1)	UHF/6-31G*	5
	132.4	B3LYP	this work
	132.0	CCSD(T)	this work
	131.4	expt	this work

[a] Values in parentheses adjusted to 298 K from original values referred to 0 K.

Let us start our analysis with HCl, whose PA has been previously evaluated by several authors, using different methods as shown in Table 5.[5,19,30−33] Li et al.[5] computed the PA_e (i.e., the proton affinity of HCl at 0 K without the inclusion of the zero-point energy correction) at the UHF/6-31G* level equal to 129.8 kcal mol^{-1}. Our PA_e value is 138.4 kcal mol^{-1} both at the B3LYP level and at the CCSD(T) level. The difference between Li's value and those reported in this work should be ascribed to correlation effects and basis set incompleteness. More recently, East et al.[19] computed the PA and GB of HCl at 298 K using G2 theory.[30] They evaluated PA_{298} and GB_{298} of HCl equal to 134.2 and 127.8 kcal mol^{-1}, respectively. These values are in excellent agreement with those computed by us (see Table 5). Curtiss et al. evaluated PA_0 at the G1 and G2 level, obtaining 132.3 and 133.0 kcal mol^{-1}, respectively, in very good agreement with our values.[30] Very recently, Ghanty and Ghosh[31] computed PA_e of HCl with the density functional theory, using different functionals and a DZVP basis set. They obtained values ranging from 131.8 to 137.1 kcal mol^{-1}, all of these values being smaller than our B3LYP value (138.4 kcal mol^{-1}). Sannigrahi et al. obtained a PA_0 of HCl = 137.3 kcal mol^{-1} at the MP4SDTQ(FC) level,[32] 3 kcal mol^{-1} higher than our value. Ochterski et al.[33] computed PA_0 of HCl with several methods, obtaining values ranging from 131.7 to 133.6 kcal mol^{-1}: all of these values, except the one computed at CBS-Q level, are close to our value. Finally, Remko et al. computed the PA_{298} of HCl by means of a CBS-Q method, obtaining a value of 132.9 kcal mol^{-1}.[34] The experimental PA_{298} of HCl has been reported to be 133.1 in the latest NIST compilation:[17] our best estimate, 134.3 kcal mol^{-1}, is in reasonable agreement with this value.

The PA of Cl_2 has been previously evaluated only by Li et al.[5] at the UHF/6-31G* level. They computed PA_e of Cl_2 equal to 123.6 kcal mol^{-1}, which should be compared with our PA_e values: 136.3 and 135.8 kcal mol^{-1} at the B3LYP and CCSD(T) level, respectively. The difference should be ascribed mainly to correlation effects, although basis set incompleteness may also play a role. Our best estimate for the PA of Cl_2 at 298 K is 132.0 kcal mol^{-1} (see Table 5), ca. 2 kcal mol^{-1} lower that the PA_{298} of HCl.

To our knowledge, the PA of FCl has not been computed so far. Our calculations suggest that the energetically preferred site of protonation is the chlorine atom and the PA_{298} of FCl is estimated to be 121.0 kcal mol^{-1}, more than 10 kcal mol^{-1} smaller than the PA_{298} of Cl_2.

Discussion

The experimental and theoretical results concur in outlining a coherent picture of the species of interest, whose structure, energetics, and reactivity will be examined in the subsequent paragraphs.

Structure of Gaseous Hydrohalonium Ions. The experimental results are consistent with the Cl−Cl−H connectivity of **1**, suggested by the following evidence:

(i) The nature of the two formation processes that yield indistinguishable Cl_2H^+ ions. In particular, reaction 1 involves addition of a proton to the Cl_2 molecule, containing a preformed Cl−Cl bond, whose fission seems most unlikely expecially when reaction 1 is moderately exothermic, or even slightly endothermic.

(ii) The observation that **1** undergoes *both* H^+ and Cl^+ transfer, which strongly supports the Cl−Cl−H connectivity.

Finally, the evidence from earlier charge-reversal experiments suggests that cations of the initial Cl−H−Cl connectivity spontaneously rearrange into the isomer of the Cl−Cl−H connectivity.[4] The above experimentally derived conclusions are supported and extended by the theoretical results, showing that the global minimum in the $[H, Cl, Cl]^+$ system is the singlet **I**, characterized by an angular structure and by Cl−Cl and H−Cl separations larger than in the Cl_2 and HCl molecules (Figure 2). Furthermore, the $[Cl-H-Cl]^+$ ions is theoretically predicted to collapse into **I**.

Passing to protonated chlorine fluoride, the experimental results favor, although not conclusively, the F−Cl−H connectivity typical of protomer **2**, based on the following considerations:

(i) the nature of the preparation route, involving fluorination of a molecule, containing a preformed H−Cl bond;

(ii) the inability of the ion to chlorinate molecules, such as CO, characterized by a large Cl^+ affinity (vide infra), that are readily chlorinated by Cl_2H^+.

The theoretical results confirm that actually the global minimum in the $[H, F, Cl]^+$ system, the singlet **II**, has the F−Cl−H connectivity typical of ion **2**, whereas protomer **III**, having the Cl−F−H connectivity of ion **3**, is less stable by 6.8 and 5.0 kcal mol^{-1} at the B3LYP and CCSD(T) levels, respectively. From Figure 2, **II** has an angular structure, with a

TABLE 6: PA (kcal mol^{-1}) at 298 K of HCl Computed at Different Levels of Theory

	B3LYP	CCSD	CCSD(T)
6-311+G (3df, 2p)	134.0	134.3	134.1
6-311++G (3df, 3pd)	134,3	136,0	135.9
cc-pVTZ	134.1	135.6	135.6
AUG-cc-pVTZ	133.7	134.7	134.5
cc-pVQZ	134.3	134.6	134.3
AUG-cc-pVQZ	134.1	134.3	133.9
cc-pV5Z	134.5	134.5	134.3

F−Cl separation *smaller* than in ClF and a H−Cl separation significantly *larger* than in HCl, consistent with the lack of chlorinating properties and with the Brønsted acid behavior of **2**. The theoretical results show, in addition, that $[F-H-Cl]^+$, the third conceivable isomer, is unstable toward conversion into **II**, which is consistent with the experimental evidence for the lack of chlorinating or fluorinating properties of protonated chlorine fluoride, in that a cation having the F−H−Cl connectivity would be expected to be an efficient halogenating agent.

At variance with previous theoretical results that identify **3** as the most stable protomer,[6] the experimental and theoretical evidence from this study in favor of protomer **2** restores the concept that, whenever possible, F is reluctant to behave as a central atom in heteropolyhalogen cations. In this connection, the present results concerning $FClH^+$ are in line with the assignment of the asymmetric structure of the strictly related Cl_2F^+ ion, based on IR and Raman spectroscopy of its solid salts[8] and a subsequent theoretical analysis.[9]

PA of Cl_2 and ClF. The best experimental estimate of the PA of Cl_2, 131.4 kcal mol^{-1}, is in excellent agreement with the result obtained at the CCSD(T) level of theory, the highest one utilized, namely 132.0 kcal mol^{-1}. Despite such rewarding consistency, a careful analysis of the absolute accuracy of both the experimental and the theoretical results is advisable and instructive from a methodological standpoint. Considering the experimental approach first, it is clear that its absolute accuracy reflects those of the absolute PA of the reference bases utilized. In this connection, the scatter of the available experimentally and theoretically derived PA values of HCl, one of the reference bases used in this work, is illustrated in Table 5. It should be noted that HCl is one of the few molecules placed at the lower end of the basicity scale whose PA estimates have undergone a significant change in the past decade.[17,21,35,37] From Table 5 it appears that the absolute PA of HCl reported in the latest NIST detabase,[17] 133.1 kcal mol^{-1}, may be slightly underestimated and its upward adjustment, and hence a better agreement with the most recent theoretical results, would require the definition of more accurate local standards at the lower end of the PA scale. Based on the above considerations, it seems appropriate to attach to the absolute experimental PA of Cl_2, 131.4 kcal mol^{-1}, an overall uncertainty conservatively estimated to amount to ± 1 kcal mol^{-1}.

Passing to the theoretical approach, rigorous evaluation of the uncertainty range is more difficult. A rough estimate can be obtained from the results reported in Table 6 that illustrate the dependence of the PA of HCl at 298 K on the level of theory and the basis set employed. It is apparent that utilizing a given basis set, the difference between the results obtained at the B3LYP, CCSD, and CCSD(T) level *decreases* in passing from the 6-311+G(3df, 2p) to the cc-pV5Z set, which gives results consistent within 0.2 kcal mol^{-1} at all levels of theory employed. Conversely, when utilizing a given level of theory, the B3LYP level appears to be the one least affected by the choice of the basis set. In conclusion, based on the data reported in Tables 5 and 6, it seems reasonable to attach a ±1 kcal mol^{-1} uncertainty range also to the theoretically calculated PA of Cl_2, 132.0 kcal mol^{-1}.

Passing to ClF, the lack of accurate experimental measurements suggests the adoption of the best theoretical estimate, PA = 121.0 kcal mol^{-1}, referred to the formation of the most stable isomer, i.e., the ion **2** protonated on the Cl atom.

The higher basicity of Cl than of F in halogen and interhalogen molecules, a trend hardly surprising on intuitive grounds, but not always supported by theoretical results,[6] is consistent with the basicity order $F_2 \ll ClF < Cl_2$, defined by the PA scale: F_2, 79,[22] ClF, 121.0; Cl_2, 131.4 kcal mol^{-1}, whose most salient feature is the remarkably large ΔPA increase, over 40 kcal mol^{-1}, following replacement of one of the F atoms of the F_2 molecule with a Cl atom.

Reactivity of Cl_2H^+ (1) and $FClH^+$ (2). A limited survey of the reactivity of gaseous hydrohalonium ion has provided useful structural information and, in the case of **1**, has allowed a comparative evaluation of the efficiency of its H^+ and Cl^+-transfer reactions to bases/nucleophiles. The results concerning Cl_2H^+ are summarized in Table 7. Owing to the specific purpose of the survey, accurate kinetic measurements have been performed only in the few cases reported in the previous sections. In Table 7 the reactions are roughly classified as follows, based on approximate estimates of their rate coefficient k: very slow ($k < 10^{-11}$ cm^3 s^{-1} molecule^{-1}); slow ($10^{-11} < k < 10^{-10}$ cm^3 s^{-1} molecule^{-1}); fast ($k > 10^{-10}$ cm^3 s^{-1} molecule^{-1}).

TABLE 7: Reactivity of Cl_2H^+ toward Gaseous Molecules

			H^+ transfer (1r)		Cl^+ transfer (4)	
molecule	IP[a] (eV)	PA[b] (kcal mol^{-1})	ΔH°[c] (kcal mol^{-1})	rate	ΔH° (kcal mol^{-1})	rate
H_2	15.4	100.9	+30.7	n.d.[d]	−45.6	slow[f]
N_2	15.6	118.0	+13.6	n.d.		very slow
Xe	12.1	118.6	+13.0	n.d.	∼0[f]	slow
CO_2	13.8	129.2	+2.4	slow		n.d.
CH_4	12.5	129.9	+1.7	n.d.	−45.5[g]	fast
Cl_2	11.5	131.4[c]	0	n.d.		fast
HCl	12.7	133.1	− 1.5	fast	0[f]	n.d.
N_2O	12.9	137.5	−5.9	fast		n.d.
CO	14.0	141.7	−10.1	fast	ca. − 48[h]	fast
H_2O	12.6	165.2	−33.6	fast	−4.1[i]	fast[f]

[a] From ref 33. [b] From ref 17. [c] Based on the PA of Cl_2 from this work. [d] Rate coefficient below 10^{-12} cm^3 s^{-1} molecule^{-1}. [e] From the ΔH°_f (Cl_2H^+) from this work. [f] See text. [g] Assuming the CH_3ClH^+ structure of the chlorinated product from thermochemical data of ref 17. [h] Based on the theoretically calculated ΔH°_f ($ClCO^+$) = 184 kcal mol^{-1}, ref 38. [i] Based on the theoretically computed ΔH°_f (H_2OCl^+) = 194.3 kcal mol^{-1}, ref 37.

The interpretation of the results reported in Table 7 is straightforward. Given its Cl−Cl−H connectivity, **1** can undergo both H^+ transfer, according to eq 1r, or Cl^+ transfer, according to eq 4. Each process can be observed provided that it is exothermic, or at least not endothermic by more than, say, 2 kcal mol^{-1} and provided that the alternative process is not much faster. Thus, the much lower basicity of H_2, Xe and N_2 than of Cl_2 makes their protonation by **1** considerably endothermic, leaving chlorination (4) as the only possible reaction channel. Such a process is highly exothermic in the case of H_2 (Table 6). Its occurrence, albeit at a low rate, in the case of N_2 and Xe suggests that the Cl^+ affinity of these molecules is comparable to, or at least not much lower than, that of HCl.

As the basicity of the neutral reagent increases, proton transfer (1r) becomes energetically more favorable. As discussed in a previous section, and according to a general trend,[14] the efficiency of reaction 1r increases with the Δ(GB) difference between the GB of the base B and that of Cl_2, leveling off at nearly unity collision efficiency when Δ(GB) exceeds a few kcal mol^{-1}. For example, in the case of CO_2, $\Delta(\mathrm{GB}) = -1.8$ kcal mol^{-1}, the collisional efficiency, k_{1r}/k_{ADO}, is ca. 0.03, whereas in the case of HCl, $\Delta(\mathrm{GB}) = +1.6$ kcal mol^{-1}, it rises to ca. 0.24. Neither CO_2 nor HCl undergoes chlorination (4), if for different reasons. In the case of carbon dioxide, reaction 4 is probably endothermic, reflecting the lower Cl^+ affinity of CO_2 than of HCl. Chlorination of HCl by **1** is of course thermoneutral, and probably could be observed in the absence of the faster, competing proton transfer (1r). The opposite situation prevails in the case of methane, $\Delta(\mathrm{GB}) \sim 0$. Here the slow proton transfer from **1** that could occur according to eq 1r is suppressed by the much faster highly exothermic Cl^+ transfer (4).

In the case of molecules, such as CO and H_2O, characterized by a much larger basicity than Cl_2, both processes 1r and 4 are fast. In the case of CO their branching ratio of 1.3 in favor of protonation can be measured, whereas in the case of water H_2OCl^+, the initial product from reaction 4, is rapidly deprotonated by water, more basic than hypochlorous acid by 11.8 kcal mol^{-1},[37] which prevents accurate evaluation of the k_{1r}/k_4 branching ratio.

The reactivity of protonated ClF, that behaves exclusively as a Brønsted acid, provides strong evidence in favor of protomer **2**, characterized by the F−Cl−H connectivity and therefore potentially capable of undergoing H^+ or F^+, but not Cl^+ transfer. The reactivity toward CO is particularly telling in that reaction 4 promoted by $FClH^+$ is *more* exothermic by ca. 40 kcal mol^{-1} than the analogous reaction promoted by Cl_2H^+ that successfully competes with proton transfer (1r). The comparison suggests that the lack of chlorinating ability of protonated ClF does not reflect operation of thermochemical or kinetic factors, but rather must be traced to the H−Cl−F connectivity typical of protomer **2**. This conclusion is supported by the theoretical results that identify the singlet **II**, having the F−Cl−H connectivity, as the global minimum.

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