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Gas-phase reactions of protonated chlorine, Cl_2H^+, with H_2(D_2) and CH_4. A mass spectrometric and theoretical study

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Abstract

FT-ICR (Fourier Transform Ion Cyclotron Resonance) experiments showed that the reaction of Cl_2H^+ with H_2 (rate coefficient 6.3 ± 1.0 cm^3 s^{-1} $molecule^{-1}$ at 298 K) yields ClH_2^+ ions, identified as protonated hydrochloric acid by CAD (Collisionally Activated Decomposition) mass spectrometry. Calculations performed at the B3LYP and CCSD(T) levels of theory show that the reaction involves insertion of the terminal Cl atom of Cl_2H^+ into the H–H bond, which accounts for the experimental observation that ClD_2^+ but not $ClHD^+$ is formed from the reaction of Cl_2H^+ with D_2. The same Cl^+ insertion mechanism characterizes the reaction of Cl_2H^+ with CH_4, whose product was identified as protonated methyl chloride, CH_3ClH^+, by CAD mass spectrometry. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Polyhalogen cations have been extensively studied in condensed phases, owing in particular to their role in the halogenation reactions promoted by cationic complexes of molecular halogens with strong acids [1–3]. We have recently extended the study to gaseous polyhalogen cations preparing and characterizing one of the most simple species, the Cl_2H^+ ion, by the joint application of mass spectrometric and theoretical methods [4]. As a natural extension, we have undertaken a study of the Cl_2H^+ reactivity towards representative molecules, utilizing the same combination of experimental and theoretical tools, and here report the electrophilic chlorination by Cl_2H^+ of H_2 and CH_4, the most simple inorganic and organic molecules.

2. Methodology

Density functional theory, using the hybrid [5] B3LYP functional [6], was used to localize the stationary points of the investigated systems and to evaluate the vibrational frequencies. Single-point energy calculations at

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the optimized geometries were performed using the coupled-cluster single and double excitation method [7] with a perturbational estimate of the triple excitations [CCSD(T) approach] [8]. Zero-point energy corrections evaluated at the 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 6-311++G(3df,3pd) basis set [9–12], while the CCSD(T) calculations were done using both the 6-311++G(3df,3pd) basis set [9–12] and for the smaller systems the correlation-consistent polarized valence set cc-pVQZ developed by Dunning and co-workers [13–15]. The choice among the basis sets was made on the ground of their performances in previous calculations on the proton affinities of Cl_2 and ClF [4]. All calculations were performed using Gaussian 94 [16]. The FT-ICR experiments were performed utilizing an APEX 47e Spectrometer (Bruker Spectrospin) equipped with an external ion source, a cylindrical 'infinity' cell [17] and a pulsed valve. The Cl_2H^+ ions generated in the external source and driven into the cell were thermalized by collision with Ar, admitted in a 20 ms pulse to a pressure up to 10^{-5} Torr, then mass selected by 'soft' ejection techniques and allowed to react with H_2, D_2 or CH_4, present at stationary pressures from 10^{-8} to 10^{-7} Torr. The readings of the Bayard–Alpert ionization gauge were calibrated and corrected according to established procedures [18]. The CAD spectra were recorded using a ZAB-Spec oa-TOF mass spectrometer (VG Micromass), under the following typical conditions: accelerating voltage 8 kV; emission current, 1 mA; repeller voltage, 0 V; electron energy, 40 eV; CI (Chemical Ionization) source temperature, 170°C; collision gas, He.

3. Results and discussion

3.1. Cl_2H^+ reactions with H_2 and D_2

Isolated and thermalized Cl_2H^+ isotopomers undergo Cl^+ transfer to hydrogen

$$Cl_2H^+ + H_2 \rightarrow ClH_2^+ + HCl, \qquad (1)$$

whose rate coefficient is 6.3 ± 1 cm^3 $molecule^{-1}$ s^{-1} at 298 K, corresponding to a collisional efficiency of 6.5%, deduced from the ion–molecule collision rate calculated utilizing the average dipole orientation (ADO) theory [19] or the trajectory algorithm [20].

Replacing H_2 with D_2, the Cl^+ transfer

$$Cl_2H^+ + D_2 \rightarrow ClD_2^+ + HCl \qquad (1a)$$

is somewhat slower ($k = 3.9 \pm 0.5$ cm^3 $molecule^{-1}$ s^{-1}) which corresponds to a k_H/k_D kinetic isotope effect of 1.6 ± 0.3. Most remarkably, no $ClHD^+$ ions are formed, and the absence of isotopic scrambling is mechanistically informative, suggesting that reaction (1) is a clean Cl^+ transfer to hydrogen. This contrasts with the complex mechanism of the deceptively similar reaction of F_2H^+ with D_2, which is *not* a simple F^+ transfer, yielding a mixture of FHD^+ and FD_2^+ ions [21]. The ClH_2^+ ions from (1) can confidently be assigned the H–Cl–H connectivity, based on the comparison (Table 1) of their CAD spectra with those of model ions obtained by CH_4/Cl of HCl, according to the mildly exothermic process, $\Delta H^\circ = -3.2$ kcal mol^{-1} [4,22]

$$CH_5^+ + HCl \rightarrow ClH_2^+ + CH_4. \qquad (2)$$

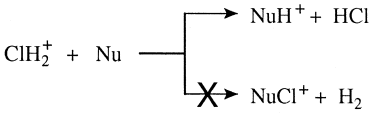
The assignment of the $[H–Cl–H]^+$ connectivity is supported by the reactivity pattern of the ClH_2^+ ions outlined by FT-ICR experiments, whose results characterize the cation as a pure Brønsted acid, devoid of the

Table 1
CAD spectra of $^{37}ClH_2^+$ and $^{37}ClD_2^+$ ions from various sources

Fragment		Source of the ions		
species	m/z	reaction (1)	reaction (2)	reaction (1a)
$^{37}Cl^+$	37	20.2[a]	18.0	18.4
$^{37}ClH^+$	38	79.8	82.0	81.6
$^{37}ClD^+$	39			

[a] Relative intensity normalized to the sum of the fragments intensities. Standard deviation of relative intensities ±5%.

chlorinating ability expected for a species of the alternative $[Cl–H–H]^+$ connectivity. Thus, proton transfer, but not Cl^+ transfer is observed, even to bases/nucleophiles of relatively high Cl^+ affinity



(Nu = CO, Cl_2, etc.)

Consistent with the experimental picture, the theoretical analysis of reaction (1) provides useful mechanistic insight. Fig. 1 illustrates the optimized geometries of the species involved and the two consecutive steps (4) and (6) of the overall reaction (1), whereas Table 2 summarizes their enthalpy changes at 298 K.

According to the theoretical description, the interaction of Cl_2H^+ with H_2 yields the intermediate **2**, which is formed by the insertion of the terminal Cl atom of **1** into the σ bond of H_2 and, based on its large Cl–Cl separation, can be regarded as a (HCl · · · **4**) cluster. The latter species at 0 K is stable with respect to dissociation into HCl and **4**, but evolves towards the more stable species **3**, i.e. the proton-bound HCl dimer, whose connectivity does not allow the occurrence of reaction (1). At 298 K, however, taking into account the entropic contributions, intermediate **2** is unstable with respect to dissociation into the products of reaction (1).

The overall process can be described as a clean Cl^+ transfer to H_2 or D_2, and in the latter case consistent with the experimental results,it is not expected to cause isotopic mixing.

Finally, the ΔH_1^o change computed at the CCSD(T) level of theory compares well with that calculated from experimental data [4,22] since the difference between the two results, -48.0 and -45.9 kcal mol^{-1}, falls well within their combined uncertainty range.

3.2. Cl_2H^+ reaction with methane

FT-ICR experiments show that thermalized Cl_2H^+ ions react with methane yielding chlorinated products, the major process, being the electrophilic chlorination

$$Cl_2H^+ + CH_4 \rightarrow CH_4Cl^+ + HCl. \quad (7)$$

The structure of the charged products was probed by CAD spectrometry, by comparing its dissociation pattern with those of model $[CH_3–Cl–H]^+$ ions obtained by CH_4/Cl of CH_3Cl, according to the equation

$$CH_5^+ + CH_3Cl \rightarrow CH_3ClH^+ + CH_4 \quad (8)$$

and by CH_3F/Cl of HCl, according to the equation

$$(CH_3)_2F^+ + HCl \rightarrow CH_3ClH^+ + CH_3F. \quad (9)$$

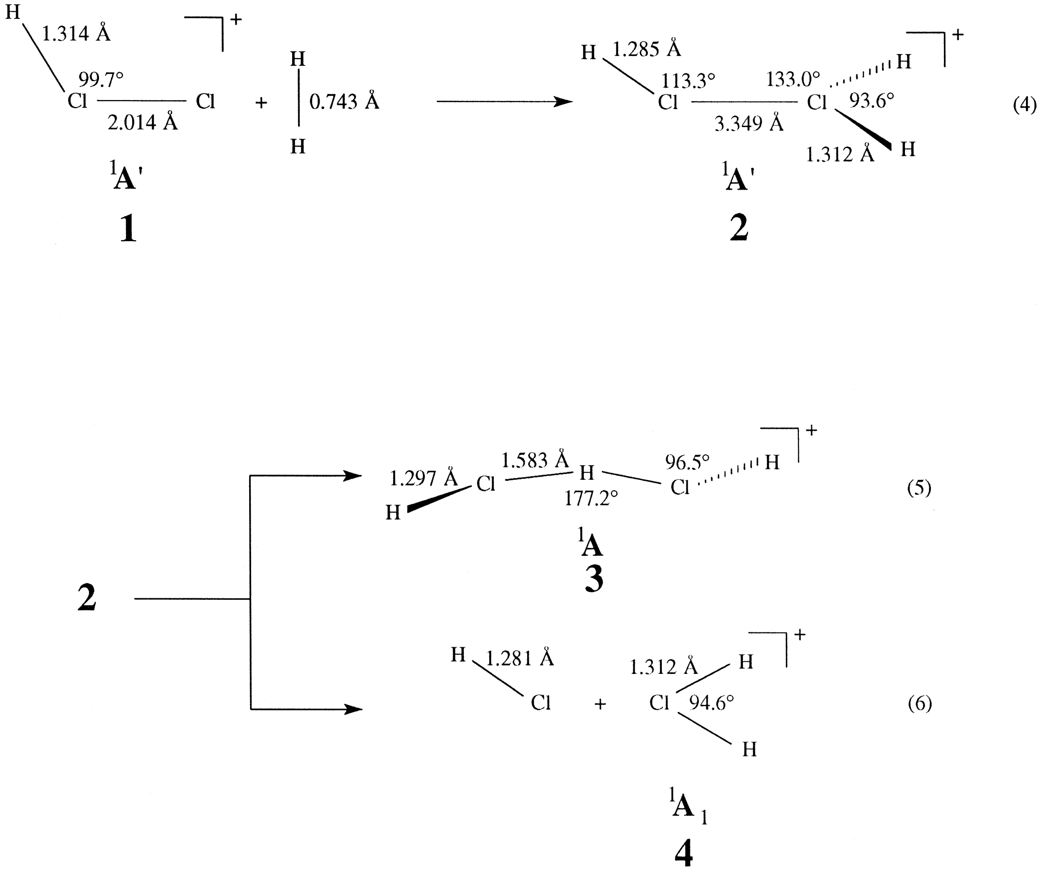


Fig. 1. Relevant reactions of the species of interest and their optimized geometries, see text.

The results, summarized in Table 3, show that the spectra of the ions from processes (7)–(9) are indistinguishable within experimental error, which allows one to assign the CH_3ClH^+ structure to the charged product from chlorination (7). Accordingly, the process can be calculated to be exothermic by 46.2 kcal mol^{-1} [4,22]. The structural assignment is consistent with the results of a FT-ICR survey of the reactivity of the CH_4Cl^+ ion from (7), showing that it behaves as a Brønsted acid, e.g. towards CH_3CN, or a methylating agent, e.g. towards H_2O, but never as a chlorinating agent.

Table 2
Energetics (kcal mol^{-1}) at 298 K of relevant processes calculated at the CCSD(T) level of theory

Process[a]	ΔH^{o}_{298}
1 + H_2 → **2**	−54.9
2 → **3**	−13.9
2 → **4** + HCl	4.7
1 + H_2 → **4** + HCl	−50.2[b]

[a] The species are labeled as in Fig. 1.

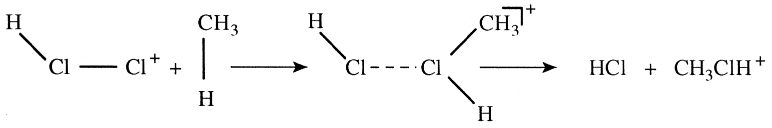
[b] The value is −48.0 at CCSD(T)/cc-pVQZ level of theory.

Table 3
CAD spectra of $CH_4{}^{37}Cl^+$ ions from various sources

Fragment		Source of the ions		
species	m/z	reaction (7)	reaction (8)	reaction (9)
CH_3Cl^+	52	24.3[a]	26.5	25.0
CH_2Cl^+	51	17.1	13.1	14.7
$CHCl^+$	50	7.2	7.2	7.0
CCl^+	49	8.3	8.9	8.5
ClH_2^+	39	3.0	3.2	3.3
ClH^+	38	12.1	13.1	12.8
Cl^+	37	6.3	6.8	6.3
CH_3^+	15	16.6	15.2	16.5
CH_2^+	14	3.7	4.3	4.3
CH^+	13	1.4	1.7	1.6

[a] Relative intensity normalized to the sum of the fragments intensities. Standard deviation of relative intensities ±5%.

By analogy with the reaction with hydrogen, and based on the structure of the charged product, the mechanism of reaction (7) most likely involves the insertion of the terminal chlorine atom of Cl_2H^+ into one of the σ bonds of methane, followed by loss of HCl according to the scheme



Support for the above mechanism, and extension of the study to other chlorination processes, is expected from the results of theoretical and experimental work currently under way in our laboratories.

4. Conclusions

The study of the gas-phase reactivity of Cl_2H^+ towards simple molecules such as H_2 and CH_4 has demonstrated its remarkable ability to promote electrophilic chlorination according to a mechanism whereby the terminal Cl atom of the cation inserts into a σ bond of the neutral molecule.

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