Gaseous $[H_3C{-}Cl{-}Cl]^+$ Ions from the Reaction of Methane with Cl_3^+, the First Example of a New Dihalogenation Process: Formation and Characterization of $CH_3Cl_2^+$ Isomers by Experimental and Theoretical Methods

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Abstract: The structure, stability, and reactivity of the $[C,H_3,Cl_2]^+$ ions from the reaction of Cl_3^+ with CH_4 were studied by structurally diagnostic mass spectrometric techniques and by computational methods. The ionic products were characterized as protonated dichloromethane $[ClH_2C{-}ClH]^+$ (**1**), the more stable isomer, that behaves exclusively as a Brønsted acid, and the hitherto unknown $[H_3C{-}Cl{-}Cl]^+$ ion (**2**), a chlorinating and methylating cation. Formation of **2** is the first example of a new class of electrophilic substitution, in which a single H atom is replaced by the diatomic $[Cl{-}Cl]^+$ dichlorinium ion. In addition, the proton affinity of dichloromethane was determined by experimental and theoretical methods to be 150.2 ± 2 and 151 kcal mol^{-1}, respectively.

Keywords: chlorine · density functional calculations · gas-phase chemistry · halogenations · mass spectrometry

Introduction

Polyhalogenation of alkanes such as the prototypal reaction of Cl_2 with CH_4 is known to proceed via intermediates, and to yield products with all Cl atoms directly bound to the carbon atom. This is also the case in the ionic chlorination of methane promoted by Cl_2 in superacid solutions, or over acidic catalysts, where dichloromethane is obtained together with methyl chloride; this is by far the major product formed via the intermediate hypervalent carbocation from the insertion of Cl^+ into a C–H bond of the alkane.[1–6] We report herein the first example of a hitherto unknown class of reactions, namely electrophilic substitution, in which a *single* H atom of methane is replaced by a *diatomic* group, the $[Cl{-}Cl]^+$ dichlorinium ion, to yield $[H_3C{-}Cl{-}Cl]^+$ as the charged product. The first hint to this unconventional substitution was provided by our recent gas-phase investigations on representative trihalogen and hydrohalonium cations.[7–9] The study of their reactivity towards simple nucleophiles disclosed a remarkable chlorinating ability, in accordance with their Lewis acid character. Among the reactions examined those of Cl_2H^+ and Cl_2F^+ with H_2 and CH_4 give products both theoretically and experimentally characterized as $[H{-}Cl{-}H]^+$ and $[H{-}Cl{-}CH_3]^+$ ions, respectively, according to a mechanism involving Cl^+ insertion into a H–H or $H_3C{-}H$ σ bond, analogous to that postulated in solution.[10] However, the reaction of Cl_3^+ with CH_4 proved to be more complex, yielding a mixture of isomeric products; this suggests the possible occurrence of a methane substitution by the dichlorinium cation. Accordingly, we have undertaken an investigation aimed at establishing the detailed course of the reaction, its mechanism and energy profile, as well as the structure and the relative stability of its isomeric products, by utilizing a combination of mass spectrometric and theoretical methods.

Experimental Section

Mass spectrometric experiments: ZABSpec oa-TOF and Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometers were used to perform all reported experiments. The ions were generated in the high-pressure chemical ionization (CI) source of the ZABSpec mass spectrometer (Micromass Ltd.) under the following typical conditions: Accelerating voltage 8 kV, emission current 0.5 mA, repeller voltage 0 V, source temperature 150 °C. The mass-selected ions were structurally assayed by mass-analyzed ion kinetic energy (MIKE) and collisionally activated dissociation (CAD) mass spectrometry. In the latter case, He was introduced into the collision cell at such a pressure as to reduce the intensity to 70 % of its original value. All the FT-ICR experiments were

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performed with a Bruker Spectrospin Apex 47e spectrometer equipped with an external CI source, a pulsed valve, a cylindrical „infinity" cell,[11] and a Bayard–Alpert ionization gauge, whose readings were corrected for its different sensitivity to the gases used.[12] 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 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) through the pulsed valve to a peak pressure of about 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. All gases and other chemicals utilized were research-grade products from commercial sources with a stated purity in excess of 99.99 mol% and were used without further purification.

Computational details: Density functional theory, based on the B3LYP functional,[13] was used to localize the stationary points of the investigated systems and to evaluate vibrational frequencies. Single-point energy calculations at the optimized geometries were performed with the coupled-cluster single- and double-excitation method[14] with a perturbational estimate of the triple excitations according to the [CCSD(T)] approach.[15] Zero-point energy (ZPE) corrections evaluated at B3LYP level were added to the CCSD(T) energies. The total energies of the species of interest at 0 K were corrected to 298.15 K by adding translational, rotational, and vibrational contributions. The absolute entropies were calculated with standard statistical-mechanistic procedures from scaled harmonic frequencies and moments of inertia relative to B3LYP/6-311G(3df, 3pd) optimized geometries. The 6-311G(3df, 3pd) basis set was used for all the investigated systems.[16] All calculations were carried out with Gaussian 94.[17]

Results

The formation reactions: $\mathrm{CH_4Cl^+}$ and $\mathrm{CH_3Cl_2^+}$ have been observed as the major products of the $\mathrm{Cl_2}$/CI of methane, performed in the high-pressure source of the ZABSpec oa-TOF mass spectrometer, probably arising from the reactions promoted by the $\mathrm{Cl_3^+}$ ion, see Equations (1) and (2).

$$\mathrm{Cl_3^+ + CH_4}\ \begin{cases}\longrightarrow \mathrm{CH_4Cl^+}\ (\mathbf{a}) + \mathrm{Cl_2} & (1)\\ \longrightarrow \mathrm{CH_3Cl_2^+}\ (\mathbf{b}) + \mathrm{HCl} & (2)\end{cases}$$

The measured $\mathrm{CH_4Cl^+/CH_3Cl_2^+}$ intensity ratio approximates unity and has been found to increase at higher pressure of $\mathrm{CH_4}$. An increase in the pressure of $\mathrm{CH_4}$, that is, of the $\mathrm{CH_4/Cl_2}$ ratio, and hence of the abundance of the $\mathrm{C}_n\mathrm{H_5^+}$ ($n = 1,2$) ions that readily undergo proton transfer to $\mathrm{Cl_2}$, turns the $\mathrm{Cl_2}$/CI of methane into a $\mathrm{CH_4}$/CI of chlorine, so that the prevailing chlorinating agent changes from $\mathrm{Cl_3^+}$ to $\mathrm{Cl_2H^+}$. Nevertheless, $\mathrm{CH_4Cl^+}$ remains abundant in the spectrum, whereas the intensity of $\mathrm{CH_3Cl_2^+}$ declines. Accordingly, it is likely that ion **a** can be formed upon chlorination of methane by a different $\mathrm{Cl^+}$ donor, such as $\mathrm{Cl_2H^+}$ and $\mathrm{Cl_2F^+}$.[10] For an enhanced elucidation of the formation process of ion **b**, $\mathrm{Cl_3^+}$, $\mathrm{Cl_2H^+}$, and $\mathrm{Cl_2F^+}$ were generated in the external source of a FT-ICR mass spectrometer by CI of neat $\mathrm{Cl_2}$, and by $\mathrm{CH_4}$/CI, and $\mathrm{XeF_2}$/CI of $\mathrm{Cl_2}$, respectively. The $\mathrm{Cl_3^+}$, $\mathrm{Cl_2H^+}$, and $\mathrm{Cl_2F^+}$ ions were isolated by selective ejection techniques and allowed to react with $\mathrm{CH_4}$ in the resonance cell. $\mathrm{Cl_3^+}$ yields both ions **a** and **b**, which were identified by accurate mass measurements of the expected isotopomers. On the contrary, $\mathrm{Cl_2H^+}$ and $\mathrm{Cl_2F^+}$ give no detectable amounts of **b**, consistent with the previously reported CI experiments, which showed that the intensity of ion **b** decreases as $\mathrm{Cl_2H^+}$ gradually replaces $\mathrm{Cl_3^+}$ as the chlorinating agent in the CI plasma.

Abstract in Italian: *La reazione di ioni* $\mathrm{Cl_3^+}$ *con il metano produce ioni* $[\mathrm{C,H_3,Cl_2}]^+$ *la cui struttura, stabilità e reattività sono state esaminate con tecniche spettrometriche di massa e con metodi teorici. L'isomero piû stabile che si ottiene é il diclorometano protonato,* $[\mathrm{ClH_2C{-}ClH}]^+$ ***(1)*** *il quale reagisce esclusivamente come acido di Brønsted. Si forma anche un isomero finora sconosciuto, lo ione* $[\mathrm{H_3C{-}Cl{-}Cl}]^+$ ***(2)*** *che reagisce come un agente clorurante e metilante. La reazione di formazione di* ***2*** *é il primo esempio di una nuova classe di sostituzioni elettrofile nelle quali un singolo atomo di H é sostituito dal catione biatomico diclorinio,* $[\mathrm{Cl{-}Cl}]^+$. *Nell'ambito della ricerca é stata determinata con metodi sperimentali e teorici, l'affinità protonica del diclorometano, ottenendo rispettivamente i valori di 150.2 ± 2 and 151 kcal mol*$^{-1}$.

Additional FT-ICR experiments were performed to ascertain whether **b** is a secondary product from the reaction of **a** with chlorine. To this end, $\mathrm{CH_4Cl^+}$ generated in an external source, isolated, and thermalized was driven into the cell containing $\mathrm{Cl_2}$. The process given in Equation (3) which would yield $\mathrm{CH_3Cl_2^+}$ was not observed.

$$\mathbf{a} + \mathrm{Cl_2} \nrightarrow \mathbf{b} + \mathrm{HCl} \qquad (3)$$

In addition, to investigate the structure and the reactivity of **b**, model $[\mathrm{C,H_3,Cl_2}]^+$ ions of known connectivity were prepared from the reactions (4) and (5).

$$\mathrm{CH_2Cl_2 + AH^+\ (A = CH_4, H_2) \longrightarrow CH_2Cl_2H^+\ (\mathbf{I}) + A} \qquad (4)$$

$$\mathrm{Cl_2 + CH_3X^+\ (X = CH_3F, CO_2, N_2) \longrightarrow CH_3Cl_2^+\ (\mathbf{II}) + X} \qquad (5)$$

Reaction (4) is expected to generate the ion **I** with the $[\mathrm{Cl{-}CH_2{-}Cl{-}H}]^+$ connectivity corresponding to protonated dichloromethane, whereas reaction (5) should give the $[\mathrm{CH_3{-}Cl{-}Cl}]^+$ ion (**II**) from the methylation of a molecule containing a preformed Cl–Cl bond.

MIKE and CAD spectrometry: Ions **I**, **II**, and **b** obtained from reactions (4), (5), and (2), respectively, were mass-selected and structurally assayed by MIKE and CAD mass spectrometry. The MIKE and CAD spectra of the m/z 85, 87, and 89 isotopomers from each reaction were recorded; those of the m/z 85 ion are reported in Table 1.

The MIKE spectrum of ion **I**, formed by $\mathrm{CH_4}$/CI of $\mathrm{CH_2Cl_2}$, shows a metastable decomposition characterized by a very narrow peak corresponding to the $\mathrm{CH_2Cl^+}$ fragment. Ions generated with a higher energy content, as in the $\mathrm{H_2}$/CI, as well as ions **II**, display no metastable decomposition.

The CAD spectra of the isotopomer of m/z 85 of ions **I** and **II** (Figure 1) proved structurally important: peaks at m/z 70 $[\mathrm{Cl_2}]^+$ and m/z 15 $[\mathrm{CH_3}]^+$ are present only in the spectrum of

Table 1. CAD spectra of m/z 85 isotopomer of $[C,H_3,Cl_2]^+$ ions **I**, **II**, and **b** obtained from reactions (4), (5), and (2), respectively.

	I	**II**		**b**[a]	
	CH_4/CI	CH_3F/CI	$ClCOOCH_3$/CI	R^1	R^2
m/z	intensities (% Σ)				
84	11.5	1.5	–	4.4	5.7
70	–	16.1	15.2	8.1	0.4
50	12.4	24.2	27.1	22.3	10.6
49	M[b]	25.6	26.5	24.0	43.8
48	25.2	9.4	8.7	13.8	12.8
47	25.7	6.4	6.8	13.9	16.7
37	3.5	–	–	2.5	2.4
36	12.6	–	–	–	4.0
35	7.2	8.4	9.8	6.9	3.5
15	–	7.0	8.2	3.4	–
14	1.9	1.4	1.7	0.8	–

[a] R^1 and R^2 ($R^1 > R^2$) denote decreasing Cl_2:CH_4 ratios. [b] M denotes a metastable transition.

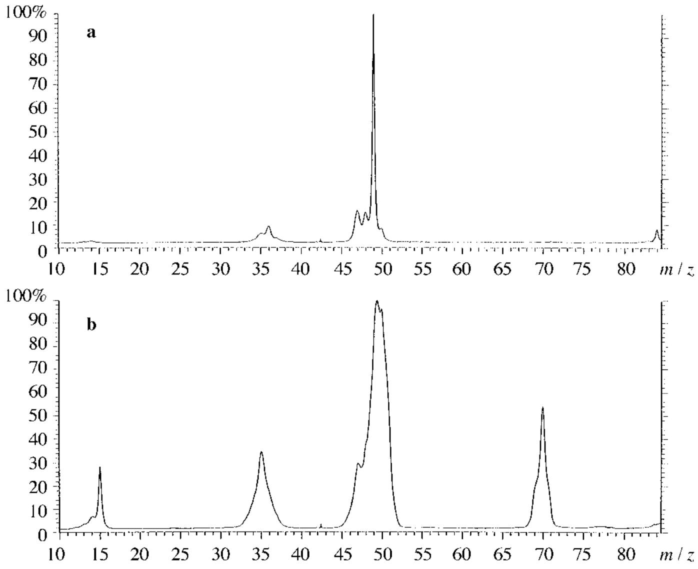

Figure 1. CAD spectra of a) ions **I** from reaction (4) and b) of ions **II** from reaction (5).

II, and that at m/z 36 $[HCl]^+$ is only formed from **I**. Moreover the fragment at m/z 50 $[CH_3Cl]^+$ is much more abundant in the spectrum of **II** than of **I**.

All these typical fragmentations are also present in the CAD spectrum of ions **b**, and their intensities change with the pressure of CH_4 within the CI source. This suggests that the ionic population sampled by CAD consists of a mixture of ions **I** and **II**, whose composition depends on the CH_4/Cl_2 ratio in the CI source.

ICR spectrometry: Ions **I**, **II**, and **b** were generated from reactions (4), (5), and (2), respectively, in the external source, and their reactivity towards selected nucleophiles was investigated to obtain structural information. The ion from reaction (4) acts essentially as a Brønsted acid, though extensive fragmentation to CH_2Cl^+ prevents accurate measurement of the proton affinity (PA) of CH_2Cl_2 by the equilibrium method, which probably accounts for the fact that this important thermochemical quantity is not reported in the literature. Nevertheless, we managed to extract useful information from the less accurate "bracketing" technique, establishing the following PA order: PA (COS), 150.2 kcal mol^{-1}, $\leq$ PA (CH_2Cl_2) $<$ PA (C_2H_2), 153.3 kcal mol^{-1}.[18] Since in the case of COS proton transfer occurs in both directions, the PA of CH_2Cl_2 and COS must be very close; our best experimental estimate is set at 150.2 ± 2 kcal mol^{-1}. The $CH_3Cl_2^+$ ion from reaction (5) displays the twofold character of Cl^+ and CH_3^+ (Me^+) donor towards nucleophiles of adequate Cl^+ and Me^+ affinity [Eq. (6) and (7)].

$$\mathrm{II + Nu} \longrightarrow \mathrm{NuCl^+ + CH_3Cl} \tag{6}$$

$$\mathrm{II + Nu} \longrightarrow \mathrm{NuCH_3^+ + Cl_2} \tag{7}$$

Reaction (6) is observed for a number of molecules such as CF_3I, CH_2F_2, C_6F_6, CH_4, CO, COS, CH_3NO_2, C_2H_2O, and CH_3OCH_3, whereas reaction (7) occurs with Nu = H_2O, CH_3OH, CF_3I, CH_3NO_2, C_2H_2O, and CH_3OCH_3. Ions **b** from reaction (2) display the same reactivity, apart from the following exceptions. Proton transfer to bases such as COS and C_6F_6 is observed whose efficiency, however, decreases at longer reaction times. In addition, if ions **b**, cooled by collisions with the neutral gas for a period of at least 2 s and isolated by "soft" single-shot ejection, are cooled by a supplementary delay time (typically 2 s), they no longer display any protonating ability. As a whole, these observations suggest that proton transfer to COS and C_6F_6 is promoted by *excited* ions **b**.

In an attempt to measure the methyl cation affinity (MCA) of Cl_2, reaction (7) was investigated in the forward and reverse direction with nucleophiles of known MCA.[19,20] The evaluation of Me^+ transfer equilibria is notoriously difficult, since kinetic factors can reduce the rate of exothermic transmethylation processes. As a consequence, the reaction is vulnerable to incursion of faster competitive processes that perturb the equilibrium measurements. Pertinent examples are the chlorination reaction (6), which can be faster than reaction (7), and the protonation of Cl_2, which can affect the reverse of reaction (7), when $NuCH_3^+$ can act also as a proton donor. As a result of these problems, we attempted to resort to the "bracketing" technique and found that the same kinetic factors can prevent the occurrence of energetically allowed transmethylation processes. An example is reaction (3), namely methyl transfer from HCl to Cl_2 described in a previous paragraph, which is too slow to be detected even in the absence of competing reaction channels. Nevertheless this observation does not necessarily imply that Cl_2 has a lower MCA than HCl, since neither the reverse Me^+ transfer from CH_3ClH^+ to Cl_2 is observed; this suggests that a sizable kinetic barrier is associated with this process. Therefore, our estimate of the MCA of Cl_2 is affected by a 9 kcal mol^{-1} uncertainty range, consistent with the following scale: MCA (CF_3I)[19,20] = 55.6 ± 3 kcal mol^{-1} > MCA (Cl_2) > MCA (Xe)[19,20] = 46.5 ± 3 kcal mol^{-1}, leading to MCA (Cl_2) = 51 ± 5 kcal mol^{-1}.

Computational results: The geometry of the neutral CH_2Cl_2 species, and that of the stationary points localized on the

$[CH_3Cl_2]^+$ potential energy surface are shown in Figure 2, whereas the energies and vibrational frequencies are reported in Table 2. Isomer **1** is the global minimum localized on the $[CH_3Cl_2]^+$ potential energy surface, whereas **2** is a less stable isomer 21.0 kcal mol^{-1} (298 K) higher in energy than **1** at the CCSD(T) level. Isomer **3** is the saddle which interconnects **1** and **2**; isomer **4** is the saddle for chlorine exchange in **2**, and **5** the saddle for the rotation of the methyl group in **2**. In saddle point **3** a hydrogen atom bridges a carbon and a chlorine atom. Both the C–H and H–Cl bond lengths are strongly elongated with respect to equilibrium values. For this reason, this structure cannot be properly described with a single reference based method such as CCSD(T). Only a multiconfigurational method like CASSCF, followed by an MRCI calculation, can provide an accurate quantitative energetic estimate, if at a very high computational cost. Therefore we refrained from performing CCSD(T) calculations on **3**, resorting to the B3LYP energies to obtain a rough estimate of the height of the barrier for the interconversion of **1** into **2**. Table 3 shows the energetics of selected reactions involving the $[CH_3Cl_2]^+$ species. From these values we can see that the PA of dichloromethane is calculated to be 151.0 kcal mol^{-1} at the CCSD(T) level.

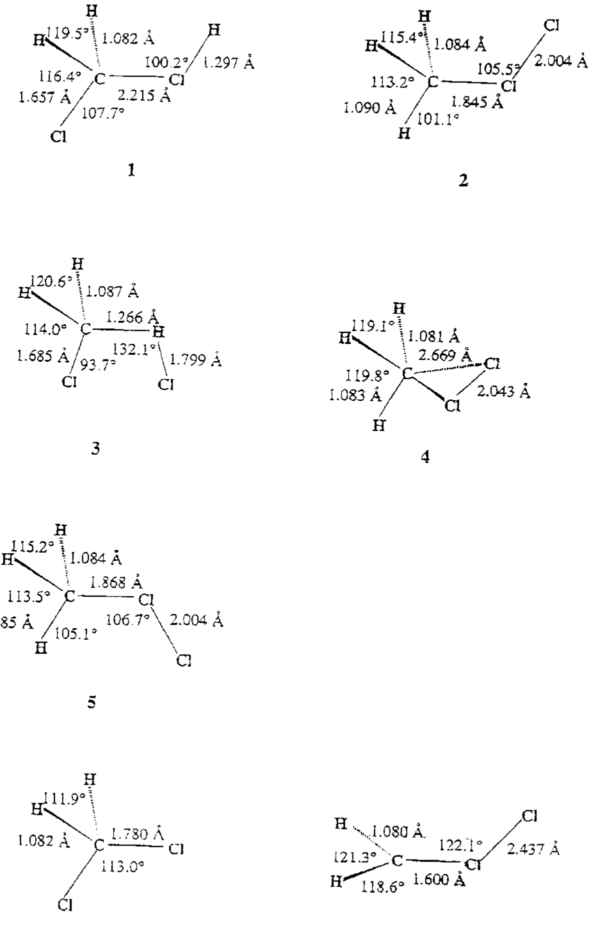

Figure 2. Stationary points localized on the potential energy surface of $[C,H_3,Cl_2]^+$ and geometry of $[CH_2Cl_2]$.

Table 3. Energetics [kcal mol^{-1}] at 298 K of selected reactions.

	ΔH_{298}	
	B3LYP	CCSD(T)
$\mathbf{1} \rightarrow \mathbf{6} + H^+$	153.5	151.0
$\mathbf{1} \rightarrow CH_2Cl^+ + HCl$	13.4	11.9
$\mathbf{2} \rightarrow CH_3^+ + Cl_2$	49.0	50.0
$\mathbf{2} \rightarrow \mathbf{7} + H^+$	191.5	194.4
$\mathbf{7} \rightarrow CH_2Cl + Cl$	15.4	13.5
$\mathbf{2} \rightarrow CH_3Cl + Cl^+$	96.2	89.1
$Cl_3^+ + CH_4 \rightarrow \mathbf{2} + HCl$	−42.2	−38.9
$Cl_2H^+ + CH_4 \rightarrow \mathbf{2} + H_2$	−3.9	−3.9
$Cl_2F^+ + CH_4 \rightarrow \mathbf{2} + HF$	−75.8	−82.1

Discussion

$[C,H_3,Cl_2]^+$ isomers: The structural evidence and reactivity probing carried out in the mass spectrometric experiments allow a clean differentiation between ions from reactions 4 and 5 that have to be taken as the model ions of connectivities **I** and **II**. The differences found reflect their intrinsic structural features.

$[Cl{-}CH_2{-}Cl{-}H]^+$ (**I**) $[CH_3{-}Cl{-}Cl]^+$ (**II**)

Table 2. Energies and frequencies of the stationary points found for $[CH_3Cl_2]^+$. Relative energies [kcal mol^{-1}] and IR intensities [km mol^{-1}] in parentheses. Total energies in Hartree, vibrational frequencies in cm^{-1}.

	1	2	3	4	5
E_{B3LYP}	−960.031147 (0)	−960.001801 (18.4)	−959.907085 (77.8)	−959.946614 (53.0)	−959.999342 (20.0)
ZPE[a]	0.035859	0.039131	0.032260	0.036058	0.038787
$E_{CCSD(T)}$	−958.928373 (0)	−958.897692 (19.3)	[b]	−958.838092 (56.7)	−958.895006 (20.9)
			vibrational frequencies		
	112.2 (36)	163.5 (0)	2037.8*i*	429.6*i*	164.5*i*
	128.4 (73)	212.7 (3)	210.4	60.5	226.8
	283.4 (75)	503.9 (8)	419.6	247.1	498.1
	606.0 (57)	544.0 (18)	424.2	526.8	528.7
	789.7 (0)	1027.5 (0)	862.3	565.9	1016.6
	898.9 (139)	1032.0 (8)	979.4	610.7	1022.7
	1071.8 (1)	1363.2 (5)	1081.9	1301.0	1359.6
	1175.0 (38)	1426.1 (20)	1123.6	1411.1	1434.1
	1456.8 (3)	1448.0 (20)	1370.4	1429.7	1441.9
	2821.9 (196)	3055.5 (28)	1425.5	3093.8	3073.6
	3133.3 (14)	3177.6 (24)	3068.8	3288.0	3207.5
	3263.0 (30)	3224.3 (17)	3194.4	3293.2	3215.8

[a] Zero-point energy. [b] See text.

In particular, i) the facile fragmentation of **I** into CH_2Cl^+ (MIKE) and HCl^+ (CAD), ii) the absence of the Cl_2^+ and CH_3^+ fragments in the CAD spectra, and iii) the ability of **I** to undergo proton, but not CH_3^+ nor Cl^+ transfer, are consistent with the assignment of the $[Cl{-}CH_2{-}Cl{-}H]^+$ structure of protonated dichloromethane to ion **I**. Conversely, i) the Cl_2^+ and CH_3^+ fragments in the CAD spectra of **II**, ii) the absence of the HCl^+ fragment, and iii) its chlorinating and methylating ability support the $[CH_3{-}Cl{-}Cl]^+$ connectivity assigned to ions from reaction (5).

The theoretical analysis has localized two minima **1** and **2** with the connectivity **I** and **II**, respectively, on the potential energy surface of the $[C,H_3,Cl_2]^+$ system. The global minimum is **1**, a $[H_2(Cl)C{-}ClH]^+$ structure characterized by a rather long C–Cl bond consistent with the narrow peak, typical of a weakly bound parent ion, observed in the metastable decomposition of **I** to CH_2Cl^+. The experimental difficulty to evaluate the PA of the corresponding neutral CH_2Cl_2 is also consistent with a picture in which the most stable protomer is an ion-molecule complex, prone to easy dissociation when not completely thermalized. This causes its depletion and a correspondent enrichment of the less stable protomer in the ionic population. From the experimental PA of CH_2Cl_2 and other available thermochemical data,[18] H_f° (**1**) = 192.6 kcal mol^{-1} can be obtained, and the endothermicity of its dissociation into CH_2Cl^+ and HCl = 14.5 kcal mol^{-1}, with an estimated error of about 3 kcal mol^{-1}. In good agreement with the experimental results, the PA of CH_2Cl_2 calculated at the CCSD(T) level is 151 kcal mol^{-1}, and the dissociation threshold of **1** is located at 11.9 kcal mol^{-1} (Table 3). The exothermicity of reaction (4) can be estimated from the H_f° value (**1**) to be about 20 kcal mol^{-1} in the case of CH_5^+ and 49 kcal mol^{-1} in the case of H_3^+.[21] Accordingly, and consistent with their low dissociation threshold to CH_2Cl^+, ions **1** generated with a large internal energy excess, as in the H_2/CI experiment, completely decompose within the source out of the metastable time window.

Isomer **2**, which is less stable than **1** by 21.0 kcal mol^{-1} (298 K) at the CCSD(T) level of theory, displays the $[CH_3{—}Cl{-}Cl]$ connectivity of **II**. In this context, the experimental and calculated MCA of Cl_2, 51 and 50 kcal mol^{-1}, respectively, compare exceptionally well, although the agreement is at least partially fortuitous and allows us to evaluate the H_f° (**2**) = 210.3 ± 5 kcal mol^{-1}. In this case reaction (5) is slightly exothermic and provides a mild route to $CH_3Cl_2^+$ from all the methylating agents employed.[21]

Remarkably, the deprotonation reaction of **2**, calculated to be endothermic by 194.4 kcal mol^{-1} (Table 3), is theoretically predicted to generate a neutral CH_2ClCl (**7**) that has been localized on the surface as a minimum, about 62 kcal mol^{-1} above the CH_2Cl_2 isomer **6**. Our attempts to investigate the protonating ability of $CH_3Cl_2^+$ ions demonstrated that proton transfer reactions actually occur to bases with PA_S values greater than 170 kcal mol^{-1}, a lower value than theoretically predicted, probably due to the ensuing decomposition of CH_2ClCl to CH_2Cl and Cl. Finally, from the H_f° of **2** the dissociation into CH_3Cl and Cl^+ is endothermic by 98.1 ± 5 kcal mol^{-1}, comparable to the calculated value of 89.1 kcal mol^{-1}, which corresponds to the Cl^+ affinity of the chlorine atom of CH_3Cl. This Cl^+ binding energy is higher than recently obtained for other chlorinated compounds,[9] probably reflecting the combined effects of the electron-rich chlorine atom and the electron-donating ability of the methyl group.

The $[C,H_3,Cl_2]^+$ ions from reaction (2): The experimental results indicate that ions **b** from the reaction of Cl_3^+ with CH_4 are a mixed population of ions **1** and **2**, whose connectivities correspond to the model ions **I** and **II**, respectively. The schematic potential energy surface reported in Figure 3 shows that the barrier of the isomerization of **2** is comparable to its dissociation threshold (51 kcal mol^{-1}) and much higher than that of **1** (14.5 kcal mol^{-1}). This makes it experimentally difficult to distinguish between the two conceivable routes to a mixed population of ions **1** and **2**, namely i) its direct formation by a highly exothermic process and ii) the partial isomerization of an initially pure population of ions **2** into **1**. The exothermicities of reaction (2) for the formation of **1** and **2** from the H_f° values of **1** and **2** are 45.5 and 63.2 kcal mol^{-1}, respectively, proving more energetic routes to $CH_2Cl_2H^+$ and $CH_3Cl_2^+$ than reactions (4) and (5), by which the model ions were obtained.[21] Nevertheless, based on the structure of the reagents involved, direct formation of **1** can in our opinion hardly be explained, and it is therefore more reasonable that initially formed ions **2** can isomerize to **1**.

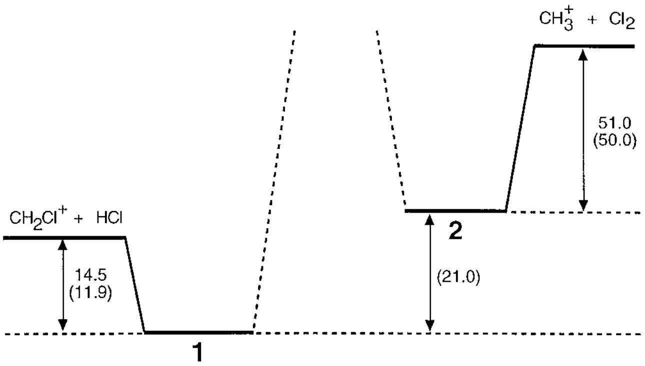

Figure 3. Potential energy surface of $[C,H_3,Cl_2]^+$ system at 298 K. The experimentally derived values and the theoretically derived values (in parentheses) are given. See text for details on the height of the interconversion barrier **1** → **2**.

As shown in Table 1, the composition of the mixed population sampled by CAD spectrometry shows a strong dependence on the pressure of CH_4; it changes from a prevalence of ions **2** at low pressures to a prevalence of **1** at higher pressures. According to the typical behavior of weakly bound complexes, the increase of the pressure causes the stabilization of a larger fraction of excited ions **1** that otherwise would easily decompose to CH_2Cl^+ and HCl. This feature seems distinctive of ions **1** from highly exothermic processes, and is observed also in the populations from the strongly exothermic protonation of CH_2Cl_2 by H_3^+. The FT-ICR results also support the hypothesis based on the isomerization of ions **2** that have sufficient energy (internal, or translational from the RF "shots" used for their isolation) to overcome the barrier to the rearrangement to give **1**. Indeed,

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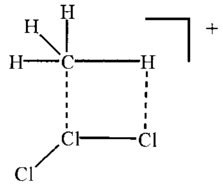
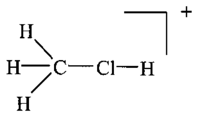
the protonating ability of the population from reaction (2) disappears after an adequate cooling period.

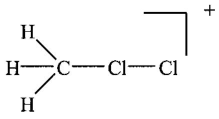
Mechanistic aspects: Formation of **b** by a formal Cl_2^+ transfer to methane with the simultaneous loss of HCl is a remarkable reaction and investigation of its mechanism is therefore of interest. A conceivable hypothesis can be based on a four-center transition state which could account, in addition, for



the failure of other chlorinating agents, such as Cl_2F^+ and Cl_2H^+, to undergo Cl_2^+ transfer to methane as a result of their varying geometries and/or to the lack of suitable leaving groups. We note, however, that the above mechanism does not account for the formation of CH_3ClH^+, the other product from the reaction. Furthermore, a four-center transition state of rigidly defined geometry is undoubtedly characterized by a highly unfavorable activation entropy. A more reasonable hypothesis can proceed from the observation that the reaction products **a** and **b** contain a CH_3 group, which requires the loss



a



b

of one of the H atoms initially present in the methane molecule. This suggests a two-step mechanism in which the loose ion-neutral complex formed upon the electrostatic association of the reagents undergoes hydride abstraction by Cl_3^+.

$$[CH_4\quad Cl_3^+]\,(INC1) \longrightarrow [CH_3^+\quad HCl\quad Cl_2]\,(INC2)$$

It then evolves into another complex formed by a methyl cation, a chlorine molecule, and a hydrogen chloride molecule. In the second step the cation can be trapped by either neutrals, according to Equations 1**a** and 2**b** yielding the observed products, namely **b** and protonated methyl chloride. As to the energetics of the process, the dissociative hydride-ion abstraction, as shown in Equation (8), is estimated to be endothermic by 5.5 kcal mol^{-1}, based on available thermochemical data[8,18] referenced to the *isolated species*.

$$[CH_3^+,HCl,Cl_2] \begin{cases} \longrightarrow CH_3ClH^+ + Cl_2 & (1\mathbf{a}) \\ \longrightarrow CH_3Cl{-}Cl^+ + HCl & (2\mathbf{b}) \end{cases}$$

$$CH_4 + Cl_3^+ \longrightarrow CH_3^+ + HCl + Cl_2 \qquad (8)$$

However, the electrostatic interaction between Cl_3^+ and CH_4 leading to INC1 is likely to release a larger amount of energy, which makes the overall process leading to INC2 energetically allowed. As to the second step, both nucleophiles, HCl and Cl_2, are present in equimolecular concentration within INC2, and their MCA are close, which accounts for the unselective character of their competitive methylation yielding comparable amounts of $CH_3Cl_2^+$ and CH_3ClH^+.

$$Cl_2H^+ + CH_4 \begin{cases} \longrightarrow \mathbf{a} + HCl & (9) \\ \nrightarrow \mathbf{b} + H_2 & (10) \end{cases}$$

The two-step mechanism provides an explanation for the formation of both products observed and does not involve the formation of a tight, entropically unfavorable four-center transition state.

In the framework of the two-step mechanism the reactivity of Cl_2H^+ towards methane is attributed to the different energetics of the first step of reactions (9) and (10). Indeed, whereas reaction (9**a**) is estimated to be nearly thermoneutral for isolated reagents ($\Delta H^\circ = +0.6$ kcal mol^{-1})[7,18] and certainly energetically allowed when occurring in the [CH_4 Cl_2H^+] INC, reaction (10**b**) is highly endothermic ($\Delta H^\circ = 44.8$ kcal mol^{-1}).[7,18]

$$CH_4 + Cl_2H^+ \longrightarrow CH_3^+ + 2\,HCl \qquad (9\mathbf{a})$$

$$CH_4 + Cl_2H^+ \longrightarrow CH_3^+ + H_2 + Cl_2 \qquad (10\mathbf{b})$$

This explains why only reaction (9) occurs, despite the fact that overall reactions (9) and (10) are both exothermic by 46.7 kcal mol^{-1} and 6.2 kcal mol^{-1}, respectively.

In the case of Cl_2F^+, the formation of **a** through the overall reaction (11) occurs because the first step [reaction (11**a**)] is thermoneutral ($\Delta H^\circ = 0$ kcal mol^{-1})[8,18] for isolated species and hence energetically allowed in the [CH_4 Cl_2F^+] complex.

$$CH_4 + Cl_2F^+ \longrightarrow \mathbf{a} + ClF \qquad (11)$$

$$CH_4 + Cl_2F^+ \longrightarrow CH_3^+ + HCl + ClF \qquad (11\mathbf{a})$$

Capture of the methyl cation by HCl then yields **a**, with an estimate of the overall exothermicity of reaction (11) of 47.3 kcal mol^{-1}.[8,18] Interestingly, no CH_3ClF^+ is formed, pointing to a selective capture of the methyl cation by HCl, rather than by ClF, the other neutral component present in the complex, which is consistent with the much lower nucleophilicity, and hence the corresponding lower MCA of chlorine fluoride. As previously noted, the reaction (12) does not occur.

$$CH_4 + Cl_2F^+ \nrightarrow \mathbf{b} + HF \qquad (12)$$

$$CH_4 + Cl_2F^+ \rightarrow CH_3^+ + HF + Cl_2 \qquad (12\mathbf{b})$$

Here the first step is highly exothermic, and $\Delta H^\circ(12\mathbf{b})$ is estimated to be as large as -30.9 kcal mol^{-1},[8,18] which causes prompt dissociation of the cluster and prevents formation of **b**.

Conclusions

The reaction of Cl_3^+ with CH_4 provides the first example of a new electrophilic substitution process, which is characterized by the formal replacement of a H atom of a saturated hydrocarbon by a $[Cl{-}Cl]^+$ dichlorinium ion. This hitherto unknown substitution is accompanied by a conventional monohalogenation reaction. The most simple mechanistic hypothesis capable of explaining the simultaneous operation of the two reactions, and their comparable rate, involves a two-step process whose first stage leads to the formation of a $[CH_3^+\ HCl\ Cl_2]$ ionic complex. With regard to the structure of the products, the present study allowed the theoretical and experimental characterization of two $[C,H_3,Cl_2]^+$ isomers with the $ClH_2C{-}{-}Cl{-}H^+$ and the $CH_3Cl{-}Cl^+$ connectivity. The more stable isomer **1** behaves as a Brønsted acid, undergoing exclusively H^+ transfer to gaseous bases. In this context, application of experimental and theoretical methods allowed evaluation of the hitherto unknown PA of dichloromethane, whose best theoretical estimate, 151 kcal mol^{-1} at the CCSD(T) level, is comparable with the experimental one, 150.2 ± 2 kcal mol^{-1}. Consistent with its connectivity, **2**, the new isomer identified, acts as a chlorinating and methylating agent towards gaseous nucleophiles. Interestingly, the theoretical study of its deprotonation suggests the intriguing possibility that the conjugate base, which exhibits $CH_2{-}Cl{-}Cl$ connectivity, may be a kinetically stable neutral species. Work to experimentally substantiate this prediction is currently under way in our laboratory.

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[21] Taking H_f^o (**1**) = 192.6 kcal mol^{-1} and H_f^o (**2**) = 210.3 kcal mol^{-1}, and combining data from refs. [8,9,18–20], ΔH° (4) = −20.3 kcal mol^{-1} (CH_4/CI) and −49.3 kcal mol^{-1} (H_2/CI); ΔH° (5) = −0.5 kcal mol^{-1} (CH_3F/CI), −6 kcal mol^{-1} ($ClCOOCH_3$/CI) and −7 kcal mol^{-1} (CH_2N_2/CI); ΔH° (**2**) = −63.2 kcal mol^{-1} for the formation of (**1**) and −45.5 kcal mol^{-1} for the formation of (**2**). For comparison the calculated ΔH° (2) (**1**) = −38.9 kcal mol^{-1} (see Table 3).

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