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Gas-Phase Chemistry of $NH_xCl_y^+$ Ions. 3. Structure, Stability, and Reactivity of Protonated Trichloramine

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The structure, stability, and reactivity of $[NCl_3]H^+$ ions from protonation of gaseous trichloramine NCl_3 with $C_nH_5^+$ ($n = 1, 2$) and H_3O^+ ions were studied by mass spectrometric techniques, Fourier transform ion cyclotron resonance (FT-ICR), and triple quadrupole (TQ) mass spectrometry and computational methods. Kinetic experiments, performed to determine the basicity of NCl_3, suggested the existence of two $[NCl_3]H^+$ populations. Consistent with the higher basicity of the nitrogen atom in NCl_3, theoretical calculations characterize the most stable isomer as the $H-NCl_3^+$ ion and suggest for the less stable one, the $HCl-NCl_2^+$ structure, corresponding to the trichloramine protonated on the chlorine atom. The calculated gas-phase basicities (GB) of NCl_3, 679.9 and 692.6 kJ/mol at the B3LYP and CCSD(T) level of theory, respectively, are fully consistent with the experimental value, 687.3 ± 8 kJ/mol. The proton affinity (PA) of NCl_3 is 721.5 ± 8 kJ/mol. The chloronium ion affinities (Cl^+ affinities) of the Cl atom of monochloramine and dichloramine were calculated from the enthalpy of formation (ΔH_f°) of $[H_2NClCl^+]$ and $[HN(Cl)Cl_2^+]$ ions. Whereas the affinity of the nitrogen atom for the H^+ and the Cl^+ ions and the affinity of the chlorine atom for the Cl^+ ion decrease on going from NH_2Cl to NCl_3, the opposite trend is observed for the proton affinities of the chlorine atom. Studies on the reactivity of $[NCl_3]H^+$ ions toward simple nucleophiles showed both a remarkable chlorinating and protonating ability, in accordance with their Lewis and Brønsted acid character.

Introduction

The reactions of chlorine, hypochlorite, or hypochlorous acid with ammonia or ammonium compounds, in solution and in the gas phase, are known to lead to the formation of inorganic chloramines, $NH_{3-n}Cl_n$ ($n = 0-3$), whose compositions depend on the relative amounts of the reactants and on the pH value of the solution.[1−4] Among inorganic chloramines, nitrogen trichloride or trichloramine (NCl_3) is the most unstable in the pure form and it is highly explosive, a strong irritant, and a lacrimator. However, in dilute acidic solutions it is moderately stable and at very low concentration the explosion hazard is eliminated or greatly reduced.

Nitrogen trichloride was first synthesized in 1811 by Dulong,[2] by the action of chlorine with a solution of an ammonium salt. Other syntheses employ hypochlorite with ammonium chloride and extraction by organic solvents or the gas-phase reaction of chlorine with ammonia.[3]

The mechanisms of formation and the reactivity of NCl_3 are of fundamental interest in environmental protection because trichloramine is formed during disinfecting potable and wastewater by reaction of chlorine or hypochlorite with ammoniacal solutions.[5] Although it is easily lost from aqueous solutions being very volatile and scarcely soluble in water, small concentrations still give a distinctive and objectionable taste to drinking water[6] and occupational exposure assessment studies proved its toxicity.[7]

Sometimes NCl_3 is an undesirable byproduct of hydrometallurgical processes,[8] of brine electrolysis, and electrolysis of NH_4Cl and ammonium compounds solutions.[9]

Nitrogen trichloride is also an important reagent in organic synthesis[3] and, at the present time, find many industrial applications as a nitrogen source in the formation of nitride thin films in the plasma-enhanced chemical vapor deposition processes or as an etching gas, in the plasma etching processes of electronic devices fabrications.[10]

Although NCl_3 has been a subject of numerous experimental and theoretical studies, owing to its unstable and explosive nature it has never been extensively studied in the free state. Only a few studies on the gas-phase ion chemistry of NCl_3 have been reported[11] and, to the best of our knowledge, the gas-phase basicity (GB) has not previously been measured nor has the reactivity of $[NCl_3]H^+$ ions been investigated.

In this work the GB and the proton affinity (PA) of NCl_3 were estimated and the reactivity of $[NCl_3]H^+$ ions investigated by combining mass spectrometric (FTICR-MS and TQ-MS) and theoretical techniques. Recently, we used the application of mass spectrometric and theoretical techniques to study the reactivity and the basicity of mono- and dichloramine.[12] Proton affinities and chloronium ion affinities (Cl^+ affinity) of the nitrogen and chlorine atoms of mono-, di-, and trichloramine,[13] as well as structural changes following protonation and chlorination, are discussed.

Experimental Section

Nitrogen trichloride is a bright-yellow liquid with a powerful irritating odor and limited solubility in water (mp below −40

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°C and bp of +70 °C). It is very volatile and is easily lost from aqueous solutions. Solutions of NCl_3 were prepared by mixing NH_4Cl solution with a three time excess of HOCl at pH 4−5 in unbuffered medium. NCl_3 was then directly allowed to expand, together with water vapor, into the external ion source of the mass spectrometer.

ICR experiments were performed using an Apex TM 47e FT-ICR spectrometer from Bruker Spectrospin AG equipped with an external ion source where protonated trichloramine (MH^+) was generated by positive chemical ionization (CI) using CH_4 as the reagent gas at a pressure of ca. 10^{-4} Torr and temperature of 150 °C. The MH^+ ions were transferred into the resonance cell (25 °C) where $[N^{35}Cl_3]H^+$ ions were isolated by broad band and “single shot” ejection pulses. After thermalization by argon, introduced by a pulsed valve, and after a delay time of 1 s, the ions were re-isolated by “single shots” and allowed to react with neutral reagents in the cell. The pressure of the neutral reactants ranging from 10^{-8} to 10^{-7} mbar was measured by a Bayard-Alpert ionization gauge, whose readings were calibrated using, as a reference, the known rate coefficient of the $CH_4 + CH_4^+ \rightarrow CH_5^+ + CH_3^\bullet$ reaction.[14] The readings were corrected for the relative sensitivity to the various gases used according to a standard method.[15] The pseudo-first-order rate constants were obtained by plotting the logarithm of $I_t/I_{t=0}$ ratio of $[N^{35}Cl_3]H^+$ as a function of the reaction time. Then the bimolecular rate constants were determined from the number density of the neutral molecules, deduced in turn from the pressure of the gas. Average dipole orientation (ADO) collision rate constants, k_{ADO}, were calculated as described by Su and Bowers.[16] Reaction efficiencies, RE, are the ratio of k_{ADO}, the collision rate constants, to the experimental rate constants, k_{exp}. The uncertainty of each rate constant is estimated to be 30%. The collisionally activated dissociation (CAD) experiments were performed using a triple quadrupole mass spectrometer model Quattro TQ from VG Micromass Ltd. The MH^+ ions generated in the CI source were driven into the collision cell, actually a RF-only hexapole, containing the neutral reagent. CAD spectra were recorded utilizing Ar as the target gas at such a pressure to reduce the main beam intensity to 80% of its initial value. The charged products were analyzed with the third quadrupole, scanned at a frequency of 150 amu s^{-1}.

Computational Details

Density functional theory, using the hybrid[17] B3LYP functional,[18] were 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[19] with a perturbational estimate of the triple excitations [CCSD(T)] approach.[20] 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. The 6-311++G(3df,3pd) basis set[21] has been used. All calculations were performed using Gaussian 98.[22]

Results

Formation of $[NCl_3]H^+$ Ions. The NCl_3 vapors distilling from an aqueous solution were directly injected into the source of the mass-spectrometer through a capillary column. The $[NCl_3]H^+$ ions (*m/z* 120, 122, 124, 126) were obtained using CI/CH_4 conditions according to process 1. The inevitable presence of

$$NCl_3 + C_nH_5^+ \ (H_3O^+) \rightarrow [NCl_3]H^+ + C_nH_4 \ (H_2O) \qquad (1)$$
$$n = 1, 2$$

water in the gaseous mixture introduced in the CI source leads to the formation of H_3O^+ ions and therefore proton transfer to trichloroamine does not occur exclusively from the C_nH^+ ions, characteristic of the CH_4 chemical ionization, but from H_3O^+ ions as well.

TABLE 1: CAD Spectra of $[N^{35}Cl_3]H^+$ Ions from Reaction 1 Taken at Different Collision Energies (Laboratory Frame)

		relative intensities				
fragment	*m/z*	5 eV	10 eV	20 eV	50 eV	100 eV
$N^{35}Cl_2H^+$	85	89.5	95.0	86.8	59.4	51.1
$N^{35}Cl_2^+$	84	10.5	5.0	4.2	5.6	4.9
$N^{35}ClH^+$	50			4.0	23.1	28.7
$N^{35}Cl^+$	49			5.0	11.9	15.3

Structural Characterization of $[NCl_3]H^+$ Ions. Three $[NCl_3]H^+$ isomers of different connectivities, **I**, **II**, and **III**, are conceivably formed from reaction 1, Whereas ions **I** and **II** are

$$\underset{\textbf{I}}{[H{-}NCl_3]^+} \quad \underset{\textbf{II}}{[HCl{-}NCl_2]^+} \quad \underset{\textbf{III}}{[H{-}N(Cl)Cl_2]^+}$$

the protomers of trichloroamine, the possible formation of isomer **III**, characterized by the Cl−Cl connectivity, is postulated on the analogy with the $H_2NCl{-}Cl^+$ ions previously observed in the CI/CH_4 plasma of dichloroamine.

Collisionally activated dissociation (CAD) mass spectrometry has been used to obtain structural information on the $[NCl_3]H^+$ population arising from protonation of trichloroamine. The low-energy CAD spectra of the $[N^{35}Cl_3]H^+$ ions (*m/z* 120) from reaction 1, recorded at nominal collision energy of 5−100 eV (laboratory frame) are reported in Table 1. The spectra are dominated by the fragment at *m/z* 85, corresponding to the loss of a Cl atom. This fragmentation is not particularly informative because it may be attributable to any of the postulated isomers. By contrast, the minor fragmentation channel leading to the ion at *m/z* 84 through the loss of a HCl molecule, speaks in favor of the isomer characterized by the connectivity **II**. In the absence of model ions of known connectivity, the CAD results do not allow a definitive conclusion as to the connectivity of the $[NCl_3]H^+$ ions.

Experimental Evaluation of GB of NCl_3. As in the case of mono- and dichloramine, the only reliable method for estimating the gas-phase basicity of nitrogen trichloride is the thermokinetic method. In fact, the evaluation of gas-phase basicity by equilibrium methods[23] presupposes the knowledge of the pressure of both neutral reagents involved. In our experiments, the presence of water and eventually of other chloramines distilling from the aqueous solution together with NCl_3 precludes the knowledge of its partial pressure. Besides, the kinetic method proposed by Cooks et al.[24] based on the dissociation of proton bound dimers is not achievable owing to the lack of proton bound dimers between NCl_3 and the reference bases. The thermokinetic method[26] allows us to reduce the uncertainty range of the GB values estimated by the “bracketing method”[25] on the bases of the empirical relationship between the measured efficiencies and the standard free energy of proton transfer from the investigated molecule (M) to reference bases (B). To evaluate the GB of trichloramine, $[N^{35}Cl_3]H^+$ ions, generated in the external CI ion source, were isolated, thermalized, re-

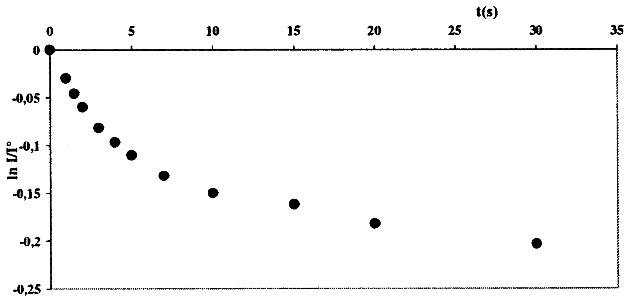


Figure 1. Time profile of the ionic intensities in the reaction of $[NCl_3]H^+$ (●) with CF_3CH_2OH ($P = 7.1 \times 10^{-8}$ Torr).

isolated by soft ejection pulses, and allowed to react with bases of different strength in the resonance cell using only bases with lone electron pairs as the basic center.

All the GB values used to establish the correlation between RE and GB are taken from ref 27, to make use of a self-consistent scale based on a single anchoring value.

As expected, the efficiency is close to zero for strongly endoergic proton-transfer reactions involving bases such as $CF_3CH(OH)CF_3$ (GB = 656.2 kJ/mol), H_2O (GB = 660.0 kJ/mol), and C_2H_5Cl (GB = 666.9 kJ/mol), whereas the efficiency is high, or equal to the unity, for exoergic processes with bases such as CF_3COCH_3 (GB = 692.0 kJ/mol), F_2CHCH_2OH (GB = 697.0 kJ/mol), CF_3COOCH_3 (GB = 709.6 kJ/mol), $ClCH_2CN$ (GB = 715.0 kJ/mol), and CH_3OH (GB = 724.5 kJ/mol).

In the range of basicity spanning from 667 to 681 kJ/mol, the semilogarithmic plot of the $[N^{35}Cl_3]H^+$ ionic intensities as a function of time shows the nonlinear profile displayed, for a typical case, in Figure 1. This feature appears to indicate a mixture of two different ionic populations, whose deprotonation reactions have different kinetic rate constants. To rule out the possibility of an artifact caused by an inefficient thermalization of the $[N^{35}Cl_3]H^+$ ions, many experiments have been performed. No changes in the ionic intensities profile were observed when methane, instead of argon, is used as the thermalization gas or if particular attention was devoted to the isolation conditions (attenuation of shots, sweep, etc.).

Increasing the basicity of the reference bases, the semilogarithmic plot of the $[N^{35}Cl_3]H^+$ ionic intensities as a function of time correctly becomes linear. Similar behavior was previously observed[12b] in the experiments performed to measure the basicity of dichloroamine ($NHCl_2$) and it was attributed to the presence of two isomeric $[NHCl_2]H^+$ ions.

Investigating the possibility that the plot of the total intensity $I(t)$ of $[N^{35}Cl_3]H^+$ ions vs reaction time was the result of bimodal kinetics, a curve fitting program was used and the individual initial intensities of two isomeric populations and the relative deprotonation rate constants were extracted from this plot.

It is well-known that the total intensity $I(t)$ of a mixture of two protonated species (M_iH^+) ($i = 1, 2$) undergoing deprotonation by a reference base, B, at reaction time t, is given by

$$I(t) = \Sigma I_o(M_iH^+)e^{-k_it}$$

where $k_i = k_{oi}[B]$ corresponds to the pseudo-first-order rate constant of the deprotonation reaction of isomer i by the base B, k_{oi} is the corresponding bimolecular rate constant, and $I_o(M_iH^+)$ is the initial concentration of isomer i.[28]

When CF_3CH_2OH (GB = 669.9 kJ/mol) is used as the reference base, the deprotonation efficiency of the less stable $[NCl_3]H^+$ isomer, M_2H^+, results in RE = k_{exp}/k_{ADO} = 38%, whereas the deprotonation of the more stable ion M_1H^+ occurs very slowly (RE=0.4%).

Increasing the basicity of the reference bases causes the disappearance of the less basic M_2H^+ ion, in accordance with its fast deprotonation accomplished in the ICR cell before starting the kinetic measurements, and makes it possible to measure the deprotonating efficiency of M_1H^+ from a linear semilogarithmic plot.

The results of the best fitting procedure, engaged to probe the existence of a mixture of two different $[N^{35}Cl_3]H^+$ ions, are reported in Table 2.

Then, to deduce GB(M_1) and GB(M_2), according to the thermokinetic method,[26] the deprotonation efficiencies of both isomers obtained by deconvolution of bimodal kinetics, are fitted by the parametric function

$$\mathrm{RE} = \mathbf{a}/\{1 + \exp[\mathbf{b}(\Delta G^\circ + \mathbf{c})]\} = \mathbf{a}/\{1 + \exp[\mathbf{b}(\mathbf{c}'' - \mathrm{GB(B)})]\}$$

with GB as a second variable, where **a** is the normalizing factor, ranging from 0.8 to 1.0, **b** = $1/RT^*$ (T^* is the effective temperature that can be different from the experimental temperature owing to a nonequilibrium distribution of the internal energy of the $[MHB^+]$ intermediate), $\mathbf{c}'' = \mathrm{GB(M)} + \mathbf{c}$, and $\mathbf{c} = \Delta G^\circ_a$. The last term was found to be of the same order of magnitude as the term $RT^* = 1/\mathbf{b}$. Thus, assuming that **c** is precisely equal to RT^*, one obtains $\mathrm{GB(M)} = \mathbf{c}'' - 1/\mathbf{b}$.

According to this method, the reaction efficiencies of the proton-transfer processes from M_1H^+ and from M_2H^+ to bases of known GB have been fitted in the equation as illustrated in Figure 2.

From the best fit of the data concerning the deprotonation of M_1H^+ we obtain **a** = 0.991, **b** = 0.353, **c″** = 690.1, T^* = 68 °C, and a M_1 gas-phase basicity value of 687.3 ± 8 kJ mol^{-1},

TABLE 2: Gas-Phase Basicities of Reference Bases, Collisional Efficiencies, and Experimental Rate Constants of Proton-Transfer Reactions of Both M_1H^+ and M_2H^+ Isomers, Calculated by the Best Fitting Procedure

			M_2H^+		M_1H^+	
B	PA[a] (kJ/mol)	GB[a] (kJ/mol)	eff %	K_{exp} (10^{-9} cm^3 s^{-1} mol^{-1})	eff %	K_{exp} (10^{-9} cm^3 s^{-1} mol^{-1})
C_2H_4	680.5	651. 5	~0[b]		~0	
$CF_3CH(OH)CF_3$	686.6	656.2	~0		~0	
H_2O	691.0	660.0	~0		~0	
C_2H_5Cl	693.4	666. 9	~0		~0	
$CF_3\,CH_2OH$	700.2	669.9	38	0.54 ± 0.1	0.4	0.006 ± 0.02
$(CF_3CH_2)_2O$	702.3	674.9	88	0.87± 0.12	3.8	0.038 ± 0.07
$CF_3\,COOH$	711.7	680.7	75	0.77 ± 0.1	2.8	0.029 ± 0.01
CF_3COCH_3	723.9	692.0	(100)[c]	(1.5)[d]	83	1.3 ± 0.1
CCl_3CN	723.2	692.6	(100)[c]	(1.8)[d]	72	1.3 ± 0.2
CF_3COOCH_3	740.5	709.6	(100)[c]	(1.5)[d]	97	1.4 ± 0.1
$ClCH_2CN$	745.7	715.1	(100)[c]	(1.7)[d]	93	1.6 ± 0.1

[a] From ref 27; [b] The efficiency is referred to the proton-transfer reaction; chlorination is not considered. [c] Deduced value. [d] k_{ADO} value

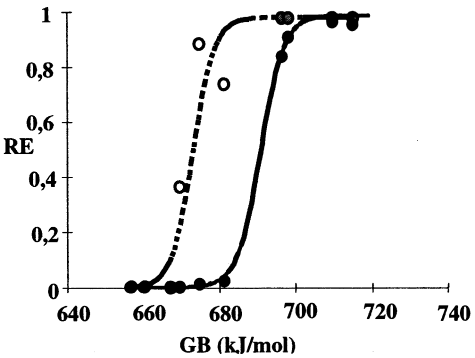


Figure 2. Reaction efficiencies (RE) of proton transfer from $[NCl_3]H^+$ to reference bases (B) vs gas-phase basicities, GB(B). Open circles refer to the deprotonation of M_2H^+(**II**), dark circles refer to the deprotonation of M_1H^+(**I**), and grey circles are deduced from experiments showing a linear decrement of semilogarithmic plot of ionic intensities as a function of the time.

TABLE 3: Optimized Geometries and Energies of NCl_3, $HNCl_3^+$ (I), $HClNCl_2^+$ (II), and $HN(Cl)Cl_2^+$ (III) in Their Singlet Ground States[a]

	NCl_3 $^1A_1$	I $^1A_1$	II $^1A'$	III $^1A'$
r(NCl)	1.772	1.753	1.634 2.715	1.635 1.688
r(NH)		1.026		1.023
r(ClH)			1.289	
r(ClCl)				2.079
∠(ClNH)		106.3		113.0
∠(ClNCl)	118.1	112.5	115.2	120.1
∠(NClH)			92.1	
∠(NClCl)				117.3
E_{B3LYP}	−1435.336894	−1435.620355	−1.435.602255	−1435.599762
ZPE[b]	0.006043	0.019905	0.013034	0.018368
$E_{\mathrm{CCSD(T)}}$	−1433.719707	−1434.007980	−1433.977759	−1433.974459

[a] Bonds lengths in angstroms, angles in degrees, total energies in hartree. [b] Zero point energy.

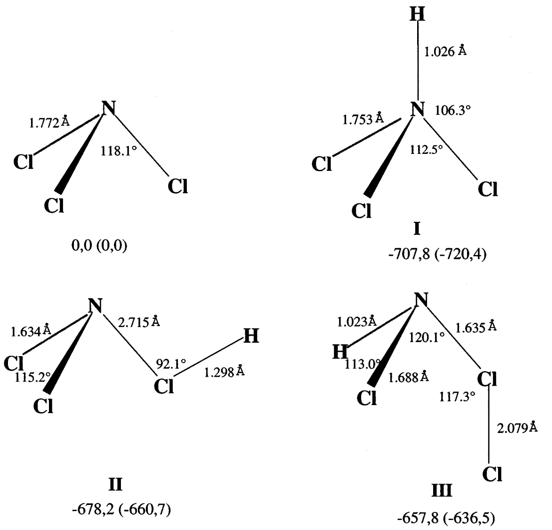


Figure 3. Optimized geometries of the investigated species in their ground states (bond lengths in ångstroms, angles in degrees). Total energies (kJ/mol), with inclusion of zero point energy, computed at the B3LYP (CCSD(T)) level are shown. The energies are relative to the total energy, corrected by the zero point energy, of NCl3: −1435.330851 hartrees at the B3LYP level and −1433.713664 hartrees at the CCSD(T) level.

TABLE 4: Optimized Geometries and Energies of NCl_3 (IV), $HNCl_3^+$(V), Cl_2NClH^+ (VI), and $HN(Cl)Cl_2^+$(VII), in Their Triplet Excited States[a]

	IV $^3A''$	V $^3A''$	VI $^3A'$	VII $^3A''$
r(NCl)	1.696 1.712	1.634 1.654	1.620 2.591	1.636
r(NH)		1.022		1.048
r(ClH)			1.292	2.134
r(ClCl)	2.813	2.892		
∠(ClNH)		117.5 118.2		118.3 118.3
∠(ClNCl)	110.7	124.4	126.5 116.7	123.3 118.3
∠(NClH)			97.3	
∠(NClCl)	101.8	178.2		
E_{B3LYP}	−1435.294055	−1435.583606	−1435.589708	−1435.587431
ZPE[b]	0.004232	0.016756	0.012705	0.016573
$E_{\mathrm{CCSD(T)}}$	−1433.665157	−1433.957764	−1433.955860	−1433.964059

[a] Bonds lengths in angstroms, angles in degrees, total energies in hartree. [b] Zero point energy.

whereas for the deprotonation of the M_2H^+ isomer, the gas-phase basicity value is about 670.0 kJ mol^{-1}.

However, considering only those experiments where the semilogaritmic decrement of $[N^{35}Cl_3]H^+$ ionic intensities is linear, the basicity of trichloramine is intermediate between that of C_2H_5Cl (GB = 666.9 kJ mol^{-1}) and CF_3COCH_3 (GB = 692.0 kJ mol^{-1}). By taking into account the large error characteristic of the bracketing method, the GB of trichloroamine can be estimated to be 679.5 ± 20 kJ mol^{-1}. In this case the uncertainty range is very broad owing to the large difference of basicity of the bases defining the interval. On the contrary, if reaction efficiencies of M_1H^+ ions deprotonation are fitted, according to the thermokinetic method, the uncertainty range is reduced to 8 kJ mol^{-1}, a value that depends on the errors of the tabulated GBs, on the absolute pressure measurements of the reactants in the cell, on the uncertainties of reaction efficiencies, etc.

Computational Evaluation of GB and PA of NCl_3. The optimized geometries and the energies of NCl_3 and its protonated species are reported in Table 3. Both the protonation on the nitrogen and chlorine atoms were investigated. The structures of the investigated species, together with the optimized geometrical parameters, are reported in Figure 3.

NCl_3 has a pyramidal structure with C_{3v} symmetry. The protonation of the nitrogen atom leads to the C_{3v} structure (**I**), whereas the protonation of the chlorine atom leads to the C_s structure (**II**) less stable than (**I**) by 61.3 kJ/ mol at the CCSD(T) level with inclusion of zero point energy. The two isomers are trapped in a deep potential well because the barrier for their interconversion is computed to be 137.7 kJ/mol at the B3LYP and 157.2 kJ/mol at the CCSD(T) levels of theory.

On the $[NCl_3]H^+$ potential energy surface we found also the low lying isomer (**III**) characterized by a Cl−Cl bond. This species has a pyramidal structure with C_1 symmetry and is less stable than (**I**) by 84.0 kJ/mol at the CCSD(T) level with inclusion of zero point energy. The barrier for the (**I**) → (**III**) interconversion is computed to be 197.9 and 171.5 kJ/mol at the B3LYP and CCSD(T) levels of theory.

The optimized geometries and the energies of NCl_3 and its protonated species in their triplet excited state are reported in Table 4. Both the protonation on the nitrogen and chlorine atoms have been investigated. The structure of the investigated species, together with the optimized geometrical parameters, are shown in Figure 4.

NCl_3 in its triplet excited state is very unstable, being more than 100 kJ/ mol higher in energy with respect to the singlet ground state. It can be described as a NCl_2^+ species slightly interacting with a chlorine atom whereas its protonated species can be described as a NCl_2^+ interacting with a HCl molecule.

TABLE 5: Calculated Proton Affinity (kJ/mol) at 0 and 298 K and Gas-Phase Basicities (kJ/mol) at 298 K of NCl$_3$

	PA$_0$		PA$_{298}$		GB$_{298}$	
	B3LYP	CCSD(T)	B3LYP	CCSD(T)	B3LYP	CCSD(T)
I → NCl$_3$ (^{1}A$_1$) + H$^+$	707.8	720.4	714.1	726.8	679.9	692.6
II → NCl$_3$ (^{1}A$_1$) + H$^+$	678.2	660.7	680.0	660.8	660.3	641.1
III → NCl$_3$ (^{1}A$_1$) + H$^+$	657.8	636.5	662.7	641.4	634.6	613.3
V → NCl$_3$ (^{1}A$_1$) + H$^+$	619.6	596.9	622.1	599.4	604.1	581.4
VI → NCl$_3$ (^{1}A$_1$) + H$^+$	646.2	602.5	647.5	603.7	631.9	588.1
VII → NCl$_3$ (^{1}A$_1$) + H$^+$	630.1	613.9	633.4	617.1	615.6	599.4
V → NCl$_3$ (^{3}A″) + H$^+$	727.4	735.5	733.2	741.3	697.9	706.0
VI → NCl$_3$ (^{3}A″) + H$^+$	754.0	741.2	758.5	745.6	725.6	712.8
VII → NCl$_3$ (^{3}A″) + H$^+$	737.9	752.5	744.4	759.0	709.4	724.0

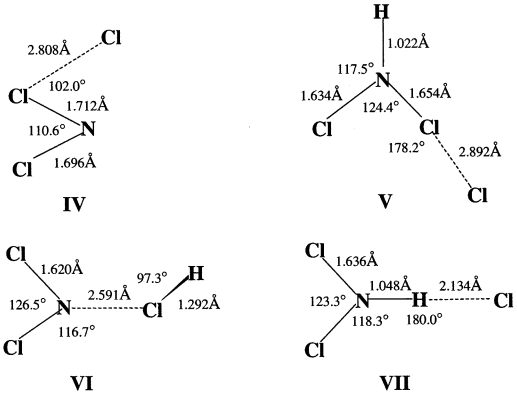


Figure 4. Optimized geometries of the investigated species in their excited states (bond lengths in angstroms, angles in degrees).

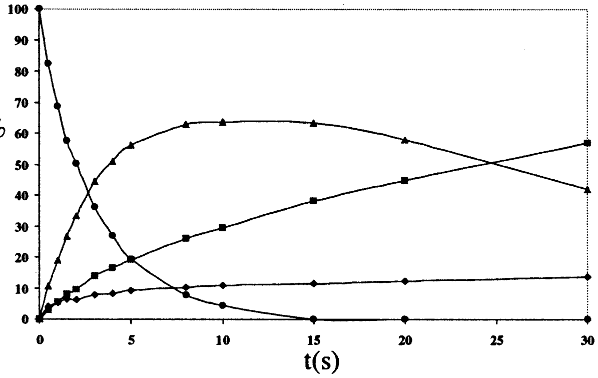
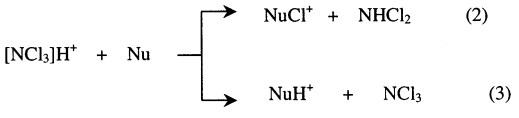


Figure 5. Time profile of the ionic intensities in the reaction of [N^{35}Cl$_3$]H$^+$ ions, m/z = 120 (●), with benzene, yielding C$_6$H$_6$^{35}Cl$^+$, m/z = 113 (▲), C$_6$H$_7$$^+$, m/z = 79 (■), and C$_6H_6$$^{\bullet+}$, m/z = 78 (◆).

Table 5 shows the proton affinities on the nitrogen and chlorine atoms at 0 and 298 K and the gas-phase basicities at 298 K of NCl$_3$. For comparison both the B3LYP and the CCSD(T) results are reported. The preferred proton site attack is the nitrogen atom at any level of calculation. The proton affinity of NCl$_3$ was recently estimated by Milburn et al.[29] at the MP2(full)/6-311++G(d,p) level obtaining a value of 734.7 kJ/mol. This value, as expected for an MP2 treatment, is slightly higher than our value of 726.8 kJ/mol at CCSD(T) level of theory.

The higher proton affinity of NCl$_3$ in its triplet excited state is obviously due to the low stability of this species.

Reactivity of [NCl$_3$]H$^+$ Ions. The [NCl$_3$]H$^+$ ions behave as a Brønsted acid and/or as a chlorinating agent, undergoing two competing processes, the nucleophilic displacement of a Cl$^+$ atom (2) and proton tranfer (3) Proton transfer is the only reaction channel observed with n-type reference bases used in the GB evaluation. By contrast a 2-fold reactivity was observed in the case of a π-system such as benzene (Figure 5). When [NCl$_3$]H$^+$ ions are allowed to react with ethylene, in accordance with its lower PA, only Cl$^+$ transfer was observed. These results are not structurally informative because this particular reactivity could be attributable to any of the isomers **I**, **II**, and **III**.



Discussion

It is legitimate to suggest the existence of two isomeric populations of [N^{35}Cl$_3$]H$^+$ ions, having slightly different stability, based on the anomalous trend of the semilogarithmic decrement of the [N^{35}Cl$_3$]H$^+$ ionic intensity as a function of the time, observed in the bracketing experiments, that may reflect a bimodal exponential function. Based on these considerations and from the theoretical results, it is reasonable to assign to the most stable [NCl$_3$]H$^+$ ions, the HNCl$_3$$^+$ structure **I**, consistent with the computed higher basicity of the nitrogen atom. The experimental gas-phase basicity of NCl$_3$, 687.3 kJ/mol, reasonably agrees with the calculated value differing by 7.4 and 5.3 kJ/mol at the B3LYP and CCSD(T) level, respectively.

The structural characterization of the less stable [NCl$_3$]H$^+$ isomer, the M$_2$H$^+$ population, is more difficult. The structurally diagnostic fragmentation observed in the CAD mass spectrum suggests the existence of an ionic population characterized by connectivity **II**. In fact, the minor fragmentation channel into ions at m/z = 84, N^{35}Cl$_2$$^+$, observed at low collision energy, likely corresponds to the easy loss of an HCl molecule from **II** ($\Delta H°$ = 48.3 and 28.2 kJ/mol at the B3LYP or CCSD(T) level) rather than from the highly endothermic consecutive loss of a Cl and H atom from **I** ($\Delta H°$ = 528 kJ/mol).

To this end, first, the chloro-protonated HCl−NCl$_2$$^+$ ion, **II**, whose existence was suggested by CAD experiments, was investigated by computational methods. The gas-phase basicity of the chlorine atom of NCl$_3$ was computed to be 660.3 and 641.1 kJ/mol at the B3LYP and at the CCSD(T) level, respectively.

The stability difference between **I** and **II** was calculated to be 34.1 kJ/mol at B3LYP and 66.0 kJ/mol at the CCSD(T) level, at 298 K.

The stability of species having a different connectivity such as the HN(Cl)−Cl$_2$$^+$ ions, **III**, and the stability of triplet states of NCl$_3$, **IV**, and of its protonated forms, **V**−**VII**, have been also theoretically investigated.

The HN(Cl)−Cl$_2$$^+$ ion, **III**, was computed to be less stable than **I** by 85.4 kJ/mol at the CCSD(T) level and by 51.4 kJ/mol at the B3LYP level at 298 K.

NCl$_3$ in its triplet state is very unstable, being more than 100 kJ/mol higher in energy with respect to the singlet state. The results listed in Table 5 show that also the triplet states of all its protonated species are less stable than the corresponding singlet states. The gas-phase basicities of NCl_3 ($^1A_1$) calculated from triplet species protonated both on the nitrogen and on the chlorine atom (604.1 and 631.9 kJ/mol at B3LYP level, respectively) and from $HNCl_2{-}Cl^+(^3A)$ (615.6 kJ/mol at B3LYP level) are far lower than the value experimentally measured for the M_2H^+ population.

In contrast, the gas-phase basicities of NCl_3 ($^3A''$) calculated for triplet species protonated on both the nitrogen and the chlorine atom and for $HN(Cl){-}Cl_2^+(^3A)$, (697.9, 725.6, and 709.4 kJ/mol at B3LYP level, respectively) are higher than the value obtained from bracketing experiments.

On the basis of thermodinamic considerations, at least in principle, both protomers **I** and **II** can be formed in the ion source by reaction 1. In fact, formation of ions **I** is exothermic by 180.7, 43.76, and 33.0 kJ/mol when protonation is accomplished by CH_5^+, $C_2H_5^+$, and H_3O^+ ions, respectively.

Depending on the relative amounts of NCl_3 and water in the CI plasma and on the total pressure of the ion source, ions **I**, formed by CH_5^+ ions, are sufficiently excited to isomerize into ions **II**, the energy barrier for this process being calculated as 137.7 and 157.2 kJ/mol at the B3LYP level and at the CCSD(T) level of theory, respectively. However, the high pressure regimes of our CI experiments and the inevitable presence of water greatly reduce the amounts of CH_5^+ ions.

The formation of ions **II** from reaction 1 is slightly endothermic or thermoneutral when the $C_2H_5^+$ and H_3O^+ are the protonating agents whereas it is exothermic by 138.9 and 117.1 kJ/mol at the B3LYP and CCSD(T) level from CH_5^+ ions.

Considering that the dissociation

$$\mathbf{II} \rightarrow HCl + NCl_2^+ \tag{4}$$

is endothermic by 48.3 and 28.2 kJ/mol at the B3LYP and CCSD(T) level, respectively, the $HCl{-}NCl_2^+$ ions formed by $C_2H_5^+$ and H_3O^+ ions are stable to the decomposition into HCl and NCl_2^+.

It is worth noting that the 3:1 ratio of chlorine on nitrogen atoms in NCl_3 should favor from a statistical point of view the chloro-protonated isomer. However, ions **II**, once formed, can undergo intermolecular isomerization to **I**, following collisions with trichloramine or water, the latter one acting as a carrier of proton from **II** to **I** owing to its intermediate PA value. This reaction can be the cause of the small amount of **II** detectable.

At least, $HN(Cl)Cl_2^+$ ions **III** could be formed in the ionic source by Cl^+ transfer from **I** to $NHCl_2$ (5), from disproportion of protonated dichloramine (6), or from isomerization of **I** (7):

$$HNCl_3^+ + NHCl_2 \rightarrow \mathbf{III} + NHCl_2 \tag{5}$$

$$H_2NCl_2^+ + NHCl_2 \rightarrow \mathbf{III} + NH_2Cl \tag{6}$$

$$\mathbf{I} \rightarrow \mathbf{III} \tag{7}$$

The absence of ions indicative of the presence of dichloramine in the CI plasma ruled out the role of processes 5 and 6 as possible routes leading to the formation of ions **III**. It is interesting to note that in the gas-phase investigation of $[NHCl_2]H^+$ ions, the disproportion of protonated monochloramine distilling in the source with dichloramine was found to be the pathway responsible for the formation of $H_2N(Cl){-}Cl^+$ ions. Moreover, the occurrence of the isomerization (7) could be excluded considering that its calculated energy barrier is 197.9 and 171.5 kJ/mol at the B3LYP and CCSD(T) level.

TABLE 6: Proton Affinity and Chloronium Affinity on the Nitrogen Atom, PA(N) and Cl^+ Affinity (N), Proton Affinity and Chloronium Affinity on the Chlorine Atom, PA(Cl) and Cl^+ Affinity (Cl) of Ammonia, Monochloramine, Dichloramine, and Trichloramine (All Values in kJ/mol)

	NH_3	NH_2Cl	$NHCl_2$	NCl_3
PA(N)	853.6[a]	797.0[b] (exp)	756.9[c] (exp)	721.5[e] (exp)
		792.9[b] (B3LYP)	748.5 [c] (B3LYP)	714.1[e] (B3LYP)
		800.4[b] CCSD(T)	758.6[c] CCSD(T)	726.8[e] CCSD(T)
		797.9[d]	755.2[d]	734.7[d]
PA(Cl)		635.1[b] (B3LYP)	626.8[c] (B3LYP)	689.9[e] (exp)
		638.1[b] CCSD(T)	613.0[c] CCSD(T)	680.07[e] (B3LYP)
		627.2[d]	601.7[d]	660.8[e] CCSD(T)
Cl^+affinity (N)	546.0[c]	523.0[c]	490.3[c]	
Cl^+ affinity (Cl)		446.8[e] (B3LYP)	429.3[e] (B3LYP)	
		430.9[e] CCSD(T)	407.9[e] CCSD(T)	

[a] Reference 27. [b] Reference 12a. [c] Reference 12b. [d] Reference 29. [e] This work.

In conclusion, although theoretical results found as a true minimum on the potential energy surface of $[NCl_3]H^+$ ions the structure corresponding to the isomer **III**, no experimental evidence on its existence was found. Finally, theoretical and experimental results identify as the most stable isomer, the M_1H^+ population, the $HNCl_3^+$ ion **I** and suggest the presence of a less stable isomer, the M_2H^+ population, which could correspond to the ion **II** having the $HClNCl_2^+$ structure.

Proton and Chloronium Ion Affinities Trend among Gaseous Inorganic Chloramines. Table 6 reports the proton affinity of the nitrogen and of the chlorine atom, PA(N) and PA(Cl), and the chloronium ion affinities of the nitrogen and of the chlorine atom, Cl^+ affinity (N) and Cl^+ affinity (Cl), of NH_2Cl, $NHCl_2$, and NCl_3.

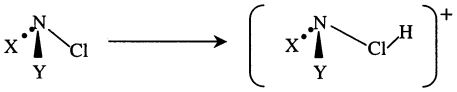
Following substitution of the hydrogen atoms of ammonia by one, two, and three chlorine atoms, the proton affinity decreases by 56.6, 40.1, and 35.4 kJ/mol, respectively, indicating that the σ electron withdrawal effect of chlorine reduces the basicity of the nitrogen of the chloramines.

Unlike PA(N), proton affinities at the chlorine atom increase in the order

$$\text{PA(Cl)} \qquad NHCl_2 < NH_2Cl < NCl_3$$

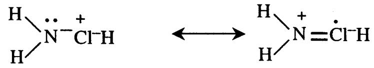
However, in NCl_3, which has the lower PA(N) and the higher PA(Cl), the basicity of the nitrogen atom exceeds that of the chlorine atom by more than 35 kJ/mol.

Structural changes following Cl^+ protonation can be briefly summarized:



the HCl−N distance increases both in the chloro-protonated dichloramine and in trichloramine by 0.391 and 0.943 Å, respectively, becoming in the latter case equal to 2.715 Å. The energy of this bond is 344 kJ/mol in the case of $HClNH_2$ but decreases to about 260.4 kJ/mol on going from NH_2Cl to $NHCl_2$ and to about 45 kJ/mol from $NHCl_2$ to NCl_3.

Increasing chloro substitution leads Cl-protonated chloramines to become unstable to the loss of a HCl moiety. A possible explanation can involve the reduced ability of the nitrogen atom to satisfy the electronic charge requirement of the chlorine atom undergoing protonation. In fact, following protonation of NH_2Cl, the HCl−N bond becomes shorter, suggesting the partial delocalization of the positive charge on the nitrogen atom, as shown in the resonance structure:



When hydrogen atoms are replaced by chlorine atom(s), the stabilization of the positive charge of chlorine undergoing protonation is prevented by the electron withdrawal effect of these substituents. Furthermore, the HCl—N bond length increases owing to the delocalization of the incipient positive charge of the nitrogen atom on the chlorine atom(s). In fact, increasing the HCl—N bond, the conjugation of the empty p orbital of nitrogen with the d orbitals of chlorine, can take place. The N−X and/or N−Y (X, Y = Cl) bond lengths both in protonated $NHCl_2$ and in NCl_3, decrease, suggesting their partial double bond character. In conclusion, the $HCl-NCl_2^+$ and $HCl-NHCl^+$ ions are more stable than the $HCl-NH_2^+$ ions, owing to the conjugation effect of Cl atom(s) responding to a charge requirement not present in the neutral molecule.

In short, the higher PA(Cl) of trichloramine reflects the different ability of the substituents to stabilize neutral and protonated species, structurally different due to the changes caused by protonation.

In Table 6 are also reported the gas-phase affinities of the nitrogen and of the chlorine atom of NH_2Cl, $NHCl_2$, and NCl_3 toward the Cl^+ ion. As previously reported for pyridines,[30] an excellent correlation exists between Cl^+ affinities and proton affinities of unhindered molecules, suggesting that the same factors affecting the stability of protonated adducts influence the stability of the chlorinated adducts. Cl^+ affinities (N) of NH_2Cl and $NHCl_2$ follow the same trend of PA(N). The electron withdrawal effect of chlorine reduces the nucleophilicity of nitrogen.

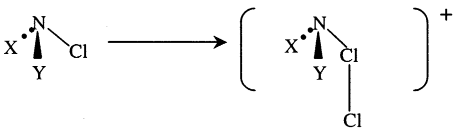
From $\Delta H_f^\circ(H_2NClCl^+)$ and from $\Delta H_f^\circ(HNCl_2Cl^+)$ we calculated the Cl^+ affinities of the chlorine atom of NH_2Cl and $NHCl_2$[31,32] corresponding to the enthalpy changes for the reactions

$$Cl^+ + NH_2Cl \rightarrow H_2NCl-Cl^+$$

$$Cl^+ + NHCl_2 \rightarrow HN(Cl)Cl_2^+$$

It is interesting to note that the Cl^+ affinities of the chlorine atom decrease on going from NH_2Cl to $NHCl_2$ (Table 6).

Structural modifications following chlorination on the Cl atoms can be briefly described.



The Cl—ClN bond length is computed to be 2.062 Å in the $H_2NCl-Cl^+$ ion and 2.079 Å in $HN(Cl)Cl_2^+$, by contrast, the ClCl—N bonds become shorter by 0.159 and 0.137 Å, respectively.

The positive charge on the chlorine atom undergoing chlorination is partially delocalized on the nitrogen, but the ClCl—N distance does not increase owing to the scarce polarization of this bond and the lack of stabilization due to the conjugation effect. On going from NH_2Cl to $NHCl_2$ the nucleophilicity of chlorine atom is depressed by the withdrawal effect of the second chlorine atom bound to the nitrogen. In other words, the scarce Cl—ClN interaction does not lead to significant structural modifications, the stabilization by charge delocalization of chlorinated products is prevented, and the same factors making $NHCl_2$ a weaker Brønsted acid than NH_2Cl depress the nucleophilicity of the chlorine atoms of NCl_3.

Conclusions

The existence of isomeric populations corresponding to the same mass-to-charge ratio and resulting indistinguishable by mass spectrometric analysis is not an uncommon event. In some cases, the gas-phase "titration" procedure combined with the thermokinetic method allows an estimate of the stability of both ionic components.[12b]

Kinetic experiments, performed to determine the basicity of NCl_3, suggests the existence of two $[NCl_3]H^+$ populations. Theoretical calculations characterize the most stable isomer as the $HNCl_3^+$ ions and suggest for the less stable one the $HClNCl_2^+$ structure. No experimental evidence on the $HN(Cl)Cl_2^+$ ions, corresponding to a true minimum on the potential energy surface of $[NCl_3]H^+$ ions, was found. The theoretical GB of NCl_3 is fully consistent with the experimental value. From the difference between the theoretical ΔG° and PA we obtain $T\Delta S = 34.2$ kJ/mol. Adding this value to the experimental GB of NCl_3 we obtain a PA of NCl_3 of 721.5 kJ/mol. From the $\Delta H_f^\circ(H_2NClCl^+)$[12b] and the $\Delta H_f^\circ(HN(Cl)Cl_2^+)$ reported in this work, the Cl^+ affinities of the Cl atom of monochloramine and dichloramine were calculated.

Whereas proton affinities of the nitrogen atom and Cl^+ affinities of the chlorine atom decrease on passing from NH_2Cl to NCl_3, the opposite trend is observed for the proton affinities of the chlorine atom.

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References and Notes

(1) Nelson, G. D. Chloramines and Bromamines. *Encyclopedia of Chemical Technology*; John Wiley & Sons: New York, 1979; Vol. 5, p 565.

(2) Mellor, J. W. *A Comprehensive Treatise on Inorganic Chemistry*; Longmans Green and Co.: New York, (a) 1928; Vol. VIII, p 598ff; (b) 1967; Vol. VIII, Suppl. II, p 409f.

(3) Kovacic, P.; Lowery, M. K.; Field, K. W. *Chem. Rev.* **1970**, *70*, 639 and references therein.

(4) Corbett, R. E.; Metcalf, W. S.; Soper, F. G. *J. Chem. Soc.* **1953**, 1927.

(5) See, for example: (a) Jafvert, C. T.; Valentine, R. L. *Environ. Sci. Technol.* **1992**, *26*, 577. (b) Kumar, K.; Day, R. A.; Margerum, D. W. *Inorg. Chem.* **1986**, *25*, 4344. (c) Kumar, K.; Shinness, R. W.; Margerum, D. W. *Inorg. Chem.* **1987**, *26*, 3430. (d) Nagy, J. C.; Kumar, K.; Margerum, D. W. *Inorg. Chem.* **1988**, *27*, 2773. (e) Boudin, S. Y.; Margerum, D. W. *Inorg. Chem.* **1990**, *29*, 2135;

(6) See, for example: (a) Welte, B.; Montiel, A. *Water Sci. Technol.* **1999**, *40*, 257. (b) Kajino, M.; Morizane, K.; Umetani, T.; Terashima, K. *Water Sci. Technol.* **1999**, *40* (6), 107.

(7) (a) Hery, M.; Hecht, G.; Gerber, J. M.; Hubert, G.; Subra, I.; Aubert, S.; Gerardin, F.; Dorotte, M. *Occup. Hyg.* **1999**, *5*, 131. (b) Hery, M.; Gerber, J. M.; Hecht, G.; Subra, I.; Possoz, C.; Aubert, S.; Dieudonne, M.; Andre, J. C. *Ann. Occup. Hyg.* **1998**, *42*, 437. (c) Massin, N.; Bohadana, A. B.; Wild, P.; Hery, M.; Toamain, J. P.; Hubert, G. *Occup. Environ. Med.* **1998**, *55*, 258.

(8) See, for example: Knothe, M.; Hasenpusch, W. *J. Hazard. Mater.* **1997**, *56*, 137;

(9) See, for example: Lyalin, B. V.; Petrosyan, V. A. *Russ. J. Electrochem.* **1999**, *35*, 523;

(10) See, for example: (a) Shr-Guang, L.; Hung-Rung, L.; Shiue-Shr, L.; Nian-Shiou, H. Method of forming pattern on steel substrate by reactive ion etching. Patent No. TW 430695 B 20010421, Taiwan, 2001. (b) Todd, M. A. CVD synthesis of silcon nitride materials having low hydrogen-content. Eur. Pat. Appl. 2001, Patent No. EP 1149934 A2 20011031. (c) Young, A. W.; Smith, D. D. Method of forming a dielectric film by plasma enhanced CVD. Patent No. US 5763021 A 19980609, 1998, 4 pp. (d) Okabe,

I. Method of supplying a chlorine gas to reactor. Eur. Pat. Appl. 1996. Patent No. EP 730902 A1 19960911, 1996. (e) Sato, J. Formation method of GaN film for semiconductor light emitting devise. Patent No. JP 08008186 A2 19960112. (f) Yamazaki, S. Plasma etching for selective patterning. Patent No. JP 07169756 A2 19950704, JP 08306675 A2 19961122.

(11) (a) Metcalf, W. S. *J. Chem. Soc*. **1942**, 148. (b) Colburn, D.; Frost, D. C.; McDowell, C. A.; Westwood, N. P. C. *J. Chem. Phys.* **1978**, *69*, 1078. (c) Exton, D. B.; Gilbert, J. V.; Coombe, R. D. *J. Phys. Chem.* **1991**, *95*, 2692. (d) Kotiaho, T., Lister, A. K.; Hayward, M. J.; Cooks, R. G. *Talanta* **1991**, *38*, 195. (e) Thorn, R. P., Jr.; Stief, L. J.; Kuo, S−K.; Klemm, R. B. *J. Phys. Chem. A* **1999**, *103*, 812;

(12) (a) Ricci, A.; Rosi, M. *J. Phys. Chem. A* **1998**, *102*, 10189. (b) Ricci, A.; Rosi, M. *J. Phys. Chem. A* **2000**, *104*, 5618;

(13) See, R. F.; Dutoi A. D.; McConnel, K. W.; Naylor, R. M. *J. Am. Chem. Soc*. **2001**, *123*, 2839.

(14) (a) Meot-Ner. *Gas-Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol 2, pp 198−268. (b) Ikezoe, Y.; Matsuoka, S.; Takebe, M.; Viggiano, A. A. *Gas-Phase Reaction Rate Constants Through 1986*; Maruzen Co.: Tokyo, 1987.

(15) Bartmess, J. E.; Georgiadis, R. M. *Vacuum* **1983**, *33*, 149.

(16) Su, T.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Phys*. **1973**, *12*, 347.

(17) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(18) Stevens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(19) Bartlett, R. J. *Annu. Rev. Phys. Chem.* **1981,** 32, 359.

(20) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479;

(21) (a) McLean, A. D.; Chandler, G. S. *J. Chem. Phys* **1980** *72*, 5639. (b) Krishman, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. (c) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294. (d) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265 and references therein.

(22) Frisch M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R: E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu. G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.7; Gaussian, Inc., Pittsburgh PA, 1998.

(23) (a) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. H.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl, 1. (b) Bohme, D. K.; Hensworth, R. S.; Rundle, H. W.; Schiff, H. I. *J. Chem. Phys.* **1973**, *58*, 3504. (c) Graul, S. T.; Squires, R. R. *Mass Spectrom Rev.* **1988**, *7*, 263.

(24) (a) McLuckey, D.; Cameron, D.; Cooks, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 1313. (b) Cooks, R. G.; Patrick, J. S.; Kotiaho, T.; McLuckey, S. A. *Mass Spectrom. Rev.* **1993**, *13*, 287−339. (c) Decouzon, M.; Gal, J.-F.; Herreros, M.; Maria, P.-C.; Murrel, J.; Todd, J. F. *Rapid Commun. Mass Spectrom.* **1996**, *10*, 242.

(25) Aue, D. H.; Bowers, M. T. *Gas-Phase Ion Chemistry*; Academic Press: New York, 1978; Vol. 2. (b) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695

(26) Bouchoux, G.; Salpin, J. Y.; Leblanc, D. *Int. J. Mass Spectrom. Ion Processes* **1996**, *153*, 37.

(27) Hunter, E. P.; Lias, S. G. Evaluated Gas-Phase Basicities and Proton Affinities of Molecules: An Update. *J. Phys. Chem. Ref. Data* **1998**.

(28) Büker, H.-H.; Crestoni, M. E.; Grützmacher, H.-F.; Ricci, A. *Int. J. Mass Spectrom. Ion Processes* **1997**, *160*, 167.

(29) Milburn, R. K.; Rodriquez, C. F.; Hopkinson, A. C. *J. Phys. Chem. B* **1997**, *101*, 1837.

(30) Eberlin, M. N.; Kotiaho, T.; Shay, B. J.; Yang, S. S.; Cooks, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 2457.

(31) From $\Delta H_f^\circ(NH_2Cl)$, 55.2 kJ/mol,[29] $\Delta H_f^\circ(Cl^+)$, 1378.8 kJ/mol,[27] and $\Delta H_f^\circ(H_2NCl-Cl^+)$, 987.0 kJ/mol at B3LYP level, 1002.9 kJ/mol at the CCDD(T).[12b]

(32) From $\Delta H_f^\circ(NHCl_2)$, 137.2 kJ/mol,[29] and from $\Delta H_f^\circ(HNCl_{2-Cl}{}^+)$, 1086.6 kJ/mol at B3LYP level, 1107.9 kJ/mol at the CCDD(T) (this work).