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Gas Phase Chemistry of $NH_xCl_y^+$ Ions. II. Structure, Stability and Reactivity of Protonated Dichloramine

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The structure and the reactivity of gaseous $(NHCl_2)H^+$ ions formed upon CH_4 chemical ionization of monochloramine and dichloramine in water were investigated by FT−ICR (Fourier transform ion cyclotron resonance) mass spectrometry and theoretical methods. Bracketing experiments performed in order to evaluate the basicity of $NHCl_2$ suggested the existence of two $(NHCl_2)H^+$ isomers. The basicity computed by MO SCF calculations allowed us to characterize the most stable $(NHCl_2)H^+$ isomer as having the $H_2NCl_2^+$ structure, corresponding to dichloramine protonated on the nitrogen consistent with the higher basicity of this atom than of the chlorine atom of $NHCl_2$ and the less stable isomer as having the $H_2NCl{-}Cl^+$ structure. The gas-phase basicity, GB, of dichloramine was estimated to be 721.4 ± 10 kJ mol^{-1} from bracketing experiments, according to the method based on the relationship between the efficiency of proton transfer and the standard free energy change of the process. This value is consistent with those from calculations at the B3LYP and CCSD(T)/6-311++G(3df,3pd) levels of theory. The proton affinity, PA, of $NHCl_2$ was evaluated to be 757 ± 10 kJ mol^{-1}. The $(NHCl_2)H^+$ ion behaves as a protonating and chlorinating agent. An excellent correlation exists between the absolute Cl^+ affinities of ammonia, monochloramine, and dichloramine, estimated 546, 523, and 490 kJ mol^{-1} respectively and their proton affinities. The results show that as substitution of H by Cl atoms in NH_3 increases, both the PA and Cl^+ binding energy, BE, of chloramines decrease, owing to the electron-withdrawing effect of the Cl atoms on the nitrogen.

Introduction

Inorganic chloramines belong to a wide class of compounds containing the N−Cl group and find a variety of applications as bleaches, disinfectants, detergents, cleansers, etc.[1] NH_2Cl, $NHCl_2$, and NCl_3 are formed in the disinfecting process of potable and wastewater by the reaction of chlorine or hypochlorite on ammoniacal solutions, their relative amounts depending on the pH of the solution.[2] NH_2Cl is formed at pH above 8 and it is relatively stable in dilute alkaline solutions; NCl_3 is the principal product at pH below 3 and it is moderately stable in dilute acidic solutions; $NHCl_2$ is formed by the disproportionation of monochloramine at pH 4.5−5 and on addition of excess HOCl to monochloramine in acidic solutions and it is not stable even in dilute solutions. In the process known as breakpoint chlorination occurring at high Cl/N molar dose ratios, the active toxic chlorine species (HOCl and inorganic chloramines) are reduced to Cl^- and ammonia is oxidized to N_2. The self-decomposition of dichloramine is frequently cited as a key step in the mechanism of breakpoint chlorination.[3] However, despite its role in the disinfecting process of water, owing to its instability and difficult preparation, $NHCl_2$ is the least characterized species among the *N*-chloro derivatives of ammonia both in the liquid and in the gas phase[3b,4,5] and its use in organic synthesis is extremely limited.

The gas-phase study of inorganic chloramines can be limited by their explosiveness when in the pure state. Yet, the study of the chemical behavior of chloroamines is of fundamental importance for understanding the possible pathways on which their disinfecting and toxic properties are based. In recent work[6] we reported a gas-phase investigation on the preparation and the reactivity of NH_3Cl^+ ions. Besides the structure of protonated monochloramine, the gas-phase basicity, GB, and proton affinity, PA, of NH_2Cl were evaluated by the joint application of FT-ICR (Fourier Transform Ion Cyclotron Resonance) mass spectrometry and theoretical techniques.

In this work the GB and PA of $NHCl_2$ were studied by the same integrated approach and the structures and the reactivity of protonated dichloramine were examined.

Experimental Section

All experiments were performed using an Apex TM 47e FT-ICR spectrometer from Bruker Spectrospin AG equipped with an external ion source where protonated dichloramine (MH^+) was generated by positive CI using CH_4 as the reagent gas at a pressure of ca. 10^{-4} Torr and a temperature of 150 °C. MH^+ ions were transferred into the resonance cell (25 °C), and $NH_2\text{-}{}^{35}Cl^{35}Cl^+$ 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 reisolated by single shots and allowed to react with the neutral in the cell. The pressure of the neutrals was measured by a Bayard−Alpert ionization gauge, whose readings were calibrated using as a reference the known rate coefficient of the $CH_4 + CH_4^+ \rightarrow CH_5^+ + CH_3^\cdot$ reaction.[7] The readings were corrected for the relative sensitivity to the various gases used according to a standard method.[8] The pseudo first-order rate constants were

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obtained by plotting the logarithm of the $NH_2{}^{35}Cl^{35}Cl^+$ intensities as a function of 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.[9] Reaction efficiencies, RE, are the ratio of experimental rate constants, k_{exp}, to the collision rate constants, k_{ADO}. The uncertainty of each rate constant is estimated to be of about 30%. Protonated dichloramine was obtained by chemical ionization of the reaction mixture resulting from the reaction of equimolar amounts of ammonia with sodium hypochlorite.[2] These reactants were introduced in a small flask fitted to a vacuum distillation apparatus connected directly to the ICR spectrometer. After cooling to liquid nitrogen temperature and reducing the pressure, the reaction mixture was allowed to return to room temperature and to distill together with water vapor, into the external ion source. A gas absorption trap packed with anhydrous copper sulfate was used for removing traces of ammonia.[10]

Computational Details

Density functional theory, using the hybrid[11] B3LYP functional,[12] was 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[13] with a perturbational estimate of the triple excitations [CCSD(T)] approach[14a] in order to include extensively correlation contributions.[14b] 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[15a] has been used. Only the spherical harmonic components of the basis set are used. We decided to add diffuse functions also to the hydrogen atoms in order to have a balanced basis, although their importance is still controversial.[15e] All calculations were performed using *Gaussian 98*[16] on a SGI Origin 2000 computer and on a cluster of IBM RISC/6000 workstations.

Results and Discussion

Experimental Evaluation of GB of $NHCl_2$. There are many methods of measuring the basicity of gaseous species. The use of equilibrium methods[17−19] presupposes the knowledge of the pressure of both neutral bases. In our experiments, the presence of water and monochloramine that evaporate together with dichloramine from the aqueous solutions precludes the possibility of determining the partial pressure of $NHCl_2$ in the ICR cell, and therefore of using equilibrium methods. The kinetic method proposed by Cooks et al.[20] is based on the dissociation of proton-bound dimers that are rarely formed under the low-pressure FT−ICR conditions and were never detected in our experiments.

As in the case of monochloramine, in the absence of pure $NHCl_2$, the only viable alternative to measure the gas-phase basicity of dichloramine is represented by the "bracketing method",[17] where the gas-phase basicity, GB(M), of the investigated molecule, M, can be estimated by measuring the efficiency of proton transfer from MH^+ to bases of known GB. For exoergic proton transfer reactions the efficiency is high; for strongly endoergic processes the efficiency drops to zero, whereas for reactions endoergic by no more than 4−8 kJ/mol the efficiency is low but still measurable. The empirical relationship between the measured efficiencies and the standard free energy of proton transfer, proposed by Bouchoux et al.,[21] allows one to reduce the uncertainty range affecting the experimental value of GB obtained by the bracketing method.

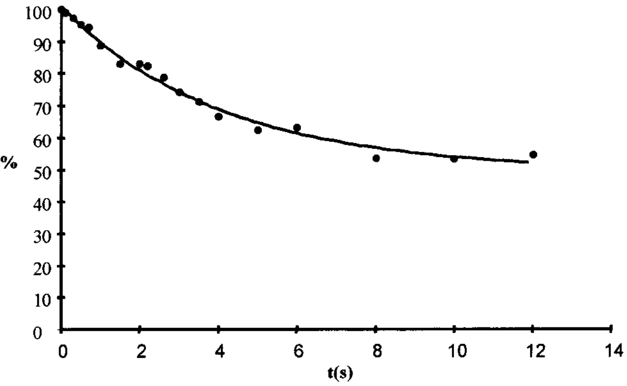


Figure 1. Time profile of the ionic intensity of $(NHCl_2)H^+$ (●) for the reaction between protonated dichloramine and CF_3CH_2OH ($P = 4.3 \times 10^{-8}$ Torr).

To evaluate the GB of dichloramine, $NH_2{}^{35}Cl^{35}Cl^+$ ions generated in an external ion source by the highly exothermic proton transfer from the $C_nH_5{}^+$ ions ($n = 1, 2$) by CH_4/CI were isolated, thermalized, and reisolated 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 of the GB values used to establish the correlation between RE and GB are taken from ref 22, to make use of a self-consistent scale based on a single anchoring value.

The efficiency of proton transfer is nearly 0% for bases such as CO, C_2H_4, H_2O, $(CF_3)_2C(CH_3)OH$, C_2H_5Cl, whose GB values span from 563 to 667 kJ/mol. Increasing the basicity of the reference bases, a peculiar behavior is observed: the plot of the $NH_2{}^{35}Cl^{35}Cl^+$ ionic intensities as a function of time indicates a mixture of two different ionic populations, whose deprotonation reactions have different kinetic rate constants. 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. The plot of total intensity $I(t)$ of $(NHCl_2)H^+$ ions vs reaction time exhibits polymodal kinetics, but, because the number of protonated species is limited, the individual initial intensities and the relative rate constants for deprotonation can be extracted from this plot by a curve fitting program.[23]

When CF_3CH_2OH (GB = 669.9 kJ/mol) is used as the reference base, the less stable of the two $(NHCl_2)H^+$ populations, M_2H^+ (**II**), is deprotonated with low efficiency whereas deprotonation of the more stable ion M_1H^+ (**I**), if occurring at all, is too slow to be detected (Figure 1). Table 1 reports the gas-phase basicities of the reference bases, GB(B), the collisional efficiencies, RE, and the experimental rate constants of proton-transfer reactions, k_{exp}, for both protomers (see discussion) calculated by the best fitting procedure.

TABLE 1: Collisional Efficiencies (eff%) and Rate Constants (k_{exp}) of Proton Transfer Reactions from M_1H^+ (I) and M_2H^+ (II) to Reference Bases (B); Gas Phase Basicities (GB), and Proton Affinities (PA) of Reference Bases; Relative Abundances of M_1H^+ (I) and M_2H^+ (II) Calculated by the Best Fitting Procedure

			(M_1H^+)			(M_2H^+)		
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})	%
CO	594.0	562.8	~0[b]			~0[b]		
C_2H_4	680.5	651.5	~0[b]			~0[b]		
H_2O	691.0	660.0	~0			~0		
$(CF_3)_2C(CH_3)OH$	691.2	660.9	~0			~0		
C_2H_5Cl	693.4	666.9	~0			~0		
CF_3CH_2OH	700.2	669.9	~0	0.0084	57	18	0.27	43
CF_3COOH	711.7	680.7	0.1	<0.001	49	100	1.0	51
$F_2CH\,CH_2OH$	727.4	697.0	0.5	0.0063	86	100	1.0	14
HCOOH	742.0	710.3	3.0	0.041	100		(1.0)	~0
CH_3OH	754.3	724.5	55	0.86	100		(1.0)	~0
CH_3NO_2	754.6	721.6	21	0.44	100		(1.0)	~0
CH_3CHO	768.5	736.5	100	2.0	100		(1.0)	~0

[a] From ref 22. [b] The efficiency refers to the proton-transfer reaction; chlorination is not considered.

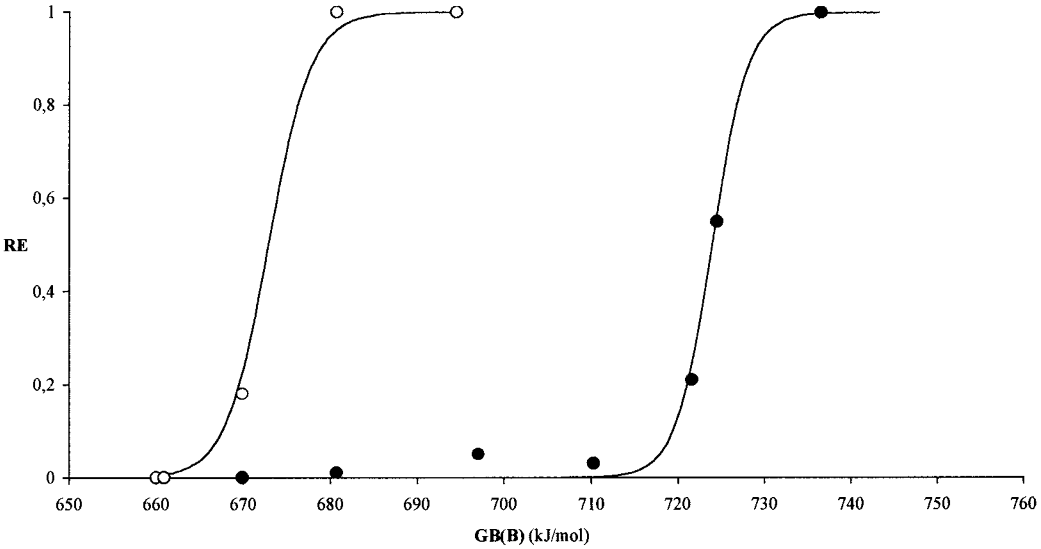


Figure 2. Reaction efficiencies (RE) of proton transfer from $(NHCl_2)H^+$ to reference bases (B) vs gas-phase basicities, GB(B). Open circles refer to deprotonation of M_2H^+(**II**), filled circles refer to deprotonation of M_1H^+(**I**).

TABLE 2: Relative Abundance of Two $(NHCl_2)H^+$ Populations Calculated by the Best Fitting Procedure When Different CI Gases Are Used in the ICR Source ($P \cong 5 \times 10^{-5}$ Torr) and CF_3COOH Is the Reference Base ($P \cong 2 \times 10^{-8}$ Torr)

CI gas	(M_2H^+) %	(M_1H^+) %
CH_4	50	50
C_2H_4	45	55
C_3H_4	20	80
C_2H_4		100

To deduce GB(M_1) and GB(M_2), the efficiency data, according to the empirical relationship proposed by Bouchoux et al.,[21] 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; $\mathbf{b} = 1/RT^*$ (where T^* is the effective temperature that can be different from the experimental temperature owing to a nonequilibrium distribution of the internal energy of the [MBH^+] intermediate); $\mathbf{c}'' = \mathrm{GB(M)} + \mathbf{c}$, and $\mathbf{c} = \Delta G^\circ_a$. The latter one 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 procedure, the reaction efficiencies of the proton-transfer processes from M_1H^+ (**I**) and from M_2H^+(**II**) to bases of known GB have been fitted to the equation as illustrated in Figure 2. From the best fit of the data concerning the deprotonation of the M_2H^+ (**II**) isomer we obtain $\mathbf{a} = 1.0$, $\mathbf{b} = 0.41$, $\mathbf{c}'' = 672.9$, $T^* = 291$ K, and a gas-phase basicity value of $M_2 = 670.5 \pm 10$ kJ mol^{-1}. From the best fit of the data concerning the deprotonation of the M_1H^+ (**I**) isomer we obtain $\mathbf{a} = 0.998$, $\mathbf{b} = 0.35$, $\mathbf{c}'' = 724.3$, $T^* = 335$ K, and a gas-phase basicity value of $M_1 = 721.4 \pm 10$ kJ mol^{-1}. The last column of Table 1 reports the abundance of M_1H^+(**I**) and M_2H^+(**II**) calculated by the best fitting procedure.

It is worth noting that an increase in the basicity of the reference base causes the abundance of the less basic M_2H^+ (**II**) ions to decrease, which is in accordance with its fast deprotonation in the ICR cell. This is accomplished before starting the kinetic measurements and during the time in which the ions transferred are isolated and thermalized. Also, the CI conditions in the external ion source are important for determining the relative amounts of the $(NHCl_2)H^+$ populations. The relative intensities of M_1H^+(**I**) and M_2H^+(**II**) are reported in Table 2 when different CI gases are used and CF_3COOH is contained at the same pressure in the cell. The non selective

TABLE 3: Optimized Geometries, Vibrational Frequencies, and Energies of $NHCl_2$, H_2NCl_2+, $HN(Cl)ClH^+$, and NH_2Cl-Cl^+ (bond lengths in Å, angles in deg, total energies in Hartree, frequencies in cm^{-1})

	$NHCl_2$ $^1A'$	$H_2NCl_2^+$ $^1A_1$	$HN(Cl)ClH^+$ ^1A	$H_2NCl-Cl^+$ $^1A'$
r(NCl)	1.761	1.746	1.635 2.152	1.602
r(NH)	1.019	1.026	1.033	1.017
r(ClH)			1.298	
r(ClCl)				2.062
∠(ClNH)	102.2	107.8	91.9	115.8
∠(ClNCl)	110.9	115.7	112.6	
∠(NClH)			89.9	
∠(NClCl)				114.7
E_{B3LYP}	−975.755517	−976.052120	−976.000086	−976.024797
ZPE[a]	0.016779	0.030624	0.023917	0.028486
$E_{CCSD(T)}$	−974.639105	−974.939500	−974.878524	−974.902430

[a] Zero point energy.

protonation of $NHCl_2$ by the $C_nH_5^+$ ions from methane is expected to yield comparable amounts of the two isomers. The GB(B) of ethylene is 651.5 kJ/mol, which is 19 kJ/mol lower than the value calculated for the less basic site of $NHCl_2$, but protonation using $C_2H_5^+$ ions from ethylene is not any more selective.

In those experiments where propylene is used as the reagent gas, if water is absent in the CI plasma and the ion at m/z = 41, $C_3H_5^+$ is the most abundant, the higher GB of C_3H_4 (723.0 kJ/mol) can account for the predominant formation of M_1H^+ (**I**) ions. Finally, if a post-delay ionization time, D_2 = 5 s, is used before transferring the ions into the resonance cell, when C_2H_4 is the reagent gas in the source the isomer M_2H^+ (**II**) disappears.

Computational Evaluation of GB and PA of $NHCl_2$. The optimized geometries and the energies of $NHCl_2$ and its protonated species are reported in Table 3. Protonation on both nitrogen and chlorine was investigated. The structures of the investigated species, together with the optimized geometrical parameters, are reported in Figure 3.

$NHCl_2$ has a pyramidal structure with C_s symmetry, and the optimized geometrical parameters are in good agreement with the experimental ones[4c] and with previous ab initio calculations.[24−26a] The protonation of nitrogen leads to a structure of C_{2v} symmetry, while the protonation of the chlorine atom leads to a C_1 structure which is a local minimum less stable than $H_2NCl_2^+$ by 142.5 kJ/mol at the CCSD(T) level with inclusion of zero point energy. This result is in reasonable agreement with the recent calculations of Milburn et al.[26a] at the QCISD(T)/6-311++G(2df,p)//MP2/6-311G(d,p) level; indeed, they found that the chlorine-protonated form is less stable than the nitrogen-protonated one by 150.2 kJ/mol. Nevertheless, a remarkable difference exists between our B3LYP optimized geometry and the one optimized by Milburn et al.[26a] at the MP2/6-311++G-(d,p) level, the distance between the nitrogen and the chlorine protonated atom being 2.152 Å in the B3LYP optimized structure and 1.853 Å in the MP2 optimized one.

Although it is well-known that density functional methods using nonhybrid functionals sometimes tend to overestimate bond lengths,[26b] hybrid functionals such as B3LYP usually provide bond lengths in excellent agreement with experiments.[26c] Moreover, the MP2 theory sometimes also overshoots bond lengths.[26d] To understand the reason for this discrepancy, we decided to optimize the geometry of this species at the MP2/6-311++G(3df,3pd) level, finding a much shorter N−Cl distance than in the B3LYP structure (1.796 Å). However, the CCSD(T) energy at this optimized geometry was lower than that of the B3LYP optimized structure by less than 1 kJ/mol. This point suggests that the problem arises from the flatness of the potential energy surface. A more accurate geometry optimization would be necessary in order to get a correct value for the N−Cl bond length, which, however, is not very relevant for the scope of the present work.

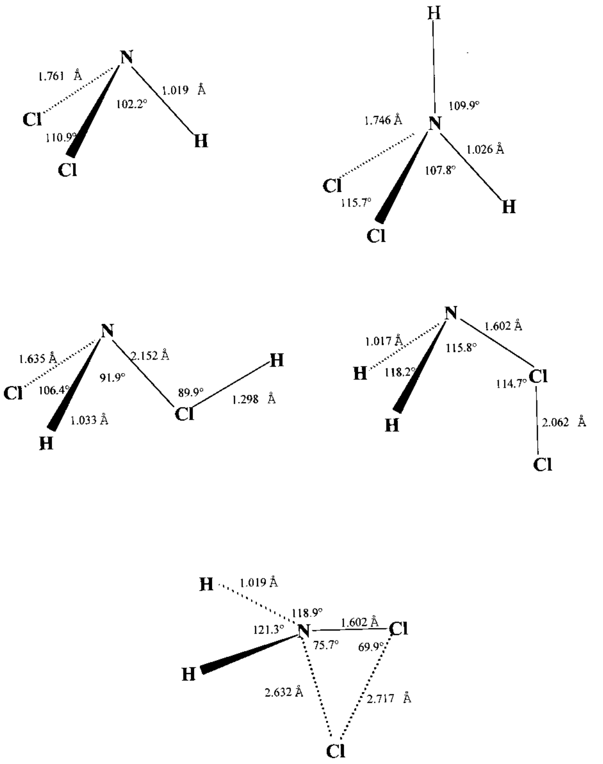


Figure 3. Optimized geometries of the investigated species in their ground states. Also shown is the saddle interconnecting $H_2NCl_2^+$ and $H_2NCl-Cl^+$. (Bond lengths in Å, angles in deg.)

On the potential energy surface of protonated dichloramine we also found a low lying isomer with a Cl−Cl bond. The geometry and energy of this species are reported in Table 3, whereas its structure is shown in Figure 3. $H_2NCl-Cl^+$ has a pyramidal structure with a C_s symmetry. In this structure, however, the pyramidality around the nitrogen center is less pronounced with respect to the other isomers, the coordination around nitrogen being almost planar. Moreover, the N−Cl bond has a partial double-bond character as is suggested by the shorter bond distance. The terminal chlorine atom prefers to be trans to the nitrogen lone pair. This structure is less stable than $H_2NCl_2^+$ by 91.7 kJ/mol at the CCSD(T) level with inclusion of zero point energy. The two species are connected by the transition state whose structure is shown in Figure 3. The barrier height for the $H_2NCl-Cl^+ \rightarrow H_2NCl_2^+$ isomerization at 298 K is 169.5 kJ/mol at the B3LYP level and 117.4 kJ/mol at the CCSD(T) level.

We investigated also the triplet states for both the nitrogen and the chlorine protonated forms as well as for dichloramine. The triplet states are less stable than the corresponding singlet states for all of the species. The optimized geometries and the energies of the triplet states are reported in Table 4. The structures and the optimized geometrical parameters are shown also in Figure 4.

Table 5 shows the proton affinities at 0 and 298 K and the gas-phase basicity at 298 K of $NHCl_2$. For comparison both the B3LYP an CCSD(T) results are reported. We considered the attack of the proton both on the nitrogen and the chlorine

TABLE 4: Optimized Geometries, Vibrational Frequencies, and Energies of the Triplet States of $NHCl_2$, $H_2NCl_2^+$, and $HN(Cl)ClH^+$ (bond lengths in Å, angles in deg, total energies in Hartree, frequencies in cm^{-1})

	$NHCl_2$ ^3A	$H_2NCl_2^+$ ^3A	$HN(Cl)ClH^+$ ^3A
r(NCl)	1.662	1.609	1.575
	2.262	3.041	2.519
r(NH)	1.025	1.018	1.029
r(ClH)			1.293
∠(ClNH)	109.3	80.8	112.0
	110.7	119.1	120.5
∠(ClNCl)	140.1	118.0	127.3
∠(NClH)			95.8
E_{B3LYP}	−975.700483	−975.994625	−975.991512
ZPE[a]	0.013890	0.026118	0.021512
$E_{CCSD(T)}$	−974.572604	−974.872972	−974.861192

[a] Zero point energy.

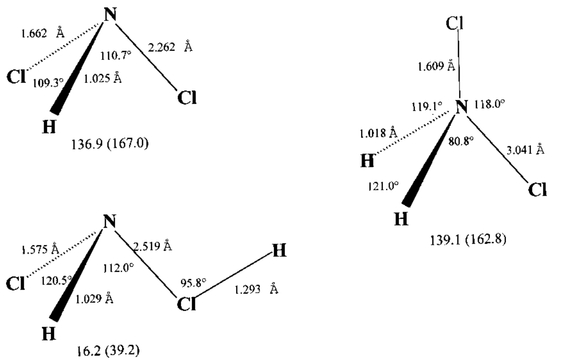
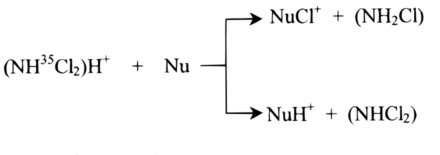


Figure 4. Optimized geometries of the triplet states. The singlet−triplet energy gaps computed at the B3LYP (CCSD(T)) level with inclusion of zero point energy are shown for each species. (Bond lengths in Å, angles in deg, energies in kJ/mol.)

atoms. The preferred site of attack by the proton is the nitrogen at any level of calculation. The proton affinity of $NHCl_2$ was recently estimated by Milburn et al.[26a] at the QCISD(T)/6-311++G(2df,p)//6-311++G(d,p) level, to be 755.2 kJ/mol; our value of 758.7 kJ/mol at the CCSD(T) level is in very good agreement with their result.

The Reactivity of $(NHCl_2)H^+$ Ions. $(NH^{35}Cl_2)H^+$ ions generated in the external ion source of the ICR spectrometer from CH_4/CI of a mixture of monochloramine, dichloroamine, and water behave as a Brønsted acid and a chlorinating agent, undergoing two competing processes, i.e. nucleophilic displacement of Cl^+ and proton tranfer: Traces of $CO^{35}Cl^+$ were detected when $(NH^{35}Cl_2)H^+$ ions were allowed to react with carbon monoxide; $C_2H_4{}^{35}Cl^+$ ions are formed from the reaction between $(NH^{35}Cl_2)H^+$ ions and ethylene. Increasing the basicity of the nucleophile favors the protonation process and suppresses the competing Cl^+ transfer channel. The reaction between $(NH^{35}Cl_2)H^+$ and 2-*trans*-butene (GB = 719.9 kJ/mol)[22] or cyclopentene (GB = 733.8 kJ/mol)[22] does not lead to formation of the respective chlorinated adducts.



(1)

(2)

Neither proton nor chlorine transfer to H_2O from $(NH^{35}Cl_2)H^+$ is observed, whereas CH_2FCH_2OH, CHF_2CH_2OH, CF_3CH_2OH, HCOOH, CF_3COOH, CH_3OH undergo only protonation.

Finally, benzene is the only reagent among those examined undergoing both protonation and chlorination reactions. The branching ratio of these competing processes is ca. 3:1 in favor of the chlorine transfer, the rate constant of proton-transfer amounting to 1.8×10^{-10} molec^{-1} cm^3 s^{-1}, whereas that of chlorine transfer is 5.6×10^{-10} molec^{-1} cm^3 s^{-1}.

Discussion

One of the most intriguing problems encountered in this work concerns the nature of the less stable $(NHCl_2)H^+$ protomer detected in the bracketing experiments. The experimental and theoretical results characterize the most stable $(NHCl_2)H^+$ ions, the M_1H^+ (**I**) populations, as having the $H_2NCl_2^+$ structure, consistent with the computed higher basicity of the nitrogen than that of the chlorine atom of $NHCl_2$.

Many hypotheses were tested in order to characterize the M_2H^+ (**II**) ion, i.e., the other protomer less stable than M_1H^+ (**I**) by 51 kJ/mol. To this end, the gas-phase basicity of the chlorine atom of $NHCl_2$ has been computed and is lower than that of the nitrogen atom by 114.3 kJ/mol at B3LYP and 137.7 kJ/mol at CCSD(T) level, which is inconsistent with the experimental results. Therefore, the stability of triplet states both for the nitrogen and the chlorine protonated forms, as well as for dichloramine, were theoretically investigated. The results listed in Table 5 show that the triplet states are less stable than the corresponding singlet states for all species, as it is shown also in Figure 4, and that gas-phase basicities of $NHCl_2$ ($^1A'$) calculated in a spin-forbidden process from protonated $NHCl_2$ (^3A) both on the nitrogen and the chlorine atom (572.3 and 552.1 kJ/mol at CCSD(T) level, respectively) are lower than the value experimentally obtained for the M_2H^+ (**II**) population. In contrast, the gas-phase basicities of $NHCl_2$ (^3A) calculated for protonation of $NHCl_2$ (^3A) both on the nitrogen and the chlorine atom, (733.5 and 713.3 kJ/mol at CCSD(T) level, respectively) are higher than the value from bracketing experiments. Having rejected the contribution of $HN(Cl)ClH^+$ and of triplet states, we were forced to consider protomers of different connectivity. The search was successful, since on the potential energy surface of protonated dichloramine we found a low lying protomer with a Cl−Cl bond, the H_2NClCl^+ isomer, computed to be less stable than $H_2NCl_2^+$ by 91.7 kJ/mol at the CCSD(T) level and by 66.1 kJ/mol at the B3LYP level, with inclusion of zero point energy. The experimental and theoretical gas-phase basicities differ by 21.6 kJ/mol at the B3LYP level and 37 kJ/mol at the CCSD(T) level, and, considering the estimated uncertainties of the two sets of results, it seems reasonable to assign the $H_2NCl{-}Cl^+$ structure to the less stable protomer M_2H^+(**II**).

Indeed, three $(NHCl_2)H^+$ isomers can conceivably be formed in the CH_4 chemical ionization experiments, namely the $H_2NCl_2^+$ ion (**I**), the H_2NClCl^+ (**II**) ion and the $HN(Cl)ClH^+$ ion (**III**). **I** can be generated by two alternative reactions, direct protonation of dichloramine (distilled from its aqueous solution) by the $C_nH_5^+$ (n = 1, 2) reactant ions:

$$NHCl_2 + C_nH_5^+ \rightarrow H_2NCl_2^+ + C_nH_4 \qquad (3)$$

This process is computed to be exothermic by 213.5 and 76.5 kJ/mol for n = 1 and n = 2, respectively, (from $\Delta H°_f$ ($NHCl_2$) = 137.2 kJ/mol[26a] and $\Delta H°_f$ ($H_2NCl_2^+$) = 911.2 kJ/mol$^{\text{this work}}$, all other $\Delta H°_f$ values being taken from ref 22). An alternative route is the disproportionation of the protonated adduct from monochloramine co-distilling from the solution utilized in this work:

$$NH_3Cl^+ + NH_2Cl \rightarrow H_2NCl_2^+ + NH_3 \qquad (4)$$

TABLE 5: Calculated Proton Affinities (kJ/mol) at 0 and 298 K and Gas-Phase Basicities (kJ/mol) at 298 K of $NHCl_2$

	PA_0		PA_{298}		GB_{298}	
	B3LYP	CCSD(T)	B3LYP	CCSD(T)	B3LYP	CCSD(T)
$H_2NCl_2^+$ ($^1A_1$) → $NHCl_2$ ($^1A'$) + H^+	742.2	752.3	748.5	758.6	713.0	723.0
						764.4
$HN(Cl)ClH^+$ (^1A) → $NHCl_2$ ($^1A'$) + H^+	623.4	610.0	626.8	613.0	598.7	585.3
$H_2NCl{-}Cl^+$ ($^1A'$) → $NHCl_2$ ($^1A'$) + H^+	676.1	660.7	681.2	665.3	648.9	633.5
$H_2NCl_2^+$ (^3A) → $NHCl_2$ ($^1A'$) + H^+	603.2	589.5	605.2	591.5	586.1	572.3
$HN(Cl)ClH^+$(^3A) → $NHCl_2$ ($^1A'$) + H^+	607.2	570.6	608.3	571.8	588.6	552.1
$H_2NCl_2^+$ (^3A) → $NHCl_2$ (^3A) + H^+	740.1	756.5	744.5	760.8	717.2	733.5
$HN(Cl)ClH^+$ (^3A) → $NHCl_2$ (^3A) + H^+	744.1	737.6	747.6	741.2	719.7	713.3

Actually, it is known that, in acidic solutions, monochloramine undergoes disproportionation[4b] to yield protonated dichloramine (vide infra).

In principle, the protomer (**III**) could be formed in the ion source by the highly exothermic and hence indiscriminate protonation of NH_2Cl by the $C_nH_5^+$ ions. However, no experimental evidence for (**III**) was obtained, likely owing to its fast decomposition,

$$NHCl_2 \xrightarrow[-\,C_nH_4]{+\,C_nH_5^+} (\mathbf{III})_{exc} \rightarrow HNCl^+ + HCl \qquad (5)$$

a process endothermic by only 7.2 kJ/mol for $n = 1$ and endothermic by 144.2 kJ/mol for $n = 2$ based on $\Delta H°_f$ ($HNCl^+$) = 1224.2 kJ/mol.[26a] A further pathway responsible for the lack of (**III**), whose conjugate base has a GB = 598.7 at B3LYP level and 585.3 kJ/mol at CCSD(T) level[this work], could be its deprotonation by water (GB = 660 kJ/mol)[22] and monochloramine (GB = 761 kJ/mol)[6] co-distilling from the aqueous solution. Water, in particular, should selectively deplete this population, acting as a catalyst to transfer H^+ from the less basic to the more basic site of dichloramine. On the contrary, the most stable protomer (**I**) can be deprotonated in an exothermic process by monochloramine but not by water.

Several processes can lead to the formation of isomeric ions (**II**), $H_2NCl{-}Cl^+$. For instance, ions (**I**), excited by the exothermicity of their formation process (3), could undergo intramolecular isomerization to $H_2NCl{-}Cl^+$, overcoming the barrier whose height is extimated to be 235.6 kJ/mol at the B3LYP level and 209.1 kJ/mol at the CCSD(T) level at 298 K. An alternative route could involve intermolecular isomerization of excited ions (**I**),

$$H_2NCl_2^+ + NH_2Cl \rightarrow NH_2Cl{-}Cl^+ + NH_2Cl \qquad (6)$$

formally a Cl^+ transfer reaction to monochloramine whose endothermicity corresponds to the stability difference between ions (**I**) and (**II**). In this connection, it is apparent that surveying the ability of protonated chloramines to transfer Cl^+ to different substrates is an important feature for the evaluation and the comparison of their oxidant properties and their stability toward the disproportionation reaction.

Occurrence of process 4 can be assessed based on the following thermochemical considerations. From $\Delta H°_f(H_3NCl^+)$, 786.9kJ/mol,[6] $\Delta H°_f(NH_2Cl)$, 55.2kJ/mol,[26a] $\Delta H°_f(NH_3)$, −45.9 kJ/mol,[22] and $\Delta H°_f(H_2NCl_2^+)$, 911.2 kJ/mol[this work], the disproportionation reaction of protonated monochloramine would be endothermic by 23.2 kJ/mol.[27] Indeed, process 4, which can be considered as the Cl^+ transfer from ammonia to NH_2Cl, is endothermic because the Cl^+ BE of NH_3 exceeds that of monochloramine, consistent with the relative Cl^+ affinity scale recently published by Cacace et al.,[28] where the Cl^+ BE of ammonia is higher than that of Cl_2 (Cl^+ BE (Cl_2) = 320.1 kJ/mol), in agreement with our previous observation[6] of the formation of NH_3Cl^+ ions from the reaction between NH_3 and Cl_3^+. However, the difference between the chloronium ion affinity of ammonia and monochloramine, 23.2 kJ/mol, is not unduly large to prevent this reaction from occurring under the conditions typical of the ICR CI source.

The Cl^+ BE (NH_3) can be estimated from the enthalpy change for the reaction:

$$Cl^+ + NH_3 \rightarrow H_3NCl^+$$

From $\Delta H°_f(H_3NCl^+)$, 786.9 kJ/mol,[6] $\Delta H°_f(Cl^+)$, 1378.8 kJ/mol,[22] and $\Delta H°_f(NH_3)$, −45.9,[22] the Cl^+ BE (NH_3) is calculated to be 546.0 kJ/mol. Untill now, no data have been reported on the absolute Cl^+ affinities of inorganic chloramines. From the enthalpy change for the reaction

$$Cl^+ + NH_2Cl \rightarrow H_2NCl_2^+$$

and from $\Delta H°_f(NH_2Cl)$, 55.2 kJ/mol,[26a] $\Delta H°_f(Cl^+)$, 1378.8 kJ/mol,[22] and $\Delta H°_f(H_2NCl_2^+)$, 911.2 kJ/mol[this work], the Cl^+ BE (NH_2Cl) results to be 523.0 kJ/mol. Finally the Cl^+ BE ($NHCl_2$) can be deduced from the ΔH value of the disproportionation reaction of dichloramine

$$H_2NCl_2^+ + NHCl_2 \rightarrow HNCl_3^+ + NH_2Cl$$

From the $\Delta H°_f(HNCl_3^+)$ computed by Milburn et al.[26a] for the N-protonation of trichloramine and the $\Delta H°_f(NHCl_2)$,[26a] the enthalpy change for the disproportion of dichloramine is of 32.7 kJ/mol. This value corresponds to the difference of the Cl^+ BE of NH_2Cl and $NHCl_2$ and allows us to estimate the Cl^+ BE ($NHCl_2$) as 490.3 kJ/mol.

Consequently, the following Cl^+ affinity order of ammonia and the inorganic chloramines is obtained:

$$Cl^+ \text{ BE} \qquad NHCl_2 < NH_2Cl < NH_3$$

As previously reported for pyridines,[29] an excellent correlation exists between the Cl^+ affinities and the proton affinities of unhindered molecules. The plot of the Cl^+ BE values vs the proton affinities, (PA), of ammonia, monochloramine, and dichloramine is linear (Figure 5), with a correlation coefficient of 0.98 which suggests that the same factors affecting the stability of the protonated adducts influence the stability of the chlorinated adducts; that is, the electron donor ability of the N atom is paramount in both proton and Cl^+ transfer. Increasing Cl for H substitution in ammonia, the PA and the Cl^+ BE decrease, owing to the electron-withdrawing effect of the Cl atoms on the nitrogen.

The correlation between PA and Cl^+ BE emerges quite clearly in the NH_xCl_{3-x} molecules, whose large basicity differences overwhelm other, more subtle effects noted in certain more simple molecules of comparable basicity.[28]

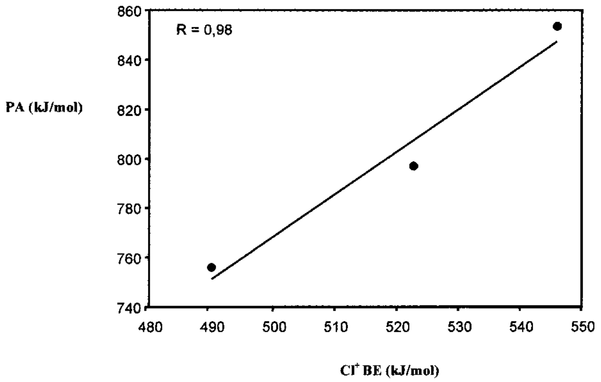


Figure 5. Proton affinities (PA) vs chloronium ion affinities (Cl^+ BE) of ammonia, NH_2Cl, and $NHCl_2$.

Utilization of the HSAB theory may help rationalize the trend noted in the competition between H^+ transfer (Brønsted acid behavior) and Cl^+ transfer (Lewis acid behavior) from protonated chloramines to gaseous bases/nucleophiles. As a matter of fact, we failed to detect Cl^+ transfer involving the soft monochloramine and hard bases such as water or alcohols, despite the fact that the alternative channel, H^+ transfer, is thermochemically unfavorable, whereas Cl^+ transfer to soft nucleophiles, such as ethylene and benzene, does occur.

Gas-phase halogenation of aromatic compounds was studied[30] in detail using as reagent ions XCO^+($X = Cl$, Br) and NH_3-Cl^+. These studies suggest that Cl^+ addition occurs at the ring to form a σ complex.

Conclusions

In summary, joint application of FT−ICR mass spectrometry and theoretical methods allowed us to determine the structure of isomeric $(NHCl_2)H^+$ ions, to evaluate their relative stability, and to survey their reactivity. The theoretical and experimental evidence identifies the $H_2NCl_2^+$ ion (**I**) as the most stable protomer, pointing as well to the existence of a less stable isomer, the $H_2NCl{-}Cl^+$ ion (**II**), whereas no evidence for the $HN(Cl)ClH^+$ isomer (**III**) was found.

This work represents the first experimental estimate of the basicity of $NHCl_2$. The theoretical $GB(NHCl_2)$ values are fully consistent with the experimental one. From the difference between the theoretical $\Delta G°$ and PA we obtain $T\Delta S = 35.6$ kJ/mol. Adding this value to the experimental $GB(NHCl_2)$ we obtain $PA(NHCl_2) = 757.0 \pm 10$ kJ/mol and from $\Delta H°_f(H^+) = 1531$ kJ/mol and $\Delta H°_f(NHCl_2) = 137.2$ kJ/mol,[26a] $\Delta H°_f(H_2NCl_2^+)$ is evaluated to be 911.2 ± 13 kJ/mol.

From the $\Delta H°_f(NH_3Cl^+)$ value obtained in a previous work[6] and the $\Delta H°_f(H_2NCl_2^+)$ value reported here, the absolute Cl^+ affinities of ammonia, monochloramine, and dichloramine were calculated.

The linear correlation obtained plotting the Cl^+ BE values of NH_3, NH_2Cl and $NHCl_2$ versus their respective proton affinities suggests that the same factors affect the stability of protonated adducts and chlorinated adducts, that is, the electrondonor ability of the N atom undergoing both proton and chlorine transfer. Increasing substitution on ammonia, the PA and Cl^+ BE decrease, owing to the electron-withdrawing effect of the Cl atoms on the nitrogen.

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