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Gas-Phase Chemistry of $NH_xCl_y^+$. 1. Structure, Stability, and Reactivity of Protonated Monochloramine

Andreina Ricci*

Dipartimento di Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive,
Università di Roma "La Sapienza", P.le A. Moro, 5 00185 Rome, Italy

Marzio Rosi

Istituto per le Tecnologie Chimiche e Centro di Studi CNR "Calcolo Intensivo in Scienze Molecolari",
Università di Perugia, 06100 Perugia, Italy

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The structure and the reactivity of gaseous NH_3Cl^+ ions obtained from direct protonation of aqueous monochloramine by CI/CH_4 and from ionization of a Cl_2 plasma containing trace amounts of ammonia have been investigated by FT-ICR mass spectrometry. The results characterized the NH_3Cl^+ ions arising from both experiments as having the NH_3-Cl^+ structure, consistent with the results of MO SCF calculations pointing to the higher basicity of the nitrogen than the chlorine atom of NH_2Cl. The gas-phase basicity of monochloramine has been estimated to be 761 ± 5 kJ mol^{-1} from bracketing experiments according to the procedure based on the relationship between the efficiency and the standard free-energy difference of proton transfer. This value is consistent with those from theoretical calculations at the B3LYP and CCSD(T)/6-311++G(3df,3pd) level. In agreement with the protonation site, the NH_3Cl^+ ions behave as a protonating and chlorinating agent but addition is also observed.

Introduction

Monochloramine, NH_2Cl, is the prototypal member of a class of compounds that includes over 1000 organic molecules containing the N−Cl group in addition to inorganic species, such as dichloro- and trichloroamine. Apart from their intrinsic fundamental interest, chloramines find a variety of applications as bleachers, disinfectants, detergents, cleansers, etc.[1]

Monochloramine itself is an important reagent in organic synthesis and is widely used as a water disinfecting agent. Owing to the great variety of applications, the chemistry of *N*-chloroamines, in particular of NH_2Cl, has received a great deal of attention in solution and, more generally, in the condensed phase.[2−6]

In contrast, apart from its preparation from the reaction of Cl_2 and NH_3,[7] little is known about the gas-phase chemistry of NH_2Cl, largely owing to the explosive nature of gaseous, undiluted chloramine and the frequent explosions caused by its attempted distillation.[8]

Only a few studies of the gas-phase ion chemistry of NH_2Cl have been reported,[9,10] including an investigation on the preparation of NH_3Cl^+ ions by protonation of the base under chemical ionization (CI) conditions, and its use as a chlorinating reagent.[10]

So far, to the best of our knowledge, no experimental studies of the two protomers

$$\underset{\mathbf{1}}{[H-NH_2Cl]^+} \qquad \underset{\mathbf{2}}{[NH_2Cl-H]^+}$$

have been reported, and the gas-phase basicity (GB) and the proton affinity (PA) of chloramine have not been measured either, despite the fundamental importance of these thermochemical data. Furthermore, no systematic survey of the manifold reactivity of protonated chloramine, which in principle can behave as a Brønsted acid, a chlorinating and an aminating agent, has been reported.

In this study, we have investigated alternative preparation methods of protonated chloramine and its structure and reactivity and evaluated the GB and PA of NH_2Cl by the joint application of FT-ICR mass spectrometry and theoretical techniques.

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 chloramine (MH^+) was generated by positive CI utilizing 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 $NH_3{}^{35}Cl^+$ ions were isolated by broad-band and "single shots" 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 the neutral molecules in the cell. The pressure of the neutrals was measured by a Bayard−Alpert ionization gauge, whose readings were calibrated utilizing the known rate coefficient of the $CH_4 + CH_4^+ \rightarrow CH_5^+ + CH_3^\bullet$ reaction as a reference.[11] The readings were corrected for the relative sensitivity to the various gases utilized according to a standard method.[12] The pseudo-first-order rate constants were obtained by plotting the logarithm of the $NH_3{}^{35}Cl^+$ intensities as a function of time. The bimolecular rate constants were then 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.[13] Reaction

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TABLE 1: Experimental and Theoretical GB and PA of Reference Bases[b]

	1		2		3		4		5		6	
	PA	GB	PA	GB	PA	GB	PA	GB	PA	GB	PA	GB
CH_3CHO	768.5	736.5			781	748.7[b]	777	744.7[b]	770.2	737.9[b]	770.2	737.9[b]
$C_2H_5NO_2$	765.7	733.2			773	740.5[c]						
$CH_2{-}CH_2O$	774.2	745.3			785	757.1[c]						
$HCOOCH_3$	782.5	751.5	787.0	755.8	788	756.8[b]	792.4	761.2[b]	781.1	749.9[b]	782.2	751.0[b]
$CH_3CH_2CH_2OH$	786.5	756.1			798	767.5[c]						
$(CH_3)_2O$	792.0	764.5	793.3	765.2[b]	80.4	776.2[b]	804.6	776.8[b]			792.0	764[b]
CH_3CH_2CN	794.1	763.0			806	775.0[b]	805.8	774.0[b]	793.7	762.7[b]	793.5	762.5[b]
$(CH_3)_2CHOH$	793.0	762.6			800	769.6[c]						
$(CH_3)_2CO$	812.0	782.1	810.4	780.3[b]	823	792.9[b]	830.1	799.9[b]	817.0	786.9[b]	811.9	781.8[b]
C_2H_5OH	776.4	746			788	757.6[c]						

[a] All values are in kJ/mol. **1**, from ref 29; **2**, from ref 30; **3**, from ref 23; **4**, from ref 3; **5**, from ref 32; **6**, from ref 33. [b] GB(B) = PA(B) + $T[\Delta S°_{1/2}(B) - S°(H^+)]$ with $T = 300$ K and $S°(H^+) = 109$ J/mol K. $\Delta S°_{1/2}$ from ref 33. [c] From $T\Delta S$ from ref 29.

TABLE 2: Efficiencies and Rate Constants of Proton Transfer from NH_3Cl^+ to Reference Bases

	K_{exp} ($\times 10^{-9}$ molecules cm^3 s^{-1})	eff%
$C_2H_5NO_2$	0.013 ± 0.001	0.5
$HCOOCH_3$	0.021 ± 0.005	1.3
$CH_3CH_2CH_2OH$	0.024 ± 0.08	1.4
C_2H_5OH	0.17 ± 0.02	10
$(CH_3)_2O$	0.65 ± 0.04	43
CH_3CH_2CN	1.3 ± 0.2	45
$(CH_3)_2CHOH$	1.4 ± 0.3	77
$(CH_3)_2CO$	2.2 ± 0.6	100

efficiencies 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%. Chloramine was prepared in water solution by reaction of equimolecular amounts of ammonia with sodium hypochlorite.[14] The pH of the solution was found to be critically important, since chloramine is the major product at pH > 8 but decomposes at pH > 10 whereas at low pH values formation of NCl_3 can occur. Monochloramine was then directly distilled, together with water vapor, into the external ion source of the ICR spectrometer, removing traces of ammonia by a trap packed with anhydrous copper sulfate.[15]

Computational Details

Density-functional theory, using the hybrid[16] B3LYP functional,[17] has been used to localize the stationary points of the systems investigated 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[18] with a perturbational estimate of the triple-excitations [CCSD(T)] approach.[19] 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[20] has been used. All calculations were performed using Gaussian 94.[21]

Results and Discussion

Experimental Evaluation of GB of NH_2Cl. Most of the GB values listed in the literature were derived from the measurement of the equilibrium constant for the reversible proton-transfer reaction between the compound of interest and reference bases of known GB. If the equilibrium constant can be evaluated over a broad temperature range, both the $\Delta H°$ and $\Delta S°$ changes can be derived.[22,23] This method requires accurate measurement not only of the ionic intensities but also of the concentrations of the neutral reagents in the cell.

Analogously, application of the alternative approach based on the determination of K_{eq} as the ratio of the forward and reverse rate constants[24] presupposes the knowledge of the concentrations of the neutral reagents.

The kinetic method proposed by Cooks et al.,[25] based on the dissociation of proton-bound dimers, is of limited application under the conditions of FT-ICR experiments where such adducts are rarely observed.

In our experiments, the presence of water, which evaporates together with chloramine from the aqueous solutions, precludes the possibility of determining the partial pressure of NH_2Cl in the cell and, therefore, of utilizing equilibrium methods. Furthermore, no proton-bound dimers are observed, which precludes application of the kinetic method.

This leaves, as the only viable alternative, the "bracketing" method[23,26] where the GB is determined by measuring the efficiency of proton transfer from the ion investigated to bases of known GB. The efficiency, high for exoergic proton-transfer reaction, falls below the detection limit when passing to strongly endoergic processes and is low for reactions endoergic by 4−8 kJ mol^{-1}. This behavior is common to bases with lone electron pairs as the basic center[27] and to olefinic and aromatic bases with π electrons as the basic system.[28]

To evaluate the GB of monochloramine, NH_3Cl^+ ions, generated in the external ion source by the highly exothermic proton transfer from the $C_nH_5^+$ ions ($n = 1,2$) in CH_4/CI, were allowed to react with bases of different strength in the resonance cell utilizing only bases with lone electron pairs as the basic center.

Experimental and theoretical GB values of the reference bases available from the literature are reported in Table 1, whereas Table 2 summarizes the collisional efficiencies of proton-transfer reactions from NH_3Cl^+ to the reference bases measured as previously described. The efficiency is large (nearly 100%) in the case of CH_3COCH_3, decreases to values <10% for bases such as $HCOOCH_3$, $C_2H_5NO_2$, $CH_3CH_2CH_2OH$, etc. and is nearly 50% for $(CH_3)_2O$ and CH_3CH_2CN. The very nature of the bracketing technique makes the results largely approximate.

To reduce the uncertainty range of the GB values obtained, Bouchoux et al.[34] proposed a procedure based on an empirical relationship between the rate of proton transfer and the standard free energy of proton transfer.

TABLE 3: Optimized Geometries, Frequencies, and Energies of NH_2Cl, NH_3Cl^+, and NH_2ClH^{+a}

	NH_2Cl $^1A'$		NH_3Cl^+ $^1A_1$		NH_2ClH^+ $^1A'$	
r(NCl)		1.758		1.747		1.727
r(NH)		1.017		1.026		1.021
r(ClH)						1.310
∠(ClNH)		104.1		109.3		105.4
∠(HNH)		106.1		109.7		110.5
∠(NClH)						97.7
	a′	677.5	a_1	741.5	a″	409.3
	a′	1068.1	e	1039.2	a′	547.0
	a″	1191.1	a_1	1467.9	a′	968.9
	a′	1595.5	e	1628.8	a′	1058.3
	a′	3455.9	a_1	3355.1	a″	1232.7
	a″	3546.2	e	3441.9	a′	1608.3
					a′	2698.9
					a′	3420.5
					a″	3526.4
E_{B3LYP}		−516.170689		−516.484557		−516.419616
ZPE[b]		0.026277		0.040516		0.035244
$E_{CCSD(T)}$		−515.556619		−515.873403		−515.806741

[a] Bonds lengths in Å, angles in deg, total energies in hartree, frequencies in cm^{-1}. [b] Zero-point energy.

According to this relationship, the efficiency of proton transfer occurring via a single intermediate

$$[MH^+] + B \underset{k_{-1}}{\overset{k_{coll}}{\rightleftarrows}} [MHB^+] \xrightarrow{k_1} M + BH^+ \qquad (2)$$

is correlated to the $\Delta G°$ change of the reaction, namely, to the Δ(GB) difference between the GB of the molecule M and B, by the equation

$$RE = 1/(1+ (k_{-1}/k_1)) = 1/(1 + \exp(\Delta G_I^{\ddagger}/RT)) = 1/(1 + \exp(\Delta G°_I + \Delta G°_a)/RT) \qquad (3)$$

where RE is the reaction efficiency expressed by the ratio of k_{exp} to k_{coll}, $\Delta G°_I$ is the difference between $\Delta G°_{-1}$ and $\Delta G°_1$, namely, the standard free-energy difference of the unimolecular decomposition of the intermediate [MHB^+], respectively, back to reactants and forward to the complex, and $\Delta G°_a$ is the difference between the intrinsic barrier $\Delta G°_a = \Delta G°_{a1} - \Delta G°_{a-1}$. In fact, the activation energy of a given process i can be correlated to its free-energy change by the equation: $\Delta G_i^{\ddagger} = \Delta G°_i - G°_{ai}$, where the latter parameter represents the intrinsic barrier, that is, the barrier that the reaction would have if it were isoergonic.

Therefore $\Delta G°_I$ = GB(M) − GB(B) and $\Delta G°_a$ is the apparent energy barrier for proton transfer, which is expected to be small and nearly constant for proton-transfer reactions between n-type bases.

To deduce GB(M) from a set of experiments, the efficiency data can be fitted in the parametric function

$$RE = a/(1 + \exp[b(\Delta G° + c)/RT) = a/(1 + \exp[b(c'' - GB(B)]/RT)$$

with GB as a second variable; a is the normalizing factor, ranging from 0.8 to 1.0; $b = 1/RT^*$ (where T^* is the effective temperature, which can be different from the experiment temperature owing to a nonequilibrium distribution of the internal energy of the [MBH^+] intermediate); c'' = GB(M) + c, and $c = \Delta G°_a$.The latter was found to be of the same magnitude order of the term $RT^* = 1/b$. Thus, assuming that c is precisely equal to RT^*, one obtains GB(M) = $c'' - 1/b$. According to this procedure, the reaction efficiencies of the proton-transfer processes from NH_3Cl^+ to bases of known GB have been fitted in the equation, as illustrated in Figure 1.

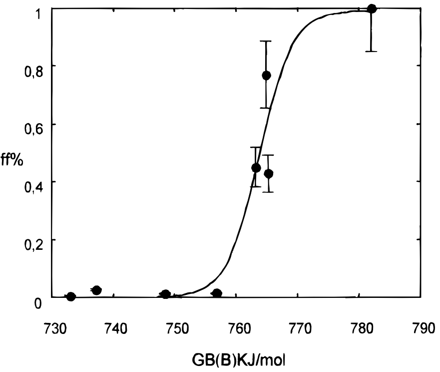


Figure 1. Reaction efficiencies (RE) vs gas-phase basicities for proton transfer between NH_3Cl^+ and reference bases.

All GB values used to establish the correlation between RE and GB are taken from ref 29, utilizing a self-consistent scale based on a single anchoring value.

From the best fitting of our data we obtain $a = 0.995$; $b = 0.36813$; $c'' = 763.83$; $T^* = 330$ K; and the gas-phase basicity of NH_2Cl is 761 ± 5kJ mol^{-1}.

Computational Evaluation of GB and PA of NH_2Cl. The optimized geometries, the energies, and the vibrational frequencies of NH_2Cl and its protonated species are reported in Table 3. Both the protonation on the nitrogen and on the chlorine have been investigated. The structures of the investigated species, together with the optimized geometrical parameters, are reported in Figure 2.

NH_2Cl has a pyramidal structure with C_s symmetry, and the optimized geometrical parameters are in good agreement with the experimental ones[35] and with previous ab initio calculations.[36−38] The protonation of nitrogen leads to a C_{3v} structure with angles very close to the tetrahedral one, while the protonation of the chlorine atom leads to a C_s structure which is a local minimum that is less stable than NH_3Cl^+ by 161.2 kJ mol^{-1} at the CCST(D) level with inclusion of zero-point energy.

This result is in reasonable agreement with the recent calculations of Milburn et al.[38] at the QCISD(T)/6-311++G-(2df,p)//MP2/6-311++G(d,p) level; indeed, they found the chlorine-protonated form less stable than the nitrogen one by 171.0 kJ mol^{-1}.

TABLE 4: Calculated Proton Affinity (kJ mol^{-1}) at 0 and 298 K and Gas-Phase Basicities (kJ mol^{-1}) at 298 K of NH_2Cl

	PA_0		PA_{298}		GB_{298}	
	B3LYP	CCSD(T)	B3LYP	CCSD(T)	B3LYP	CCSD(T)
$NH_3Cl^+ \rightarrow NH_2Cl + H^+$	786.6	794.1	792.9	800.4[a]	756.9	764.4
$NH_2ClH^+ \rightarrow NH_2Cl + H^+$	630.1	633.0	635.1	638.1	603.3	606.7

[a] 800.8 kJ mol^{-1}at QCISD(T)/6-311++G(2df,p)//MP2/6-311++G(d,p) level, as computed by Milburn et al.[38]

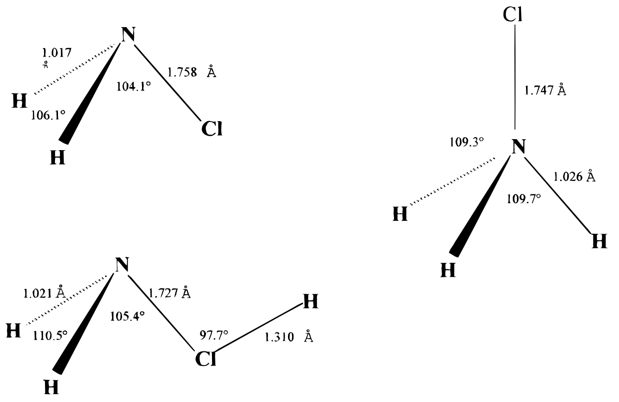
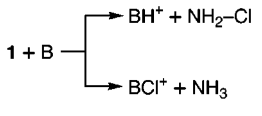


Figure 2. Optimized geometries of the investigated species. Bond lengths in Å, angles in deg.

Table 4 shows the proton affinities at 0 and 298 K and the gas-phase basicities at 298 K of NH_2Cl. We considered the attack of the proton both on the nitrogen and the chlorine atoms. For comparison, both the B3LYP and the CCSD(T) results are reported.

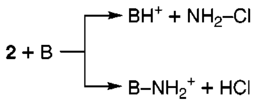
The preferred site of attack by the proton is the nitrogen at any level of calculation, the energy difference being around 160 kJ mol^{-1}. The proton affinity of NH_2Cl was estimated several years ago by Jolly and Bakke[39] (795.0 kJ mol^{-1}) and by Kollman and Rothenberg[40] (856.9 kJ mol^{-1}). The first value is in reasonable agreement with the value computed by us for the protonation of the nitrogen, while the second value seems to be somewhat overstimated. More recently, Kotiaho et al.[10] estimated the proton affinity of NH_2Cl supposing that the proton affinities of NH_3 and NH_2Cl differ by the same amount as those of HCN and ClCN. They obtained the value 871.5 kJ mol^{-1}, which is 71 kJ mol^{-1} higher than the value computed by us. However, their assumption is somehow questionable. The values computed at the AM1 level by Protashchuk et al.,[41] 794.5 and 638.9 kJ mol^{-1} for the protonation of the nitrogen and the chlorine atoms, respectively, agree well with our PA_{298} values. Very recently, Milburn et al. computed the PA of NH_2Cl at the QCISD(T)/6-311++G(2df,p)//MP2/6-311++G(d,p) level, obtaining a value of 800.8 kJ mol^{-1}; our value at the CCSD(T) level is in perfect agreement with their result.

The Reactivity of NH_3Cl^+. Depending on the site of protonation, NH_3Cl^+ can conceivably behave as a Brønsted acid and/or a chlorinating agent



$$\mathbf{1} + B \rightarrow BH^+ + NH_2{-}Cl \quad (2)$$
$$\mathbf{1} + B \rightarrow BCl^+ + NH_3 \quad (3)$$

or as a protonating and/or aminating agent



$$\mathbf{2} + B \rightarrow BH^+ + NH_2{-}Cl \quad (2a)$$
$$\mathbf{2} + B \rightarrow B{-}NH_2^+ + HCl \quad (3a)$$

In acidic solutions, both proton transfer and Cl^+ transfer are known to occur,[42,43] whereas *direct* amination is not observed. In the only gas-phase study dealing with the NH_3Cl^+ reactivity, chlorination and protonation of benzene and other aromatic molecules have been reported,[10] although the latter process, traced to the occurrence of reaction 2, should be energetically unfavorable in view of the larger PA of NH_2Cl than that of benzene.

Since, however, the PA of NH_2Cl is referred to the formation of the most stable isomer **1**, the reported ability of $(NH_2Cl)H^+$ ions obtained from the reaction of strong Brønsted acids with NH_2Cl is of interest. In fact, unselective protonation of chloramine could yield a mixed population of **1** and **2** isomers.

Owing to the lower basicity of the Cl than of the N atom of chloramine demonstrated by the present theoretical study, NH_2ClH^+ could conceivably undergo exothermic proton transfer to C_6H_6, a process that is endothermic if promoted by the more stable protomer **1**.

To verify this hypothesis, which requires formation of **2**, we have utilized an alternative preparation route that yields exclusively model ions **1**. To this end, trace amounts of NH_3 were introduced into a Cl_2/CI plasma, containing Cl_3^+ as an effective chlorinating cation,[44] whose reaction with ammonia

$$Cl_3^+ + NH_3 \rightarrow \mathbf{1} + Cl_2 \qquad (4)$$

gives the desired population of model ion **1** having the $H_3N{-}Cl^+$ connectivity.

A systematic investigation performed by FT-ICR mass spectrometry has shown that the reactivity of model ions **1** from eq 4 is indistinguishable from that of $(NH_2Cl)H^+$ from the CH_4/CI of NH_2Cl, in particular concerning the rate of proton transfer to all bases investigated.

This shows that only protomer **1** is formed in the CH_4/CI of NH_2Cl, despite the fact that proton transfer from $C_nH_5^+$ (n = 1,2) to the Cl atom, yielding the less stable ion **2**, would be energetically allowed. A simple explanation is based on the presence of water codistilled with NH_2Cl into the CI source. According to the theoretical results from this study, the PA of H_2O of 691 kJ/mol[29] is intermediate between those of the basic sites of NH_2Cl. Thus, any ions **2** from the exothermic reaction

$$C_nH_5^+ + NH_2Cl \rightarrow C_nH_4 + \mathbf{2} \qquad (5)$$

should undergo fast exothermic deprotonation by H_2O

$$\mathbf{2} + H_2O \rightarrow NH_2Cl + H_3O^+ \qquad (6)$$

a process that selectively depletes the population of **2** but not that of **1**, whose deprotonation by water is endothermic.

Whereas the above results provide a neat explanation for the exclusive formation of **1**, from the CH_4/CI of NH_2Cl, a problem arises as to the reported[10] ability of NH_3Cl^+ to protonate benzene, whose PA is significantly *lower* than that of NH_2Cl. To clarify this point, ions **1** were allowed to interact with C_6H_6 in the resonance cell of the FT-ICR spectrometer. The results, illustrated in Figure 3, show that the Cl^+-transfer process

$$\mathbf{1} + C_6H_6 \rightarrow C_6H_6Cl^+ + NH_3 \qquad (7)$$

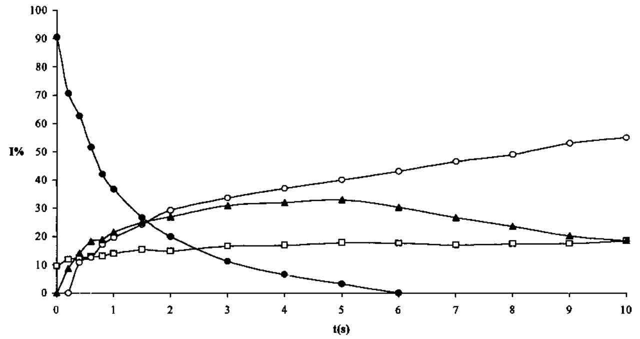


Figure 3. Time profile of the ionic intensities of the reaction between protonated monochloramine and benzene ($P = 1.8 \times 10^{-8}$ Torr). $NH_3{}^{35}Cl^+$ (●); $C_6H_7^+$ (○); $C_6H_6{}^{35}Cl^+$(▲); $C_6H_6^{+\cdot}$ (□).

is the primary process, whereas no H^+ transfer from **1** to benzene occurs. Only in a subsequent stage the chlorobenzenium ions formed react with benzene according to the process

$$C_6H_6Cl^+ + C_6H_6 \rightarrow C_6H_5Cl^+ + C_6H_7^+ \tag{8}$$

which is allowed by the very close PA of chlorobenzene (PA(C_6H_5Cl) = 759,[23] 753,[29] kJ mol^{-1}) and of benzene (PA(C_6H_6) = 758.6,[23] 750.2,[29] 753.1[30] kJ mol^{-1}), and by the large excess of the latter base.

The secondary nature of process 8 is clearly apparent from the plot of Figure 3.

We conclude that no direct H^+ transfer from 1 to C_6H_6 occurs, and that the reported[10] formation of $C_6H_7^+$ is rather to be traced to the secondary process (eq 8).

Disproportionation of Chloramine. One of the most interesting reactions of NH_2Cl, long known to occur in acidic solutions, is its disproportionation into ammonia and dichloramine. Two alternative mechanisms have been proposed, i.e., direct Cl^+ transfer

$$NH_3Cl^+ + NH_2Cl \rightarrow NH_2Cl_2^+ + NH_3 \tag{9}$$

or hydrolysis to protonated hypochlorous acid[43]

$$NH_3Cl^+ + H_2O \rightarrow H_2ClO^+ + NH_3 \tag{10}$$

followed by the reaction of the latter with chloramine

$$H_2ClO^+ + NH_2Cl \rightarrow NH_2Cl_2^+ + H_2O \tag{11}$$

Interestingly, the CH_4/CI spectrum of NH_2Cl/H_2O mixtures displays, besides H_3O^+, a major $NH_2Cl_2^+$ triplet of the correct isotopic composition, showing that cationic disproportionation of NH_2Cl occurs in the gas phase as well. The most likely source of $NH_2Cl_2^+$ is process 9, which is exothermic by 81.9 kJ/mol based on the heat of formation of **1** from this work and the heat of formation of $NH_2Cl_2^+$ estimated in turn from the PA of $NHCl_2$.[41] The sequence of eqs 10−11 appears unlikely because no H_2ClO^+ ions are detectable in the CH_4/CI experiments and process 10 is appreciably endothermic, based on the heat of formation of **1** from this work and the calculated heat of formation of H_2ClO^+.[45]

In accordance to the chlorinating ability of **1**, $C_3H_6Cl^+$ ions are formed from the reaction of NH_3Cl^+ with propylene. As for benzene, $C_3H_7^+$ and other ions arising from secondary reactions of $C_3H_6Cl^+$ are observed.

Other Reactions. The reaction of NH_2Cl with aldehydes and ketones has been extensively studied in solution.[46] From the fast decomposition of the unstable hemiaminal, ald−chlorimines are formed according to the mechanism

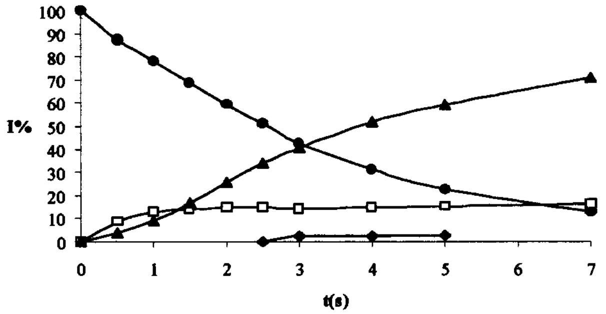
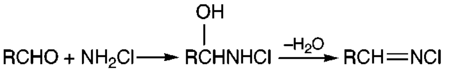


Figure 4. Time profile of the ionic intensities of the reaction between protonated monochloramine and ethylene oxide ($P = 2.7 \times 10^{-8}$ Torr). $NH_3{}^{35}Cl^+$ (●); $C_2H_5N^{35}Cl^+$ (▲); $C_2H_5O^+$ (□); $C_4H_9O^+$ (◆).

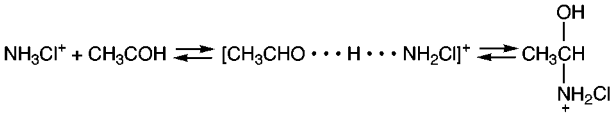


$$RCHO + NH_2Cl \longrightarrow \overset{OH}{\overset{|}{R\text{C}}}HNHCl \xrightarrow{-H_2O} RCH{=}NCl \tag{12}$$

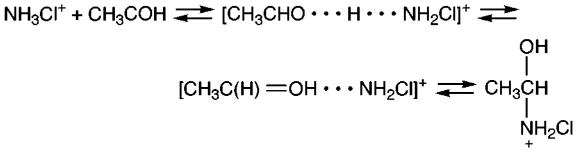
The reaction between $NH_3{}^{35}Cl^+$, **1**, and acetaldehyde yields the ion at m/z = 96 corresponding to $C_2H_7{}^{35}ClNO^+$ besides protonated acetaldehyde as a relatively low-intensity ion and the proton-bound cluster $(CH_3COH)_2H^+$ ion. Structural analysis by CID spectrometry, showing the fragment at m/z = 78 from water loss, characterizes this ion as a true addition product rather than a proton-bound dimer of **1** and acetaldehyde.

The reaction between $NH_3{}^{35}Cl^+$, **1**, and ethylene oxide displays the same reactivity pattern, except that addition yields the deprotonated $C_2H_5N^{35}Cl^+$ ion of m/z = 78 (Figure 4).

A reasonable explanation of the ability of NH_3Cl^+ to undergo addition involves a mechanism whose first step is the formation of a proton-bound complex between **1** and CH_3COH or ethylene oxide, followed by proton transfer to the oxygen atom and by the concerted or subsequent nucleophilic attack by the N atom of chloramine; e.g. for acetaldehyde:



$$NH_3Cl^+ + CH_3COH \rightleftharpoons [CH_3CHO\cdots H\cdots NH_2Cl]^+ \rightleftharpoons CH_3\underset{\overset{|}{\overset{+}{N}H_2Cl}}{\overset{\overset{OH}{|}}{C}}H \tag{13a}$$



$$NH_3Cl^+ + CH_3COH \rightleftharpoons [CH_3CHO\cdots H\cdots NH_2Cl]^+ \rightleftharpoons [CH_3C(H){=}OH\cdots NH_2Cl]^+ \rightleftharpoons CH_3\underset{\overset{|}{\overset{+}{N}H_2Cl}}{\overset{\overset{OH}{|}}{C}}H \tag{13b}$$

Following a facile intramolecular proton transfer, the addition product from the reaction of **1** with ethylene oxide, eliminates water.

It is worthy to note that protonated ethylene oxide and protonated acetaldehyde are structural isomers and that the latter has been recognized as the most stable one.[47−50]

The different reactivity of ethylene oxide toward **1** can be reasonably traced to a mechanism involving a protonated oxirane that does not isomerize to the most stable structure $CH_3C(H){=}OH^+$.

In fact, ICR studies of the ion−molecule reaction in a mixture of ethylene oxide with PH_3 or H_2S established the cyclic structure of protonated ethylene oxide, rearranging to the more stable protonated acetaldehyde only when excited by a large exothermicity of its formation process.[49]

However, if protonated acetaldehyde is formed from the fast isomerization of protonated oxirane, the different reactivity observed can be explained on the basis of energetic considerations.

The addition products arising from CH_3CHO and ethylene oxide contain a different excess of internal energy, owing the different heats of formation of the two neutrals, making the ethylene oxide reaction much more exothermic. For this reason, the addition product formed from the reaction of **1** and oxirane can undergo fast water elimination.

Conclusions

These results provide the first experimental estimate of the basicity of NH_2Cl and represent the first systematic study on the gas-phase reactivity of NH_3-Cl^+ ions. The theoretical GB(NH_2Cl) values are fully consistent with the experimental one. From the difference between the theoretical $\Delta G°$ and PA, we obtain $T\Delta S = 35.98$ kJ/mol. Adding this value to the experimental GB(NH_2Cl), we get PA(NH_2Cl) = 797.05 kJ/mol and $\Delta H°_f$ (NH_3Cl^+) = 786.95 kJ/mol from $\Delta H°_f(H^+) = 1531$ kJ/mol and $\Delta H°_f$ (NH_2Cl) = 53 kJ/mol.[23]

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