

Theoretical Enthalpies of Formation of NH_mCl_n : Neutral Molecules, Cations, and AnionsR. K. Milburn, C. F. Rodriguez,[†] and A. C. Hopkinson*

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Ab initio molecular orbital calculations are reported for all neutrals, anions, and cations of the formula NH_m ($m = 1-3$) and for their chlorinated analogues NH_mCl_n ($m + n = 1, 2$, or 3). Structures were optimized using gradient techniques at HF/6-31++G(d,p) and at MP2(full)/6-311++G(d,p). Single-point calculations are reported at MP4SDTQ(fc)/6-311++G(2df,p) and at QCISD(T)(full)/6-311++G(2df,p) levels using geometries optimized at MP2. Standard enthalpies of formation have been calculated at MP4SDTQ(fc)/6-311++G(2df,p) and at QCISD(T)(full)/6-311++G(2df,p) and, where possible, are compared to experimental and previous theoretical results. These same two levels of theory give adiabatic ionization energies that are within ± 0.12 eV of experimental values and proton affinities for neutrals and anions that are within at least 3 kcal mol⁻¹ of experimental values. Electron affinities, anchored on the experimental value of NH, are reported at MP4 and QCI for NCl, NH₂, NHCl, and NCl₂.

Introduction

There are few experimental thermochemical and structural data on chloramines and on chloroamidogens and chloronitrene. Some structural information is available for the amines; for example, NH₂Cl, NHCl₂, and NCl₃ have each been subjected to microwave structure determinations,¹⁻³ but there are few reliable thermodynamic data on these molecules. NCl₂ was first observed in flash photolysis experiments⁴ on NCl₃ and was subsequently generated by the reaction of Cl with NCl₃ in a microwave discharge.⁵ Its bond angle has been estimated to be $111 \pm 4^\circ$ from infrared spectra on solid matrices in which NCl₂ was trapped.⁶ NCl is also formed in the photolysis⁷ of NCl₃, and there has been considerable interest recently in using the ¹Δ excited state of NCl to pump an I* laser.⁸⁻¹⁰ The bond length of NCl in its ³Σ⁻ ground state has been established to be 1.0107 Å from microwave spectroscopy.¹¹

There have been several theoretical studies of NCl_m compounds.¹²⁻²² NCl₂ has been shown to have a ²B₁ ground state, but there are four other states within 4 eV.¹⁷ Nitrenes, NX, have triplet ground states, and for X = H, the lowest singlet state is estimated to be 36 kcal mol⁻¹ higher.²³ Configuration interaction calculations found the triplet-singlet difference to be 41 kcal mol⁻¹ for NH.²⁴ NCl has been studied by a variety of high-level molecular orbital techniques, including MCSCF,¹² multireference CI,¹³ MP4SDTQ and full CI,¹⁷ and CEPA-1 and CASSCF calculations.¹⁴ All the theoretical studies estimate the dissociation energy of NCl to be around 60 kcal mol⁻¹, and these compare with experimental values of 80 ± 2 kcal mol⁻¹^{25a} and more recently 75.8 kcal mol⁻¹.^{25b-d} All the experimental values are based on an estimate of the enthalpy of the reaction of N₃ with Cl established by measuring the chemiluminescence energy of the excited NCl formed in this reaction.

High-level *ab initio* molecular orbital theory has been used to calculate the total atomization energies of molecules, and combining these with experimental enthalpies of formation for the atoms²⁶ provides enthalpies of formation for the molecules that are within at least ± 3 kcal mol⁻¹ of experimental values. For molecules containing only single bonds, the agreement is usually much better.²⁷⁻³⁵ Recently, using QCISD(T)(full)/6-

311G(2df,p)/QCISD(full)/6-311G(d,p) and MP4SDTQ(full)/6-311G(2df,p)/MP2(full)/6-311G(d,p) calculations, we have established and validated reliable thermochemical properties for a series of CH_mCl_n molecules and related cations.³⁵ Here we apply similar levels of theory to the calculation of structural parameters and standard enthalpies of formation of molecules and ions with the general formulas NH_mCl_n ($n = 0-3$ and $n + m = 1-3$). These data then are used in the determination of proton affinities of the neutral molecules and anions and in evaluating ionization energies and electron affinities of the neutral molecules.

Computational Details

Standard *ab initio* molecular orbital calculations were carried out using the Gaussian 90,³⁶ Gaussian 92, and Gaussian 94 programs.^{37,38} Geometries were optimized using gradient techniques^{39,40} at two levels, HF/6-31++G(d,p) and MP2(full)/6-31++G(d,p),⁴¹⁻⁴⁴ for all molecules and ions studied. At both levels of theory, the optimized structures were characterized by harmonic frequency calculations to be at minima (that is, they have no imaginary frequencies). The frequency calculations also yielded both zero-point energies and the thermal corrections required to calculate enthalpies at 298 K. The zero-point energies from the harmonic frequency calculations were scaled by a factor of 0.89^{45,46} for the HF-level and by 0.94⁴⁷ for the MP2 calculations. Single-point calculations using fourth-order Møller-Plesset theory^{48,49} and using spin annihilation for radicals⁵⁰ were done with a frozen core, at a 6-311++G(2df,p) basis set with the geometry optimized at MP2(full)/6-311++G(d,p). Using Pople's notation, this is denoted as MP4SDTQ-(fc)/6-311++G(2df,p)/MP2(full)/6-311++G(d,p), which we abbreviate to MP4. Similarly, single-point calculations at the QCISD(T) level⁵¹ were performed with a 6-311++G(2df,p) basis set using geometries optimized at the MP2(full)/6-311++G(d,p) level, and we abbreviate this to QCI. The total energies, ground state configurations, and scaled zero-point values from these calculations are given in Table 1. Structural details are illustrated in Figure 1.

Results and Discussion

Structural Details. Where comparisons with experimental data are possible,^{1-3,6,52-57} the structures calculated at the HF/

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TABLE 1: Total Energies (hartrees) and Zero-Point Vibration Energies (kcal mol⁻¹)^a

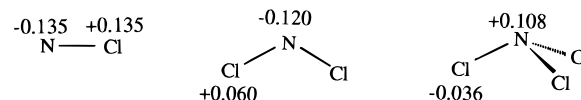
molecule	energies from optimization		single-point at MP2(full)/6-311++G(2df,p) structure	
	HF/6-31++G(d,p) [ZPE] ^b	MP2(full)/6-311++G(2df,p) ^c [ZPE] ^b	MP4 ^d	QCI ^e
NH(³ Σ ⁻)	-54.965 21 [4.5]	-55.112 25 [4.6]	-55.135 06	-55.155 75
NH ₂ (² B ₁)	-55.568 49 [11.4]	-55.758 10 [11.5]	-55.785 29	-55.806 33
NH ₃ (¹ A ₁)	-56.201 15 [20.5]	-56.434 68 [20.6]	-56.462 50	-56.484 12
NCl(³ Σ ⁻)	-513.851 19 [1.1]	-514.208 73 [1.2]	-514.261 27	-514.345 21
NCl ₂ (² B ₁)	-973.297 61 [2.7]	-973.906 58 [2.8]	-973.990 02	-974.135 71
NCl ₃ (¹ A ₁)	-1432.739 51 [5.1]	-1433.597 83 [4.8]	-1433.706 40	
NHCl(² A'')	-514.436 14 [7.5]	-514.831 94 [7.5]	-514.888 05	-514.972 46
NH ₂ Cl(¹ A')	-515.052 44 [16.1]	-515.486 46 [15.9]	-515.541 17	-515.624 83
NHCl ₂ (¹ A')	-973.899 58 [10.9]	-974.542 50 [10.6]	-974.623 71	-974.768 62
NH ⁺ (² Π)	-54.491 91 [4.2]	-54.618 18 [4.3]	-54.639 79	-54.663 07
NH ⁺ (⁴ Σ ⁻)	-54.525 70 [3.7]	-54.632 19 [3.8]	-54.642 60	-54.664 39
NH ₂ ⁺ (³ B ₁)	-55.217 69 [10.2]	-55.362 53 [10.5]	-55.380 05	-55.400 92
NH ₂ ⁺ (¹ A ₁)	-55.135 98 [10.8]	-55.298 36 [10.8]	-55.326 21	-55.351 95
NH ₃ ⁺ (² A ₁)	-55.885 55 [19.6]	-56.070 85 [19.7]	-56.093 74	-56.115 211
NH ₄ ⁺ (¹ A ₁)	-56.546 04 [30.0]	-56.775 07 [29.6]	-56.800 25	-56.822 66
NCl ⁺ (² Π)	-513.437 34 [2.3]	-513.817 25 [2.5]	-513.866 36	-513.948 84
NCl ₂ ⁺ (¹ A ₁)	-972.910 40 [3.1]	-973.548 06 [3.3]	-973.629 30	-973.772 78
NCl ₂ ⁺ (³ B ₁)	-972.872 66 [2.4]	-973.478 93 [2.7]	-973.562 91	-973.709 06
NCl ₃ ⁺ (² A ₁)	-1432.415 88 [5.1]	-1433.252 37 [5.3]	-1433.353 08	
NHCl ⁺ (¹ A')	-514.040 35 [7.7]	-514.453 33 [7.8]	-514.508 65	-514.592 80
NHCl ⁺ (³ A'')	-514.080 17 [7.0]	-514.455 60 [7.5]	-514.504 41	-514.590 15
NH ₂ Cl ⁺ (² B ₁)	-514.732 59 [15.7]	-515.140 38 [15.7]	-515.189 65	-515.274 79
NHCl ₂ ⁺ (² B ₁)	-973.576 11 [10.2]	-974.198 06 [10.5]	-974.272 34	-974.419 46
NH ₃ Cl ⁺ (C _{3v} ,N-prot.)	-515.371 09 [24.6]	-515.806 57 [24.4]	-515.856 21	-515.941 04
NH ₃ Cl ⁺ (C ₁ ,Cl-prot.)	-515.293 58 [21.6]	-515.734 35 [21.8]	-515.786 66	-515.871 74
NH ₂ Cl ₂ ⁺ (C _{2v} ,N-prot.)	-974.198 79 [19.1]	-974.845 85 [18.8]	-974.920 51	-975.067 17
NH ₂ Cl ₂ ⁺ (C ₁ ,Cl-prot.)	-974.126 93 [16.1]	-974.779 73 [16.0]	-974.858 74	-975.005 43
NHCl ₃ ⁺ (C _{3v} ,N-prot.)	-1433.025 23 [13.4]	-1433.888 60 [13.0]		
NHCl ₃ ⁺ (C _s ,Cl-prot.)	-1432.984 77 [9.8]			
NH ⁻ (² Π)	-54.909 27 [4.3]	-55.107 75 [4.4]	-55.137 03	-55.156 56
NH ₂ ⁻ (¹ A ₁)	-55.527 68 [11.0]	-55.774 58 [11.1]	-55.803 15	-55.822 45
NCl ⁻ (² Π)	-513.831 45 [0.7]	-514.217 40 [0.9]	-514.279 87	-514.362 40
NCl ₂ ⁻ (¹ A ₁)	-973.327 39 [2.2]	-973.962 04 [2.5]	-974.054 29	-974.196 87
NHCl ⁻ (¹ A')	-514.435 16 [6.9]	-514.865 69 [7.1]	-514.928 47	-515.010 57

^a Total energies for the smaller atom and molecules used in calculating the atomization energies at MP4SDTQ/6-311++G(2df,p) and at QCISD(T)/6-311++G(2df,p), respectively, are N(⁴P) -54.510 90, -54.531 34; Cl(²P) -459.658 53, -459.719 95; Cl(¹A) -459.776 83, -459.843 32; H(²S) -0.499 82, -0.499 82; H₂(¹Σ_g⁺) -1.167 76, -1.168 37. ^b The HF zero-point energies are scaled by 0.89,^{45,46} and the MP2 zero-point energies are scaled by 0.94.⁴⁷ ^c For open-shell wave functions, PMP2 and PMP4 energies are quoted. ^d MP4 refers to MP4SDTQ(fc)/6-311++G(2df,p)/MP2(full)/6-311++G(d,p). ^e QCI refers to QCISD(T)(full)/6-311++G(2df,p)/MP2(full)/6-311++G(d,p).

6-31++G(d,p) mostly have bond lengths that are too short. The only exceptions to this generalization are the nitrenes, NH and NCl, where the calculated bond distances are too long by 0.023 and 0.049 Å, respectively. The structures calculated at MP2-(full)/6-311++G(d,p) have bond lengths that, in general, are closer to the experimental values than those calculated at HF/6-31++G(d,p). At the MP2 level the largest difference between theory and experiment is for NH and is 0.028 Å. All the N-H distances from the Hartree-Fock calculations are shorter than those from MP2 calculations, but there is no such trend in the N-Cl distances, where approximately half are increased by the inclusion of electron correlation and the remainder are decreased. The largest decrease resulting from inclusion of electron correlation is 0.112 Å in NHCl⁻, the anion with the longest bond. The bond length of 1.816 Å is to be compared with a distance of 1.685 Å in NHCl, indicating that the N-Cl bond is substantially weakened by the addition of an electron to NHCl. Dissociation of NHCl⁻(¹A') into NH(³Σ⁻) and Cl⁻(¹S) is symmetry forbidden and is endothermic by only 7.3 kcal mol⁻¹ using enthalpies of formation calculated at QCI along with the experimental value for Cl⁻. Dissociation into NH(¹Δ) and Cl⁻(¹S) is endothermic by 48.8 kcal mol⁻¹.

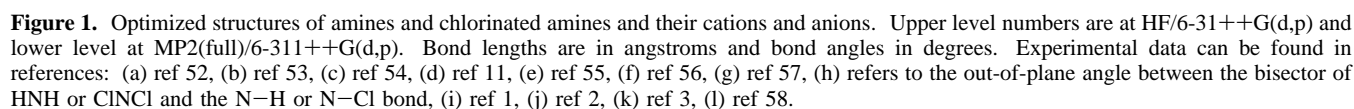
Comparison of molecules NCl_n shows the N-Cl distance to be very sensitive to the coordination number of nitrogen, varying from 1.623 Å in NCl to 1.697 Å in NCl₂ and to 1.767 Å in NCl₃. These distances suggest that there is considerable double-bond character in both NCl and NCl₂. This implies donation of π -electron density from Cl to N, making resonance structure

$\text{N}=\text{Cl}^+$ an important contributor. The charges as obtained from a Mulliken population analysis support this conclusion. In both NCl and NCl₂ the nitrogen carries some negative charge, while in the pyramidal NCl₃ molecule the charge on nitrogen is positive.

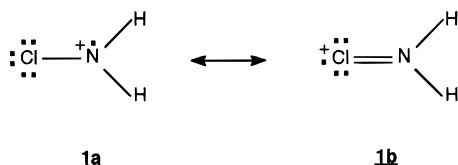


The parent nitrene is isoelectronic with carbene, and both NH and CH₂ have triplet ground states.^{35,58} In the nitrenes, unlike in the carbenes, substitution by chlorine does not lead to a singlet ground state.¹⁷ In nitrenium ions stabilization by Cl becomes more important. Protonation of the parent nitrene, NH(³Σ⁻), leads to nitrenium ion NH₂⁺(³B₁), and this is the ground state, 31 kcal mol⁻¹ below the singlet NH₂⁺(¹A'). Singlet NHCl⁺ is stabilized by π -donation from the lone pair on Cl to the formally vacant p-orbital on N⁺, and while the triplet has lower energy at Hartree-Fock and MP2 levels, the MP4 and QCI calculations favor the singlet (by 2.4 and 1.4 kcal mol⁻¹, respectively). Additional substitution by chlorine leads to further stabilization, and NCl₂⁺(¹A') is lower than the ³B₁ state at all levels of theory, with the difference (41 kcal mol⁻¹) being largest at MP4.

Protonation of amidogens, NH₂, NHCl, and NCl₂, results in planar radical cations. The structural changes accompanying



protonation are increases in bond angles from 103–112° to ~120°, slight decreases in N–H distances, and large decreases in N–Cl distances (0.108 Å on protonation of NHCl and 0.075 Å on protonation of NCl₂). Ions NH_mCl_n⁺ ($n + m = 3$) are also produced by removal of an electron from the chloramines. Comparison of the structures of the amines and the cations shows the N–Cl bond to be much shorter in the cations (by 0.168 Å when $m = 1$, by 0.130 Å when $m = 2$ and by 0.116 Å when $m = 3$). The shorter N–Cl bond lengths in the cations are consistent with delocalization of some of the positive charge onto the chlorine, as shown in resonance structure **1b**. Com-



parison of the charges from a Mulliken population analysis supports this conclusion. The increase in positive charge on the chlorine atom on removing an electron from NH₂Cl is 0.438, while on protonation of NHCl the increase is 0.579.

Protonation of the chloramines on nitrogen also results in a shortening of the N–Cl bonds and a lengthening of the N–H bonds, both by approximately the same small amount. The largest changes (both 0.017 Å) occur in the protonation of NH₂Cl (N–H lengthening) and of NCl₃. Chloramines can also undergo protonation at chlorine, and we have located high-energy minima for H₂NClH⁺, H(Cl)NClH⁺, and Cl₂NClH⁺, ions in which the proton is attached to a chlorine atom. The N–Cl⁺ distances in these three molecules differ greatly. In H₂NClH⁺ the N–Cl distance of 1.722 Å is shorter than that in NH₂Cl (1.745 Å), and the energy required to dissociate the ion into NH₂⁺ + HCl is 83.3 kcal mol^{−1} (at MP4). The N–Cl⁺ distance in H(Cl)NClH⁺ is sensitive to the level of theory used in the optimization, but the value obtained from the MP2 optimization (1.853 Å) is considerably longer than that in NHCl₂ (1.752 Å). The dissociation energy for this bond is small (16.2 kcal mol^{−1} at MP4). Finally, chlorine-protonated NCl₃ was investigated only at the Hartree–Fock level, as the N–Cl⁺ distance of 3.399 Å indicates that the bond has been broken and that the ion at the minimum is NCl₂⁺ solvated by HCl. At this relatively low level of theory the dissociation energy of NCl₂⁺⋯HCl is 3.7 kcal mol^{−1}.

Standard Enthalpies of Formation. The method used to calculate standard enthalpies of formation has been described in detail previously,³¹ but briefly the procedure was as follows. The atomization energy for a molecule was calculated from *ab initio* molecular orbital energies using an isogyric reaction involving H atoms and H₂ to balance the spins²⁷ and then compensating for the addition of H atoms by using the experimental *D*_e for H₂.⁵⁹ The theoretical atomization energy at 0 K was then combined with the experimental enthalpies of formation for the constituent atoms⁶⁰ to give Δ*H*_{f,0}^o. This was then converted into Δ*H*_{f,298}^o by using standard heat capacities for the elements⁶¹ and theoretical thermal corrections for the molecule. Ions were treated in an identical way but with an electron being added into the atomization reaction. The stationary electron convention was used.

There is good agreement between the enthalpies of formation as calculated at MP4 and at QCI (Table 2). The largest disagreement (3.4 kcal mol^{−1}) is for NH⁺(⁴Σ[−]), and here the QCI result appears to be the more reliable, as the MP4 calculation gives the incorrect order for the relative stabilities of the two states of NH⁺.⁶² The only other disagreement above

2 kcal mol^{−1} is for NH₂⁺(¹A'), where the difference is 2.5 kcal mol^{−1}. The good agreement between the enthalpies calculated at two different levels of theory, coupled with our previous finding that similar levels of theory gave enthalpies of formation of CH_mCl_n molecules within ±3 kcal mol^{−1} of experimental values, encourages us to believe that the values given in Table 2 are also within ±3 kcal mol^{−1} of the correct value. There are solidly established experimental enthalpies of formation only for the NH_m molecules,²⁶ and comparison of the calculated values listed in Table 2 shows that for all species except NH₂[−] there is agreement to within ±2 kcal mol^{−1}.

There are no reliable experimental Δ*H*_{f,298}^o values for any of the NH_mCl_n species, but estimates for six of these molecules, the three chloroammonia molecules NH₂Cl, NHCl₂, and NCl₃ and the cations formed by the removal of an electron from these amines, were included in the Lias compilation.²⁶ There is good agreement between the calculated and estimated values for NH₂Cl and NHCl₂⁺, but the estimated enthalpies of formation of NHCl₂ and NCl₃ are higher than the calculated values by 5.1 and 11.8 kcal mol^{−1}, respectively. For the cations the difference between the calculated and estimated values is even higher, 11.7 kcal mol^{−1} for NHCl₂⁺ and 18.6 kcal mol^{−1} for NCl₃⁺. By contrast, estimates of enthalpies of formation for NCl and NCl₂^{25b–d} are lower than the calculated values by 5.2 and 3.2 kcal mol^{−1}, respectively.

From the enthalpies of formation in Table 2, it is possible to draw some general conclusion about the effect of chlorine substitution on bond energies. Bond energies calculated at QCISDTQ(fc)/6-311++G(2df,p)//MP2(full)/6-311++G(d,p) are given in Table 3. In all the neutral molecules containing both H and Cl, the N–H bond has a higher dissociation energy than the N–Cl bond. Using the results of the QCI calculations, combined with experimental enthalpies of formation for the atoms,²⁶ the bond energy of the diatomic chloronitrene, NCl, is calculated to be 62.8 kcal mol^{−1}, and this is smaller than that calculated for NH (78.2 kcal mol^{−1}). The N–Cl bond energy of 62.8 kcal mol^{−1} compares with an estimated value for *D*₀(N–Cl) of 75.8 kcal mol^{−1}.^{25b–d} This latter estimate, however, has been questioned and, in light of a subsequent theoretical value for *D*₀(N–Cl),¹³ has been modified to 67.1 ± 6 kcal mol^{−1}.^{25d}

Along the series NH, NH₂, and NH₃ the N–H bond energies increase by increments of 14.3 and 15.2 kcal mol^{−1}. By contrast, along the series NCl, NCl₂, and NCl₃ the N–Cl bond energies decrease by 16.2 and 7.5 kcal mol^{−1}. For the ammonia molecules, the relative N–H bond energies are NH₃ > NH₂Cl > NHCl₂, with the decrease between the first two being 15.4 kcal mol^{−1} and between the last two 11.5 kcal mol^{−1}. The N–Cl bonds exhibit similar behavior, with the bond energy order being NH₂Cl > NHCl₂ > NCl₃, with each additional chlorine resulting in a decrease in the N–Cl bond by ~12 kcal mol^{−1}. Similarly the N–H in NH₂ (92.5 kcal mol^{−1}) is larger than that in NHCl (77.9 kcal mol^{−1}), whereas the N–Cl in NHCl (62.5 kcal mol^{−1}) is larger than that of NCl₂ (46.6 kcal mol^{−1}).

The bond energies of cations NH_m⁺ are larger than those of the neutral molecules, reflecting the stabilization of the ion resulting from charge delocalization over a large number of atoms. This stabilization is also reflected in the order of the N–H bond energies, NH₂⁺ > NH₃⁺ > NH₄⁺, being the reverse of that in the neutral NH_m molecules. Chlorine is more effective than hydrogen at delocalizing the positive charge, and in the NCl_n⁺ ions ($n = 2$ and 3) the N–Cl bond energies of 69.0 kcal mol^{−1} ($n = 2$) and 39.6 kcal mol^{−1} ($n = 3$ and assuming formation of NCl₂⁺ in its ¹A₁ state), while larger than those of the neutral molecules, are small compared with the bond

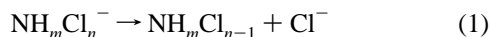
TABLE 2: Calculated and Experimental Standard Enthalpies of Formation ($\Delta H^\circ_{f,298}$) in kcal mol⁻¹

molecule	MP4 ^a	QCI ^b	experimental [theory]
$\text{NH}(\text{}^3\Sigma^-)$	86.7	86.9	84.0, ^c 90.0 \pm 4, ^d [87.0], ^e [86.9] ^f
$\text{NH}_2(\text{}^2\text{B}_1)$	46.1	46.5	45.5 \pm 1.5, ^{g,h} [46.1], ^e [45.8], ^f [45.5] ^p
$\text{NH}_3(\text{}^1\text{A}_1)$	-9.5	-9.1	-10.97 \pm 0.1, ^g [-11.0], ^e [-10.8], ^f [-9.7] ^p
$\text{NCl}(\text{}^3\Sigma^-)$	80.7	79.2	65.3 est., ^q 74 est., ^s [76] ^r
$\text{NCl}_2(\text{}^2\text{B}_1)$	62.3	61.6	58.4 est. ^q
$\text{NCl}_3(\text{}^1\text{A}_1)$	52.2		64.0 est. ^g
$\text{NHCl}(2\text{A}''')$	54.2	53.4	
$\text{NH}_2\text{Cl}(\text{}^1\text{A}')$	13.2	13.2	13.0 est. ^g
$\text{NHCl}_2(\text{}^1\text{A}')$	32.8	32.9	38.0 est. ^g
$\text{NH}^+(\text{}^2\Pi)$	397.2	395.8	394.0 \pm 1, ⁱ [399.2] ^j
$\text{NH}^+(\text{}^4\Sigma^-)$	395.1	398.5	
$\text{NH}_2^+(\text{}^3\text{B}_1)$	303.4	303.5	300.5, ⁱ [305.6] ^j
$\text{NH}_2^+(\text{}^1\text{A}_1)$	333.6	331.0	
$\text{NH}_3^+(\text{}^2\text{A}_1)$	225.0	225.1	223.6, ⁱ 224.5, ^k [226.6], ^j [225.4] ^p
$\text{NH}_4^+(\text{}^1\text{A}_1)$	152.0	151.9	152.5, ^k \sim 151, ^l [152.4], ^j [152.7] ^p
$\text{NCl}^+(\text{}^2\Pi)$	329.8	329.7	
$\text{NCl}_2^+(\text{}^1\text{A}_1)$	289.0	289.7	
$\text{NCl}_2^+(\text{}^3\text{B}_1)$	334.1	332.8	
$\text{NCl}_3^+(\text{}^2\text{A}_1)$	278.4		297.0 est. ^g
$\text{NHCl}^+(\text{}^1\text{A}')$	292.6	292.6	
$\text{NHCl}^+(\text{}^3\text{A}''')$	298.9	296.8	
$\text{NH}_2\text{Cl}^+(\text{}^2\text{B}_1)$	237.5	236.2	240.0 est. ^g
$\text{NHCl}_2^+(\text{}^2\text{B}_1)$	257.3	255.6	269.0 est. ^g
$\text{NH}_3\text{Cl}^+(\text{}^3\text{B}_1, \text{N-prot.})$	188.2	187.5	
$\text{NH}_3\text{Cl}^+(\text{}^1\text{A}_1, \text{Cl-prot.})$	229.2	228.6	
$\text{NH}_2\text{Cl}_2^+(\text{}^2\text{B}_1, \text{N-prot.})$	219.1	218.0	
$\text{NH}_2\text{Cl}_2^+(\text{}^3\text{B}_1, \text{Cl-prot.})$	254.9	253.9	
$\text{NHCl}_3^+(\text{}^2\text{A}_1, \text{N-prot.})$	245.2 ^m		
$\text{NH}^-(\text{}^2\Pi)$	81.3	82.6	81.26 \pm 5, ⁿ [79.3] ^p
$\text{NH}_2^-(\text{}^1\text{A}_1)$	30.7	32.5	27.01 \pm 1, ^o [27.7] ^p
$\text{NCl}^-(\text{}^2\Pi)$	64.7	65.0	
$\text{NCl}_2^-(\text{}^1\text{A}_1)$	17.8	19.4	
$\text{NHCl}^-(\text{}^1\text{A}')$	24.3	25.3	

^a MP4 refers to MP4SDTQ(fc)/6-311++G(2df,p)/MP2(full)/6-311++G(d,p). ^b QCI refers to QCISD(T)(full)/6-311++G(2df,p)/MP2(full)/6-311++G(d,p). ^c Cornford, A. B.; Frost, D. C.; Herring, G.; McDowell, C. A. *J. Chem. Phys.* **1971**, *54*, 1872. ^d Kaskan, W. E.; Nadler, M. P. *J. Chem. Phys.* **1972**, *56*, 2220. ^e Melius, C. F.; Ho, P. *J. Phys. Chem.* **1991**, *95*, 1410. ^f Reference 27a. ^g Reference 60. ^h Lide, D. R. *JANAF Thermochemical Tables* (Supplement) *J. Phys. Chem. Ref. Data* **1985**, *14*. ⁱ Baumgärtel, H.; Jochims, H. W.; Rühl, E.; Bock, H.; Dammel, R.; Minkwitz, J.; Nass, R. *Inorg. Chem.* **1989**, *28*, 943. ^j Reference 27c. ^k Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695. ^l Reference 26. ^m Calculations done at MP2(full)/6-311++G(d,p). ⁿ Reference 54. ^o MacKay, G. J.; Hemsworth, R. S.; Bohme, D. K. *Can. J. Chem.* **1976**, *54*, 1624. ^p Yu, D.; Rauk, A.; Armstrong, D. A. *Can. J. Chem.* **1994**, *72*, 417. ^q Reference 25b. ^r Reference 13. ^s Reference 25d.

energies of the NH_m^+ ions. In all positive ions containing both hydrogen and chlorine, as in the neutral molecules, the N-Cl bonds are weaker than the N-H bonds except in NHCl^+ , where the N-Cl bond energy of 132.2 kcal mol⁻¹ is much larger than that in any other NH_mCl_n molecule or ion and is larger than the N-H bond energy (89.2 kcal mol⁻¹) in the same ion. We attribute the anomalously high N-Cl bond energy in both NHCl^+ and in NCl^+ to the ability of chlorine to carry a large fraction of the positive charge.

Homolytic breaking of the N-Cl bond of anions NH_mCl_n^- produces chlorine atoms and leaves the negative charge on the N-containing fragment. The energies for these reactions, given in Table 3, are larger than those in neutral NH_mCl_n molecules.



The thermodynamically most favorable dissociation paths for NH_mCl_n^- ions involves the loss of Cl^- . For all three Cl^- -containing anions examined here, heterolytic dissociation to form Cl^- leaves the remaining $\text{NH}_m\text{Cl}_{n-1}$ neutral molecules in excited states. For the bond-breaking reaction in eq 1, ΔH_f values as calculated at QCI are for NCl^- 53.1 kcal mol⁻¹, for NHCl^- 48.8 kcal mol⁻¹, and for NCl_2^- 37.5 kcal mol⁻¹. However, if the product molecules are allowed to relax to their ground electronic states, the energies for reaction 1 are lowered substantially. For NCl^- , dissociation into $\text{N}(\text{}^4\text{S})$ and $\text{Cl}^-(\text{}^1\text{S})$ is calculated to be exothermic by 6.3 kcal mol⁻¹, while heterolytic

TABLE 3: Bond Energies (kcal mol⁻¹) for Homolytic Fission of N-X Bonds from QCI Calculations

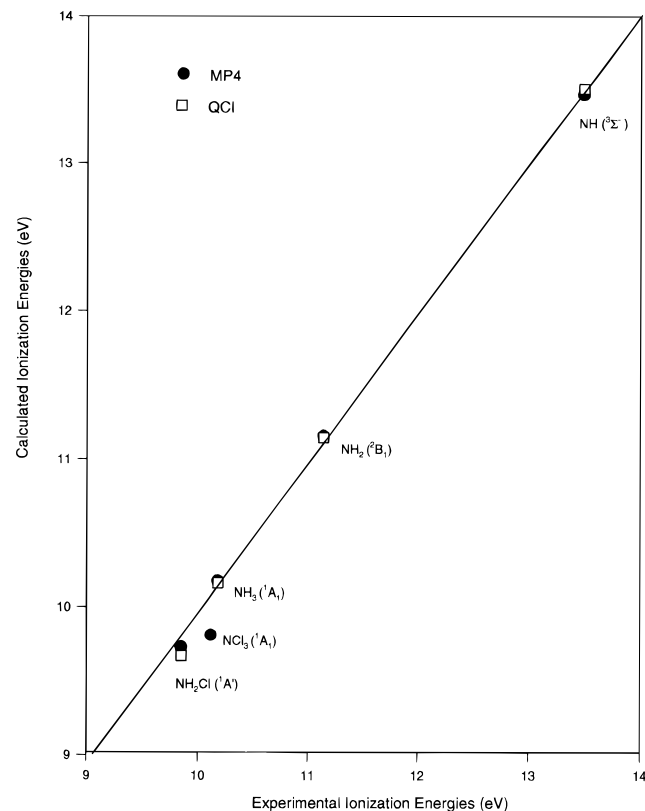
molecule or ion	neutral molecules		cations		anions	
	N-H	N-Cl	N-H	N-Cl	N-H	N-Cl
NH	78.2		104.5		84.1	
NH ₂	92.5		147.1		102.2	
NH ₃	107.7		130.5			
NH ₄			125.3			
NCl		62.8		147.5		78.6 ^a
NCl ₂		46.6		69.0		74.6 ^b
NCl ₃		39.1 ^c		84.7 ^d		
NHCl	77.9	62.5	89.2	132.2	91.8	86.3 ^e
NH ₂ Cl	92.3	62.3	112.7	96.3		
NH ₃ Cl			100.8	66.6		
NHCl ₂	80.8	49.5	129.3 ^f	70.2 ^g		

^a Derived from the electron affinity of N (-0.07 eV).⁶⁵ Formation of $\text{N}(\text{}^4\text{S})$ and $\text{Cl}^-(\text{}^1\text{S})$ is exothermic by 6.3 kcal mol⁻¹, but the formation of these products requires heterolytic dissociation followed by quenching of the initially formed $\text{N}(\text{}^2\text{P})$. ^b Formation of $\text{NCl}(\text{}^3\Sigma^-)$ and $\text{Cl}^-(\text{}^1\text{S})$ is endothermic by 5.5 kcal mol⁻¹, but the formation of these products requires heterolytic dissociation followed by quenching of the initially formed $\text{NCl}(\text{}^1\Delta)$. ^c At MP4SDTQ(fc)/6-311++G(2df,p)/MP2(full)/6-311++G(d,p). ^d Assuming formation of $^3\text{B}_1$ state of NCl_2^+ . If the ground state $^1\text{A}_1$ of NCl_2^+ is formed, then the bond energy is 39.6 kcal mol⁻¹. ^e Heterolytic cleavage followed by quenching of the initially formed $\text{NH}(\text{}^1\Delta)$ state to give the ground state products $\text{NH}(\text{}^3\Sigma^-)$ and $\text{Cl}^-(\text{}^1\text{S})$ is endothermic by only 7.3 kcal mol⁻¹. ^f Assumes formation of NCl_2^+ in the excited $^3\text{B}_1$ state. The reaction $\text{NHCl}_2^+(\text{}^2\text{B}_1) \rightarrow \text{NCl}_2^+(\text{}^1\text{A}_1) + \text{H}(\text{}^2\text{S})$ has $\Delta H_f = 86.2$ kcal mol⁻¹. ^g Assumes formation of NHCl^+ in the excited $^3\text{A}''$ state. The reaction $\text{NHCl}_2^+(\text{}^2\text{B}_1) \rightarrow \text{NHCl}^+(\text{}^1\text{A}') + \text{Cl}(\text{}^2\text{P})$ has $\Delta H_f = 66$ kcal mol⁻¹.

TABLE 4: Calculated and Experimental Adiabatic Ionization Energies (in eV)

molecule	MP4 ^a	QCI ^b	experiment [theory]
NH(³ Σ ⁻)	13.47, ^c 13.37 ^d	13.40, ^c 13.51 ^d	13.49 ± 0.01, ^e [13.49] ^f
NH ₂ (² B ₁)	11.16	11.15	11.14 ± 0.01, ^g [11.26] ^f
NH ₃ (¹ A ₁)	10.17	10.16	10.18 ± 0.01, ^h [10.28], ^f [10.19] ⁱ
NCl(³ Σ ⁻)	10.80	10.86	
NCl ₂ (² B ₁)	9.84	9.90	
NCl ₃ (¹ A ₁)	9.81		10.12 est. ^h
NHCl(² A'')	10.34, ^j 10.61 ^k	10.37, ^j 10.56 ^k	
NH ₂ Cl(¹ A')	9.73	9.67	9.85 est. ^h
NHCl ₂ (¹ A')	9.74	9.66	

^a MP4 refers to MP4SDTQ(fc)/6-311++G(2df,p)//MP2(full)/6-311++G(d,p). ^b QCI refers to QCISD(T)(full)/6-311++G(2df,p)//MP2(full)/6-311++G(d,p). ^c For formation of the ²Π state. ^d For formation of the ⁴Σ⁻ state. ^e Dunlavey, S. J.; Dyke, J. M.; Jonathan, N.; Morris, A. *Mol. Phys.* **1980**, 39, 1121. ^f Reference 27c. ^g Gibson, S. T.; Greene, J. P.; Berkowitz, J. *J. Chem. Phys.* **1985**, 83, 4319. ^h Reference 26. ⁱ Calculated by Yu, D.; Rauk, A.; Armstrong, D. A. *Can. J. Chem.* **1994**, 72, 471, using the G2 data in ref 29. ^j For formation of ¹A'. ^k For formation of ³A'.

**Figure 2.** Plot of calculated ionization energy (in eV) against experimental values.

N–Cl breaking in NHCl⁻ (to form NH(³Σ⁻)) is endothermic by 5.5 kcal mol⁻¹ and in NCl₂⁻ is endothermic by 7.3 kcal mol⁻¹.

Ionization Energies. The adiabatic ionization energy of a molecule is defined as the standard enthalpy change in reaction 2, assuming that the cation is allowed to relax to its optimum structure. There is good agreement between the ionization



energies calculated at QCI and MP4, with the largest difference being 0.08 eV for NHCl₂ (Table 4). The calculated ionization energies are in excellent agreement with the experimental values for the NH_m molecules, but for NCl₃ and NH₂Cl, molecules for which there are only estimated experimental ionization energies, the calculated values are lower (Figure 2).

The relative magnitude of the ionization energies is dictated by the ability of the cation to delocalize the positive charge, an ability that increases with the coordination number of the nitrogen atom and also when hydrogen is replaced by chlorine.

TABLE 5: Calculated and Experimental Proton Affinities (in kcal mol⁻¹)

molecule	MP4 ^a	QCI ^b	experimental [theory]
N(⁴ S)	79.7 ^c	80.6 ^c	
NH(³ Σ ⁻)	149.0	149.1	
NH ₂ (² B ₁)	186.9	187.0	186.2 ± 2, ^d [186.6] ^e
NH ₃ (¹ A ₁)	204.4	204.9	203.5 ± 0.8, ^f [204.0], ^{g,hi} [204.1] ^e
NCl(³ Σ ⁻)	147.5	148.0	
NCl ₂ (² B ₁)	170.8	171.7	
NCl ₃ (¹ A ₁)	175.6 ⁱ		
NHCl(² A'')	182.4	182.9	
NH ₂ Cl(¹ A')	190.7	191.4	
NHCl ₂ (¹ A')	179.4	180.5	
NH ⁻ (² Π)	400.9	401.8	403.7 ± 1, ^k [405.9], ^l [400.1] ^e
NH ₂ ⁻ (¹ A ₁)	405.7	407.2	405.13, ^k [412.4], ^l [403.9] ^e
NCl ⁻ (² Π)	376.3	377.5	
NCl ₂ ⁻ (¹ A ₁)	350.9	352.4	
NHCl ⁻ (¹ A')	376.6	377.5	

^a MP4 refers to MP4SDTQ(fc)/6-311++G(2df,p)//MP2(full)/6-311++G(d,p). ^b QCI refers to QCISD(T)(full)/6-311++G(2df,p)//MP2(full)/6-311++G(d,p). ^c For formation of NH(⁴Σ⁻). ^d DeFrees, D. J.; Hehre, W. J.; McIver, R. T.; McDaniel, D. H. *J. Phys. Chem.* **1979**, 83, 232. ^e Yu, D.; Rauk, A.; Armstrong, D. A. *Can. J. Chem.* **1994**, 72, 471, using the G2 data in ref 29. ^f Reference 63. ^g Reference 27b. ^h DeFrees, D. J.; McLean, A. D. *J. Comput. Chem.* **1986**, 7, 321. ⁱ Reference 29. ^j Calculations done at MP2(full)/6-311++G(d,p). ^k Reference 26. ^l Pople, J. A.; Schleyer, P. v. R.; Kanet, J.; Spitznagel, G. W. *Chem. Phys. Lett.* **1988**, 145, 359.

For example, along the NH_m series, the ionization energies are 14.53 eV for N, 13.40 eV for NH, 11.15 eV for NH₂, and 10.16 eV for NH₃ (all numbers from the QCI calculations). NCl_m molecules all have lower ionization energies than the NH_m molecules with the same coordination number *m*, with the difference being largest when *m* = 1 (2.54 eV) and the smallest when *m* = 3 (0.36 eV). These differences indicate that chlorine is most stabilizing in NCl⁺ and least stabilizing in NCl₃⁺, a conclusion that is consistent with the structural changes discussed previously for the NCl_m⁺ ions.

Proton Affinities. The proton affinity of a molecule B is defined as the enthalpy change for the reaction in eq 3.



Calculated proton affinities for the neutral molecules and anions are given in Table 5, along with experimental and other theoretical values. In a recent study⁶³ the proton affinity of ammonia was evaluated to be 203.5 ± 0.8 kcal mol⁻¹, and our calculated values of 204.4 kcal mol⁻¹ at MP4 and 204.9 kcal mol⁻¹ at QCI are in good agreement with this value.

The proton affinity of NH_m molecules increases with *m*, with the differences in proton affinities becoming smaller as the number of H atoms increases (Table 4). These changes are attributed to an increase in the number of H atoms over which

TABLE 6: Calculated and Experimental Electron Affinities (in eV)

molecule	direct QCI ^a	relative to $\text{NH}^- \rightarrow \text{NH} + \text{e}^-$		experimental [theory]
		MP4 ^b	QCI ^a	
$\text{NH}(\Sigma^-)$	0.18	(0.370)	(0.370)	0.381 ± 0.014 , ^c 0.370 ± 0.004 , ^d [0.29], ^e [0.338] ^h
$\text{NH}_2(^2\text{B}_1)$	0.59	0.77	0.80	0.779 ± 0.037 , ^f 0.744 ± 0.022 , ^c [0.68], ^g [0.77], ^e [0.763], ^h [0.773] ⁱ
$\text{NCl}(\Sigma^-)$	0.60	0.78	0.79	
$\text{NCl}_2(^2\text{B}_1)$	1.82	2.03	2.03	
$\text{NHCl}(^2\text{A}')$	1.19	1.38	1.39	

^a QCI refers to QCISD(T)(full)/6-311++G(2df,p)//MP2(full)/6-311++G(d,p). ^b MP4 refers to MP4SDTQ(fc)/6-311++G(2df,p)//MP2(full)/6-311++G(d,p). ^c Mead, R. D.; Stevens, A. E.; Lineberger, W. C. *Gas Phase Ion Chemistry*; Academic Press: New York, 1984. ^d Reference 64. ^e Pople, J. A.; Schleyer, P. v. R.; Kanetti, J.; Spitznagel, G. W. *Chem. Phys. Lett.* **1988**, 145, 359. ^f Celotta, R. J.; Bennett, R. A.; Hall, J. L. *J. Chem. Phys.* **1974**, 60, 1740. ^g Baker, J.; Nobes, R. H.; Radom, L. *J. Comput. Chem.* **1986**, 7, 349. ^h Montgomery, J. A.; Ochterski, J. W.; Peterson, G. A. *J. Chem. Phys.* **1994**, 101, 5900. ⁱ Calculated by Yu, D.; Rauk, A.; Armstrong, D. A. *Can. J. Chem.* **1994**, 72, 471, using the G2 data from ref 29.

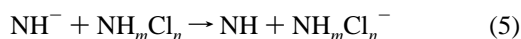
the positive charge is spread. The proton affinities of NCl_m exhibit the same trend, although the proton affinity of each NCl_m molecule is always lower than that of the NH_m molecule with the same coordination number. These changes are largest in the chloramines NH_mCl_n ($m + n = 3$), where one chlorine substituent reduces the proton affinity by 13.5 kcal mol⁻¹, the second chlorine by a further 10.9 kcal mol⁻¹, and the third by 4.9 kcal mol⁻¹. These decreases indicate that σ -electron withdrawal by chlorine reduces the basicity of the chloroamines. Substitution by chlorine also reduces the basicity of the less saturated NCl_m molecules ($m = 1$ and 2), although here the effect is smaller due to the stabilization of the cation by π -donation from the chlorine.

Chloro-substituents reduce the proton affinities of the anions, and the effect is much larger than in the neutral compounds. From the limited data in Table 5, the proton affinity of NCl^- is lower than that of NH^- by 24.3 kcal mol⁻¹. Similarly, the proton affinity of NHCl^- is lower than that of NH_2^- by 29.7 kcal mol⁻¹, while the proton affinity of NCl_2^- is lower than that of NHCl^- by 25.1 kcal mol⁻¹. In these anions, then, each chlorine substituent reduces the proton affinity by ~25–30 kcal mol⁻¹, and this is attributed to the σ -electron withdrawing ability of chlorine stabilizing the anions.

Electron Affinities. The electron affinity of a molecule is defined as the enthalpy of the reaction in eq 4 at 0 K. Direct



evaluation using molecular orbital calculations generally underestimates electron affinities,^{31b} and using this procedure the QCI calculations in Table 6 gives values ~0.2 eV lower than the experimental values. The electron affinities of NH have recently been determined very accurately by photodetachment,⁶⁴ and we have combined these experimental values with energies from our molecular orbital calculations to obtain the electron affinities for other molecules using the charge transfer reaction in eq 5.



The electron affinities of the NH_mCl_n molecules increase with the coordination number of nitrogen and also when hydrogen is replaced by chlorine. Substitution of hydrogen by chlorine in nitrene, NX, increases the electron affinity by 0.43 eV. Similarly, substitution of one hydrogen of NH_2 results in an increase in electron affinity of 0.59 eV, and substitution of the second hydrogen leads to a further increase of 0.64 eV.

Conclusions

MP4 and QCI calculations give enthalpy of formation values that are generally within ± 2 kcal mol⁻¹ of each other. For the

NH_m molecules, where accurate experimental enthalpies of formation are available, the values calculated at the QCI level are within ± 3 kcal mol⁻¹ of the experimental values, with the exception of that for NH_2^- . Most of the enthalpies of formation for chloramines in the literature are estimated from experimental data and are higher than the calculated values. These differences are generally quite large, with the largest being 18.6 kcal mol⁻¹ for NCl_3^+ . On the basis of the excellent correlation between the theoretical and experimental enthalpies where accurate experimental values are available, it would appear that the calculated values in Table 2 are more reliable than the estimated values.

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