Thermodynamic Calculations for Reactions Involving Hydrogen Halide Polymers, Ions, and Lewis Acid Adducts. 2. Polychlorohydrogenate(1−) Anions (H$_n$Cl$_{n+1}^-$), Polychlorohydrogen(I) Cations (H$_{n+1}$Cl$_n^+$), and Hydrogen Chloride Polymers (HCl)$_n$

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Semiempirical (MNDO, AM1, and PM3) and *ab initio* (HF/3-21+G(d,p), BVWN/3-21+G(d,p), MP2/3-21+G(d,p), HF/6-311+G(d,p), BVWN/6-311+G(d,p), and MP2/6-311+G(d,p)) energy minimization and frequency calculations have been carried out on three hydrogen chloride polymers, (HCl)$_n$, $n = 2-4$ (the semiempirical methods were employed for $n = 5$ and 6 as well); on four polychlorohydrogenate(1−) anions, H$_n$Cl$_{n+1}^-$, $n = 1-4$; and on two polychlorohydrogen(I) cations, H$_{n+1}$Cl$_n^+$, $n = 1$ and 2. From the results, $\Delta G°$, $\Delta H°$, and $\Delta S°$ values have been calculated for a number of reactions involving these species. The thermodynamic data are presented for 21 reactions using calculations at the MP2/6-311+G(d,p) level, along with a comparison of $\Delta G°$ values obtained from all nine molecular orbital methods. ^{1}H NMR shielding data have also been calculated for three species, HCl, HCl$_2^-$, and H$_2$Cl$^+$, using the gauge-independent atomic orbital (GIAO) and the continuous set of gauge transformations (CSGT) methods and density functional techniques with large basis sets.

Introduction

Recent investigations in this laboratory[1] established that the chemistry of HCl added to ambient-temperature ionic liquids,[2] e.g. AlCl$_3$−ImCl (Im$^+$ ≡ 1-ethyl-3-methyl-1*H*-imidazolium),[3] is more complex than previously suggested[4] although actually quite systematic. In HCl−ImCl liquids, the successive addition of HCl to Cl$^-$ takes place with the formation of first HCl$_2^-$ (with an equilibrium formation constant of $\geq 10^5$ L mol^{-1}),[5] then H$_2$Cl$_3^-$,[6] and even some H$_3$Cl$_4^-$. Proton speciation both in HCl−ImCl and in strongly Lewis basic AlCl$_3$−ImCl melts is governed largely by the equilibrium

$$Cl^- + H_2Cl_3^- \rightarrow 2HCl_2^- \qquad (1)$$

with the equilibrium constant ranging from 220 in HCl−ImCl to 100 in an $X_{AlCl_3} = 0.49$ melt. Molecular HCl is not present in these systems, as confirmed by infrared spectroscopy.[5]

Earlier work by Smith *et al.*[7] demonstrated that HCl in Lewis acidic melts ($X_{AlCl_3} > X_{ImCl}$) behaves as a Brønsted superacid, being able to protonate a variety of arenes. This behavior was ascribed merely to the maintenance of low chloride ion activity with the dissolved HCl as the active species. There is no evidence in the literature to support the formation of HAlCl$_4$ or HAl$_2$Cl$_7$. The autosolvolysis of liquid HCl[8] is believed to produce a small concentration of H$_2$Cl$^+$ which, analogous to H$_2$F$^+$,[9] should show superacidic properties. Moreover, the formation of H$_2$Cl$^+$ in Lewis acidic melts was anticipated in the light of H$_2$F$^+$ and H$_3$F$_2^+$ formation in mixtures of HF with the Lewis acid SbF$_5$.[10] To our surprise, HCl was more soluble in Lewis neutral ImAlCl$_4$ than in Lewis acidic AlCl$_3$−ImCl mixtures and, in fact, showed a solubility linear in both HCl partial pressure and melt composition; thus H$_2$Cl$^+$ was not formed but rather 1:1 compounds of HCl with AlCl$_4^-$ and Al$_2$Cl$_7^-$. Evidence favors Al$_2$Cl$_7$·HCl$^-$ over simple HCl as the superacidic entity in the melts.[1]

As the work progressed, it became apparent that theoretical data concerning the stability of many of the lesser-known, as well as the new, species proposed above would be useful. It is now possible to calculate thermodynamic, structural, vibrational, and magnetic properties for hydrogen−chlorine and aluminum−chlorine species with reasonable efficacy and precision. In this paper we report the results of these calculations for the

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hydrogen−chlorine species and their significance to our experimental studies; the work related to the aluminum chlorides and chloroaluminates will be dealt with in a subsequent paper. The approach and reliability of the data have been discussed previously in relation to hydrogen−fluorine species,[9] so that they will only be outlined here. However, we note that calculations based on density functional theory are now possible and so have been added to the repertoire of methods employed.

Some of the considerable body of literature dealing with the synthesis, properties, structure, and *ab initio* energies of some of these ions and polymers, particularly of the fluorine analogs, has been reviewed previously.[9] Of particular interest for the chlorine species being treated in this paper is the experimental work on HCl_2^-,[4bc,11] H_2Cl^+,[11g,j,12] and $(HCl)_n$, $n = 2$ and 3.[13] At the same time, there have been numerous theoretical treatments of structures and energies for HCl_2^-,[11d,14] H_2Cl^+,[14a,e,15] $H_3Cl_2^+$,[14e] and $(HCl)_n$.[11c,14a,16]

Our major interest, as an adjunct to studying melt compositions by various experimental techniques, is to use molecular orbital calculations in estimating thermodynamic data for a number of reactions. These data permit us to predict which hydrogen−chlorine species would be expected to occur in the melts and what their relative concentrations might be. Previous theoretical studies have tended to provide relative energies,

sometimes corrected for zero-point energies, at 0 K (ΔU) for some of the reactions which interest us. However, if theoretical calculations are to be truly helpful in predicting the outcomes of reactions at equilibrium, they should provide $\Delta G°$, $\Delta H°$, and $\Delta S°$. The difference between ΔH at 298 K and ΔU at 0 K, even with zero-point-energy differences taken into account, involves thermal energy (usually small) as well as the term ΔnRT, where Δn is the change in the total number of moles of gas during the reaction (eq 2). This PV work term can be as much as 12 kJ/mol for reactions we are interested in although it more frequently ranges from 2.5 to 5.0 kJ/mol. At the same time, while $T\Delta S$ can be as large as 80 kJ/mol in cluster formations, it is usually found to be less than 30 kJ/mol. Clearly, the ΔE or ΔU values usually reported by theoreticians for reactions, while informative, simply do not provide the most reliable picture of how a chemical change should be viewed under equilibrium conditions.

Our purpose in this paper is to use thermodynamic data obtained from semiempirical and *ab initio* molecular orbital calculations to explore the feasibility of a number of reactions involving polychlorohydrogenate(1−) anions, polychlorohydrogen(I) cations, and small hydrogen chloride polymers.

Calculations

Ab initio and semiempirical calculations were performed using Gaussian 92/DFT and Gaussian 94.[17] Geometries were optimized by using MNDO, AM1, and PM3 semiempirical methods, as well as with 3-21+G(d,p) and 6-311+G(d,p) basis sets at the Hartree−Fock and MP2 *ab initio* levels and BVWN or Becke3LYP density functional approaches. Vibrational frequencies were also calculated using the same methods and basis sets. From the latter calculations, it was possible (a) to determine that a structure represented a true minimum and not a saddle point in the energy surface, (b) to estimate entropies ($S°$) at 298 K, and (c) to obtain zero-point-energy corrections and thermal energies at 298 K and 1 atm pressure. All *ab initio* and density functional energies were corrected for thermal energies, including zero-point vibrations (Hartree−Fock zero point energy values were scaled by 0.90[18] and MP2 values by 0.95[14a]), to give U values at 298 K. The reaction internal energies ($\Delta U°$) were converted to reaction enthalpies ($\Delta H°$) by means of eq 2 which assumes ideal gas behavior for all

$$\Delta H° = \Delta U° + \Delta nRT \qquad (2)$$

species.[19] $\Delta S°$ values were obtained using $S°$'s taken from frequency

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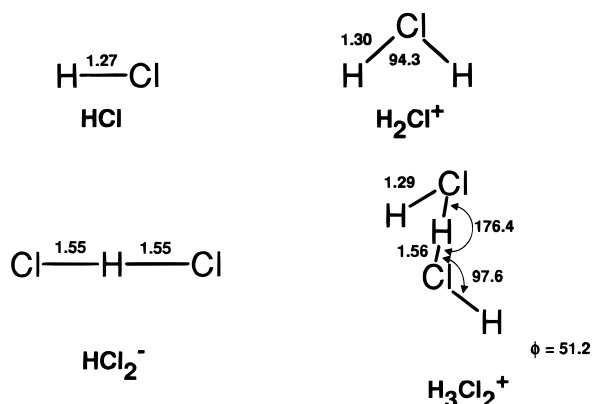
Figure 1. Structures of HCl, the dichlorohydrogenate(1−) anion, and two chlorohydrogen(I) cations determined by MP2/6-311+G(d,p) *ab initio* methods. Bond lengths are in angstroms and angles in degrees.
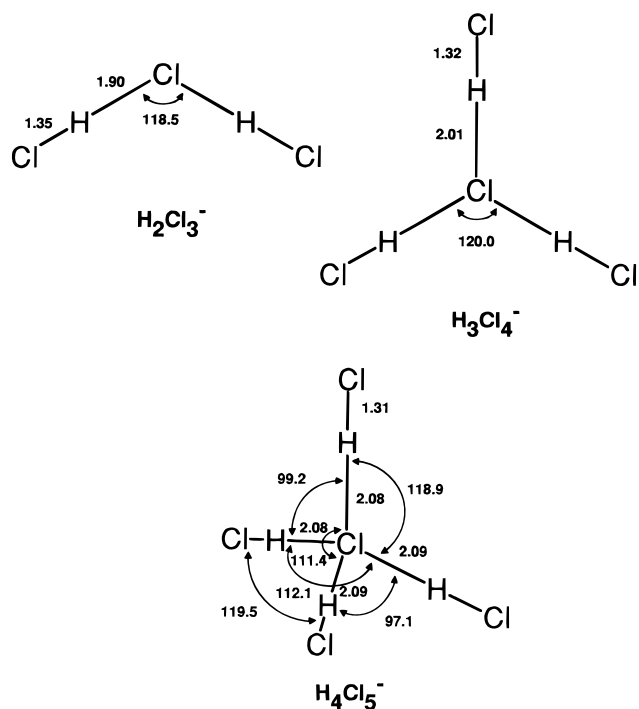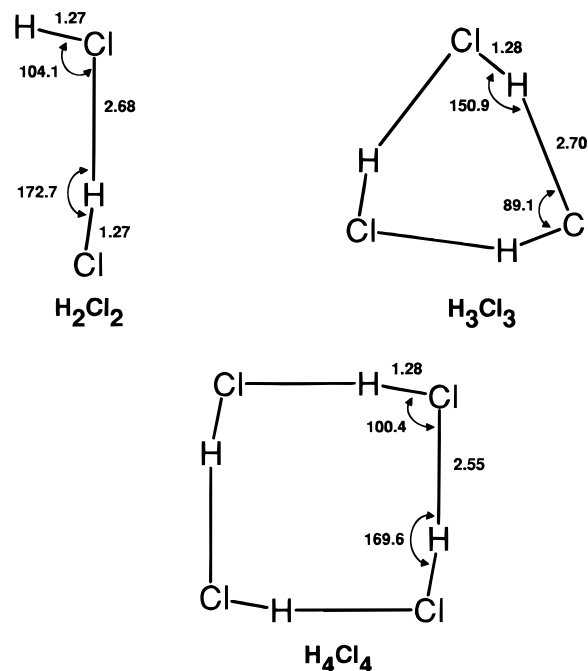

Figure 2. Structures of three chlorohydrogenate(1−) anions determined by MP2/6-311+G(d,p) *ab initio* methods. Bond lengths are in angstroms and angles in degrees.

calculations for polyatomic ions and molecules and employing the Sackur−Tetrode equation for monatomic ions.[19]

^{1}H NMR absolute shielding data and relative chemical shifts were calculated for HCl, HCl_2^-, and H_2Cl^+, using the gauge-independent atomic orbital (GIAO) and the continuous set of gauge transformations (CSGT) methods and density functional techniques (BVWN, Becke3LYP, BPW91, and Becke3PW91) available in Gaussian 94 with large basis sets such as 6-311++G(3df,3pd), AUG-cc-pVTZ, and AUG-cc-pVQZ.

Results

Figures 1−3 provide structures of the species studied as determined by MP2/6-311+G(d,p) optimizations. Structures for some (HCl, HCl_2^-, H_2Cl^+, $H_3Cl_2^+$, H_2Cl_2, and H_3Cl_3) have been presented in the literature previously in some form (*vide supra*), and our results are essentially the same as the most reliable of them. The agreement with experimental data, where the latter are available, is exceptionally good (Table 1[20]). The structures are qualitatively similar to those of the corresponding fluorine

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Figure 3. Structures of three hydrogen chloride polymers determined by MP2/6-311+G(d,p) *ab initio* methods. Bond lengths are in angstroms and angles in degrees.

Table 1. Comparison of Experimental and Calculated Structures

species	parameter	exptl	ref	calcd[b]
HCl	R_{HCl}	1.275	20	1.273
HCl_2^-	R_{ClCl}	3.147	11e	3.100
		3.117	11c	
H_2Cl^+	R_{HCl}	1.304	12b	1.300
	∠HClH	94.24	12b	94.3
H_2Cl_2	dist between centers of mass of two HCl monomers	3.746	13b	3.916
		3.797	13g	
	angles between line connecting the two centers of mass and the two short HCl bands	89.8, 9	13b	78.2, 5.5
		87, 16	13g	

^{a} All lengths are in angstroms, and angles are in degrees. ^{b} Calculated structures were obtained from MP2/6-311+G(d,p) optimizations.

compounds;[9] as *n* increases from 1 to 4 in the anionic series, $H_nCl_{n+1}^-$, the shorter of the HCl bond lengths decreases (1.550, 1.351, 1.323, and 1.309 Å respectively). There is a similar bond length decrease with the two cations studied, $H_{n+1}Cl_n^+$ (1.300 and 1.289 Å). These results indicate that, as ionic species become larger, HCl molecules increasingly act in a solvating capacity around either a Cl^- or a H^+ ion, with less true covalent bonding occurring. The trends are, however, smaller in the chlorine series than for their fluorine counterparts. The XHX bond angle in $H_3Cl_2^+$ is 176.4° as opposed to exactly 180° in $H_3F_2^+$. Another slight difference involves $H_4Cl_5^-$, which does not have the tetrahedral T_d symmetry exhibited by $H_4F_5^-$, the longer HCl bond lengths are not all the same but vary slightly between 2.082 and 2.086 Å. The solvated structures $Cl(HCl)_n^-$ shown in Figure 2 for $H_3Cl_4^-$ and $H_4Cl_5^-$ are about 20 and 40 kJ/mol, respectively, **lower** in energy than the the linear, open structures $ClHClHClHCl^-$ and $ClHClHClHClHCl^-$ when all calculations are done at the MP2/6-311+G(d,p) level.

While it is known that the cyclic H_2Cl_2, with C_{2h} symmetry, is a saddle point and not a minimum in the energy surface,[14,16] the cyclic C_{nh} structures **are** the minima for the other two hydrogen chloride polymers like their hydrogen fluoride counterparts.[14a]

Table 2. Thermodynamic Data Calculated at 298 K for a Number of Reactions Involving H_nCl_n, $H_nCl_{n+1}^-$ and $H_{n+1}Cl_n^+$ Species[a]

	$\Delta H°/$ kJ mol^{-1}	$\Delta S°/$ J mol^{-1}K^{-1}	$\Delta G°/$ kJ mol^{-1}
$HCl \rightarrow Cl^- + H^+$	1406.9	75.7	1384.4
$Cl^- + HCl \rightarrow HCl_2^-$	−103.4	−106.6	−72.5
$H^+ + HCl \rightarrow H_2Cl^+$	−570.2	−89.6	−543.5
$3HCl \rightarrow H_2Cl^+ + HCl_2^-$	733.3	−117.5	768.4
$HCl + HCl_2^- \rightarrow H_2Cl_3^-$	−57.5	−91.8	−30.2
$2HCl_2^- \rightarrow Cl^- + H_2Cl_3^-$	45.9	11.8	42.3
$HCl + H_2Cl^+ \rightarrow H_3Cl_2^+$	−73.8	−113.0	−40.1
$HCl + H_2Cl_3^- \rightarrow H_3Cl_4^-$	−51.9	−102.3	−21.4
$HCl + H_3Cl_4^- \rightarrow H_4Cl_5^-$	−41.8	−69.2	−21.2
$H_2Cl_2 \rightarrow Cl^- + H_2Cl^+$	842.3	53.2	826.5
$H_2Cl_2 \rightarrow H^+ + HCl_2^-$	1309.2	39.1	1297.5
$H_3Cl_3 \rightarrow Cl^- + H_3Cl_2^+$	781.0	51.8	765.6
$H_3Cl_3 \rightarrow H^+ + H_2Cl_3^-$	1264.1	58.9	1246.6
$HCl_2^- \rightarrow H^+ + 2Cl^-$	1510.3	179.3	1456.9
$2HCl \rightarrow H_2Cl_2$	−5.62	−67.0	14.4
$3HCl \rightarrow H_3Cl_3$	−18.1	−178.6	35.1
$4HCl \rightarrow H_4Cl_4$	−30.0	−275.4	52.1
$H^+ + H_2Cl_2 \rightarrow H_3Cl_2^+$	−638.4	−135.5	−598.0
$Cl^- + H_2Cl_2 \rightarrow H_2Cl_3^-$	−155.3	−128.4	−117.0
$Cl^- + H_3Cl_3 \rightarrow H_3Cl_4^-$	−195.8	−97.8	−166.7
$Cl^- + H_4Cl_4 \rightarrow H_4Cl_5^-$	−224.7	−91.5	−197.4

[a] All data were obtained using MP2/6-311+G(d,p) optimizations and frequency determinations.

Structures obtained from the other methods (Hartree−Fock, MP2, density functional, and semiempirical) are qualitatively the same as those shown in Figures 1−3, with the following exceptions:

(i) All HF optimizations of HCl_2^- find a minimum structure with two HCl bonds of **different** lengths. Semiempirical and density functional optimizations, however, agree much more closely with that of MP2/6-311+G(d,p).

(ii) Hartree−Fock optimizations using the 3-21+G(d,p) and 6-311+G(D,p) basis sets suggest that $H_2Cl_3^-$ should be linear.

(iii) For $H_3Cl_2^+$, the semiempirical structures have C_{2h} symmetry like that of $H_3F_2^+$. Both of the MP2 structures and all density functional structures have C_2 symmetry. The dihedral angle formed by two HCl bonds about a central H−Cl is 51.2° (MP2/6-311+G(d,p)). HF optimizations do not have any symmetry at all since all HCl bond lengths, both HClH bond angles, and the two dihedral angles are different.

(iv) The semiempirical (except for AM1), HF, and MP2 optimizations of $H_3Cl_4^-$ give a D_{3h} structure. For AM1, the bonds are about 16° from being planar, so the symmetry is C_{3v} rather than trigonal planar. All density functional calculations produce slightly distorted planar structures with unequal HCl bond lengths. As noted above, the D_{3h} structure is lower in energy than the open, linear one ($ClHClHClHCl^-$) for MP2/6-311+G(d,p) calculations. The same result is obtained for all the other methods studied except PM3, which predicts that the open structure has the lower energy by about 3 kJ/mol.

(v) MP2/6-311+G(d,p) and the density functional optimizations of $H_4Cl_5^-$ give distorted tetrahedral structures. All other methods predict T_d symmetry. Except for PM3, which finds an open structure, all methods calculate this structure to be the global minimum.

(vi) In contrast to **all** other methods, MNDO predicts that the global energy minimum occurs for the cyclic H_2Cl_2 of C_{2h} symmetry. The remaining semiempirical, HF, and post-HF methods suggest an open, planar structure with three different bond lengths. The density functional methods give an optimized structure that is open but not planar although the dihedral angle, in the case of Becke3LYP/6-311+G(d,p) optimization, is only about 2°.
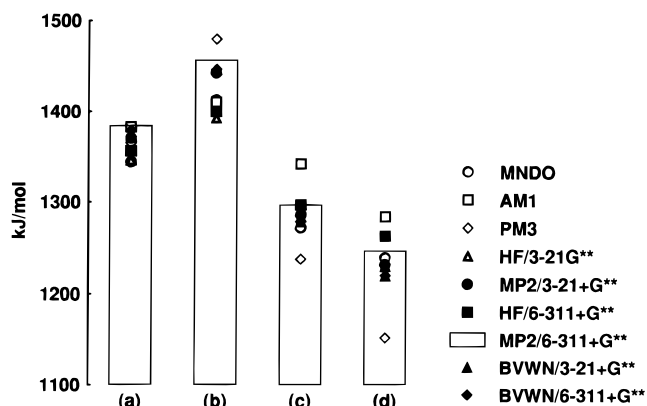
Figure 4. Comparison of $\Delta G°$ values determined by various semiempirical and *ab initio* methods: (a) $HCl \rightarrow Cl^- + H^+$; (b) $HCl_2^- \rightarrow H^+ + 2Cl^-$; (c) $H_2Cl_2 \rightarrow H^+ + HCl_2^-$; (d) $H_3Cl_3 \rightarrow H^+ + H_2Cl_3^-$.
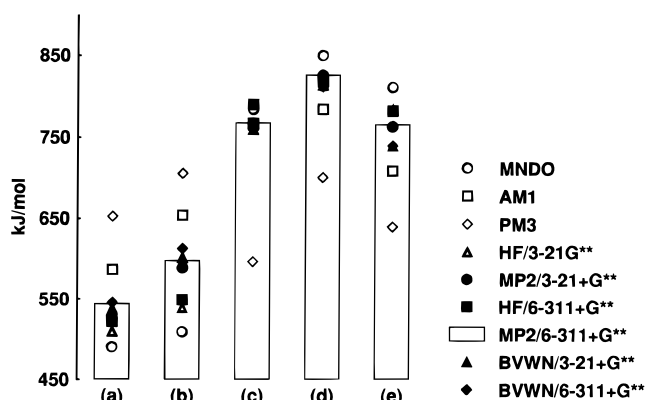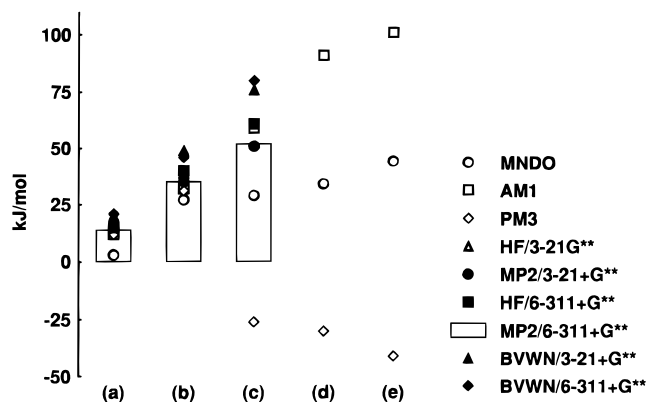

Figure 5. Comparison of $\Delta G°$ values determined by various semiempirical and *ab initio* methods: (a) $H_2Cl^+ \rightarrow H^+ + HCl$; (b) $H_3Cl_2^+ \rightarrow H^+ + H_2Cl_2$; (c) $3HCl \rightarrow H_2Cl^+ + HCl_2^-$; (d) $H_2Cl_2 \rightarrow Cl^- + H_2Cl^+$; (e) $H_3Cl_3 \rightarrow Cl^- + H_3Cl_2^+$.
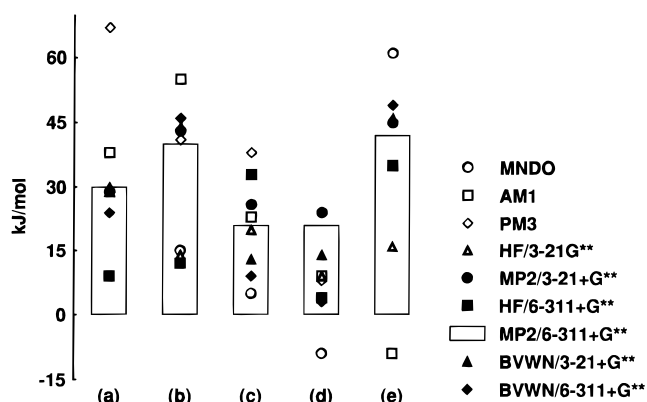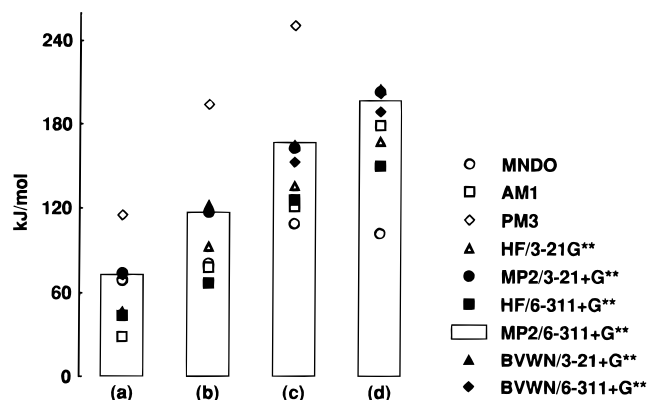

Figure 6. Comparison of $\Delta G°$ values determined by various semiempirical and *ab initio* methods: (a) $H_2Cl_3^- \rightarrow HCl + HCl_2^-$; (b) $H_3Cl_2^+ \rightarrow HCl + H_2Cl^+$; (c) $H_3Cl_4^- \rightarrow HCl + H_2Cl_3^-$; (d) $H_4Cl_5^- \rightarrow HCl + H_3Cl_4^-$; (e) $2HCl_2^- \rightarrow Cl^- + H_2Cl_3^-$

(vii) H_3Cl_3 and H_4Cl_4 have C_{nh} symmetry for all methods except the density functional optimizations. In those cases, the molecules, although cyclic, are not planar and the bond lengths do not fall into two sets.

Table 2 presents thermodynamic data calculated at the MP2/6-311+G(d,p) level for 21 reactions. Figures 4−8 are comparisons of the $\Delta G°$ values calculated for these reactions by the various *ab initio*, semiempirical, and density functional molecular orbital methods; since the data using the BVWN and Becke3LYP density functional methods are so similar, only the former are presented in the figures. The data for these reactions are qualitatively similar to those of the corresponding reactions

Figure 7. Comparison of $\Delta G°$ values determined by various semi-empirical and *ab initio* methods: (a) $2HCl \rightarrow H_2Cl_2$; (b) $3HCl \rightarrow H_3Cl_3$; (c) $4HCl \rightarrow H_4Cl_4$; (d) $5HCl \rightarrow H_5Cl_5$; (e) $6HCl \rightarrow H_6Cl_6$.

Figure 8. Comparison of $\Delta G°$ values determined by various semi-empirical and *ab initio* methods: (a) $HCl_2^- \rightarrow Cl^- + HCl$; (b) $H_2Cl_3^- \rightarrow Cl^- + H_2Cl_2$; (c) $H_3Cl_4^- \rightarrow Cl^- + H_3Cl_3$; (d) $H_4Cl_5^- \rightarrow Cl^- + H_4Cl_4$.

in the fluorine series;[9] generally, the chlorine reactions have a smaller **absolute value** of $\Delta G°$ so that the reactions, as shown in Table 2, are either less exergonic or endergonic. A most notable exception is the formation of H_2Cl^+ from HCl (reaction 3), for which $\Delta G°$ is -543.5 kJ/mol, nearly 20% lower than

$$HCl + H^+ \rightarrow H_2Cl^+ \qquad (3)$$
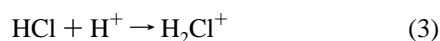
that for H_2F^+ formation. The other exceptions involve the gas phase formation of the three polymers $(HCl)_n$, $n = 2-4$ (reactions 4–6). Each of these reactions has a larger $\Delta G°$ than

$$2HCl \rightarrow H_2Cl_2 \qquad (4)$$

$$3HCl \rightarrow H_3Cl_3 \qquad (5)$$

$$4HCl \rightarrow H_4Cl_4 \qquad (6)$$

its fluorine counterpart, and the free energy changes increase in a consistent way as n increases, unlike the case with HF polymers. MNDO and AM1 (but not PM3) calculations suggest that the trend should continue for $n = 5$ and 6 (Figure 7).

The calculated value of $\Delta H°$ for the gas phase heterolytic bond energy of HCl (reaction 7) agrees well with the experi-

$$HCl \rightarrow Cl^- + H^+ \qquad (7)$$

$$HCl + H_2Cl^+ \rightarrow H_3Cl_2^+ \qquad (8)$$

mental value of 1395 kJ/mol (obtained from a thermodynamic cycle using bond dissociation energies, Cl electron affinity, and

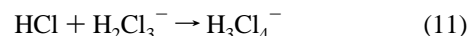*H* ionization energy)[19,20,22] and the best calculated value of 1397 kJ/mol.[21] Similarly, our $\Delta H°$ value for the formation of H_2Cl^+ (reaction 3) of -570.2 kJ/mol is remarkably near the experimental proton affinity enthalpies between -538.1[22] and -565 kJ/mol.[12e,f] The currently accepted "best" experimental value is -556.5 kJ/mol.[23] The formation of the two members of the cation series monochlorodihydrogen(I), H_2Cl^+, and dichlorotrihydrogen(I), $H_3Cl_2^+$ (reactions 3 and 8), from H^+ and H_2Cl^+, respectively, is spontaneous, a result qualitatively the same for all methods of calculation. These results suggest that, if there are sufficient concentrations of HCl and H^+ present for reaction, either or both H_2Cl^+ and $H_3Cl_2^+$ could be present in measurable quantities.

The calculated value of -103.4 kJ/mol for $\Delta H°$ of reaction 9, the formation of HCl_2^-, compares well with experimental

$$Cl^- + HCl \rightarrow HCl_2^- \qquad (9)$$
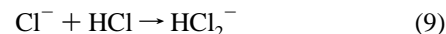
gas phase data of -96.7[24] and -99.2 kJ/mol.[11f] Ikuta, Saitoh, and Nomura[11d] calculated $\Delta H°$, $\Delta S°$, and $\Delta G°$ at 298 K to be -98.3 kJ/mol, -98.3 J/(mol·K), and -69.0 kJ/mol, respectively. In molecular solvents such as nitrobenzene and tetrachloroethane the equilibrium constant for reaction 9 is of the order of 5×10^2 L/mol, implying a $\Delta G°$ of about -15 to -16 kJ/mol.[25] In HCl–ImCl liquids, the equilibrium constant has been estimated to be $\geq 10^5$ L/mol,[5] while in chloroaluminates the thermodynamic parameters, ΔH and ΔS, have been determined to be -9.8 kJ/mol and 4.8 J/(mol·K), respectively.[4b] Clearly, although the reaction is highly exergonic, the amount of HCl_2^- present is very much dependent on the phase and dielectric constant of the medium.

The experimental equilibrium constant for reaction 10 in HCl–ImCl ionic liquids is about 5×10^2 L/mol, implying a

$$HCl + HCl_2^- \rightarrow H_2Cl_3^- \qquad (10)$$

$$HCl + H_2Cl_3^- \rightarrow H_3Cl_4^- \qquad (11)$$

$$HCl + H_3Cl_4^- \rightarrow H_4Cl_5^- \qquad (12)$$

$\Delta G°$ of -15 kJ/mol,[5] as compared with our calculated value of -30 kJ/mol. The measured equilibrium constant for the disproportionation reaction (reaction 1) in the same melts is 218 $\pm$ 25, with ΔH, ΔS, and $\Delta G(297 \text{ K})$ having values of -22.8 kJ/mol, -31.8 J/(mol·K), and -13.3 kJ/mol, respectively.[5] Again, the condensed-medium results suggest less reaction than do our calculations in the gas phase.

Our results indicate that the four members of the polychlorohydrogenate(1−) anion series, $H_nCl_{n+1}^-$, are all favored with respect to the previous homologue or Cl^- (reactions 9–12), with the equilibrium constant decreasing as n increases from 1 to 2 but remaining nearly constant for $n = 2-4$. Clearly, once chloride ion exists, the concentration or partial pressure of any one member of the series will depend on the chloride ion:HCl ratio as the HCl–ImCl melt work shows.[5,6,9] PM3 tends to overestimate the stability of members of the series relative to the preceding homologue except for $H_4Cl_5^-$; in general, one would expect that the thermodynamic parameters calculated

(21) Gronert, S. *Chem. Phys. Lett.* **1996**, *252*, 415.
(22) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. Gas Phase Ion and Neutral Thermochemistry. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.
(23) Adams, N. G.; Smith, D.; Tichy, M.; Javahery, G.; Twiddy, N. D.; Ferguson, E. E. *J. Chem. Phys.* **1989**, *91*, 4037.
(24) Yamdagni, R.; Kebarle, P. *Can. J. Chem.* **1974**, *52*, 2449.
(25) (a) Fujiwara, F. Y.; Martin, J. S. *J. Chem. Phys.* **1972**, *56*, 4091. (b) Herbrandson, H. F.; Dickerson, R. T., Jr.; Weinstein, J. *J. Am. Chem. Soc.* **1954**, *76*, 4046.

Table 3. Comparison of Experimental and Calculated ^{1}H NMR Absolute Shieldings and Chemical Shifts

species/method	abs shielding/ppm			rel chem shift^a/ppm	
	exptl	IGAIM/ CSGT	GIAO	IGAIM/ CSGT	GIAO
HCl	30.4^b				
	29.5−30.2^c				
BVWN/6-311++G(3df,3pd)		31.64	31.76		
BPW91/6-311++G(3df,3pd)		31.07	31.17		
BPW91/AUG-cc-pVTZ		30.87	31.21		
BPW91/AUG-cc-pVQZ		30.88	31.13		
BVWN/AUG-cc-pVQZ		31.46	31.72		
B3LYP/6-311++G(3df,3pd)		31.07	31.18		
B3PW91/6-311++G(3df,3pd)		30.97	31.07		
H$_2$Cl$^+$					
BVWN/6-311++G(3df,3pd)		24.77	24.88	6.9	6.9
BPW91/6-311++G(3df,3pd)		24.32	24.42	6.8	6.8
BPW91/AUG-cc-pVTZ		24.22	24.46	6.7	6.8
BPW91/AUG-cc-pVQZ		24.23	24.41	6.7	6.7
BVWN/AUG-cc-pVQZ		24.67	24.86	6.8	6.9
B3LYP/6-311++G(3df,3pd)		24.36	24.46	6.7	6.7
B3PW91/6-311++G(3df,3pd)		24.29	24.40	6.7	6.7
HCl$_2^-$	18.1^c				
	17.5^d				
BVWN/6-311++G(3df,3pd)		15.22	15.06	16.4	16.7
BPW91/6-311++G(3df,3pd)		14.59	14.45	16.5	16.7
BPW91/AUG-cc-pVTZ		14.03	14.40	16.8	16.8
BPW91/AUG-cc-pVQZ		13.83	14.20	17.1	16.9
BVWN/AUG-cc-pVQZ		14.47	14.83	17.0	16.9
B3LYP/6-311++G(3df,3pd)		13.92	13.74	17.2	17.4
B3PW91/6-311++G(3df,3pd)		13.57	13.46	17.4	17.6

^{a} Chemical shifts are relative to HCl at the same level of calculation. ^{b} Reference 26. ^{c} Reference 4bc. ^{d} Reference 6. Where shifts relative to TMS are given, the absolute shieldings were calculated using that of TMS as 31.06 ppm.[25a]

using semiempirical methods are less reliable than those using *ab initio* methods, particularly MP2 and density functional methods with basis sets incorporating diffuse functions.[21]

Although the dimerization and trimerization reactions (reactions 4 and 5) both are exothermic (−5.62 and −18.1 kJ/mol respectively), the large unfavorable ΔS causes the free energy change to be positive. The experimental binding energies for (HCl)$_2$ (D_e and D_0)[13b,f] of −8.3 and −5.15 kJ/mol agree exceptionally well with our $\Delta H°$ of −5.62 kJ/mol. Unlike our earlier results which predicted that 13% of gaseous HF could exist in various polymeric forms,[9] the data in Table 2 suggest that less than 1% of HCl would be a polymer (mainly a dimer). It should be noted that the thermodynamic calculations involve a classical evaluation of $S°$; as a result, they will underestimate the entropy for nonrigid molecules like the polymers if conformations other than the lowest energy one are significantly populated.[13,16] This entropy of mixing may mean that these molecules or ions are actually **less disfavored,** by several kilojoules per mole, relative to their more rigid precursors than one would infer from our calculations.

The data of Table 2 clearly suggest that either HCl$_2^-$ or H$_2$Cl$^+$ could exist in the gas phase and, presumably, in liquid melts, depending on the conditions. Several groups have used proton NMR studies to identify HCl$_2^-$,[6,4b,c] but there has been more difficulty in finding the resonance of H$_2$Cl$^+$. Table 3 presents calculated absolute proton shieldings and chemical shifts relative to HCl.[26] The calculated chemical shift of HCl$_2^-$, relative to HCl, is 16.5−17.5 ppm. There is little difference depending on the density functional method used, on the nature of the extended basis set, or on the method of calculating the absolute

(26) Schneider, W. G.; Bernstein, H. J.; Pople, J. A. *J. Chem. Phys.* **1958**, *28*, 601.

shielding. However, the shift is significantly higher than the 11.4−12.7 ppm estimated in liquid melts.[6,4bc] The gas phase data predict the proton signal for H$_2$Cl$^+$ will occur at about 6.5−7.0 ppm relative to HCl, upfield by approximately 10 ppm from HCl$_2^-$. If the liquid melt data are valid, one might expect to find the H$_2$Cl$^+$ resonance at 5 ± 2 ppm relative to HCl in these melts.

Summary

On the basis of our calculations, the following conclusions may be drawn for reactions of HCl, Cl$^-$, and H$^+$ occurring in the gas phase:

(i) At 298 K and 1 atm, only a small amount of HCl, unlike HF, will exist in a polymeric form, (HCl)$_n$.

(ii) Reactions that form ions are extremely unlikely in the gas phase although one would expect solvation and other forces present in media of medium to high dielectric constant to increase the equilibrium constants substantially in condensed phases. For example, whereas $\Delta G°$ is around 1400 kJ/mol for the ionization of gaseous HCl, it is 40 kJ/mol under aqueous conditions.[19]

(iii) Once the chloride ion is available, the formation of the various polychlorohydrogenate(1−) anions, according to reaction 13, can proceed. The values of $\Delta G°$ are all less negative than

$$\text{HCl} + \text{H}_n\text{Cl}_{n+1}^- \rightarrow \text{H}_{n+1}\text{Cl}_{n+2}^- \ (n = 0, 1, 2, 3) \quad (13)$$
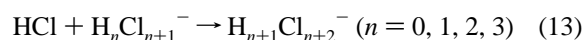
those of the comparable reactions in the fluorine series, meaning that one would expect a smaller concentration of any of the polychlorohydrogenate(1−) ions. Since $\Delta G°$ becomes less negative as n increases, any one or several of the four anions could occur depending on the relative amounts of HCl and Cl$^-$.

(iv) Once H$^+$ is available, the formation of the polychlorohydrogen(I) cations according to reaction 14 can occur. $\Delta G°$ is less negative for $n = 0$ than for $n = 1$, and either or both of the cations are possible depending on conditions.

$$\text{HCl} + \text{H}_{n+1}\text{Cl}_n^+ \rightarrow \text{H}_{n+2}\text{Cl}_{n+1}^+ \ (n = 0, 1) \quad (14)$$
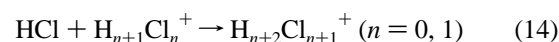
(v) The reactions of either H$^+$ or Cl$^-$ with hydrogen chloride polymers to produce larger cations and anions are highly probable. As a result it is unlikely that any amount of polymer formation could occur (see conclusion i above).

(vi) The proton chemical shifts of HCl$_2^-$ and H$_2$Cl$^+$ relative to HCl have been calculated to be about 17 and 7 ppm, respectively.

In addition, the use of pure Hartree−Fock or density functional calculations or of the 3-21+G(d,p) basis set does not make a substantial difference in the thermodynamic results. Generally speaking, the semiempirical methods give results qualitatively similar to those of the *ab initio* methods although they may be quantitatively different especially when $\Delta G°$ is small. Of the three, PM3 appears to do the poorest job; unlike all other methods, PM3 predicts that (HCl)$_4$ (as well as the pentamer and hexamer) would exist relative to HCl and that the anions, H$_n$Cl$_{n+1}^-$, are **all** open in structure. Differences among the various methods appear to be less pronounced than was the case for the corresponding fluorine reactions.[9]