Thermodynamic Calculations for Reactions Involving Hydrogen Halide Polymers, Ions, and Lewis Acid Adducts. 3. Systems Constituted from Al^{3+}, H^+, and Cl^-

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Semiempirical (MNDO, AM1 and PM3), ab initio (HF/3-21+G(d,p), MP2/3-21+G(d,p), HF/6-311+G(d,p), and MP2/6-311+G(d,p)), and density functional (BVWN/3-21+G(d,p) and BVWN/6-311+G(d,p)) energy minimization and frequency calculations have been carried out on $AlCl_3$, $AlCl_4^-$, $AlCl_2^+$, $HAlCl_4$, $HAlCl_3^+$, and $ClHAlCl_4^-$. The same computational set, except for MP2/6-311+G(d,p) frequency calculations, was performed on Al_2Cl_6 and $Al_2Cl_7^-$. For $ClHAl_2Cl_7^-$, only semiempirical calculations, as well as Hartree−Fock and BVWN optimizations using the 3-21+G(d,p) and 6-311+G(d,p) basis sets, were carried out along with Hartree−Fock frequency determinations. $\Delta G°$, $\Delta H°$, and $\Delta S°$ values have been calculated for a number of reactions involving these species along with a variety of ions derived from HCl. Thermodynamic data and equilibrium constants at 298 K are presented for 22 reactions using calculations at the best level, along with a comparison of $\Delta G°$ values obtained from all molecular orbital methods used.

Introduction

Mixtures of $AlCl_3$ and ZCl, where ZCl is an alkali chloride or an organic chloride such as 1-ethyl-1*H*-imidazolium chloride (ImCl), are Lewis acidic when $AlCl_3$ is in excess and Lewis basic when ZCl is in excess.[1] The governing equilibria are

$$Cl^- + AlCl_3 \rightarrow AlCl_4^- \quad (1)$$

$$AlCl_3 + AlCl_4^- \rightarrow Al_2Cl_7^- \quad (2)$$

and the combination reaction

$$Cl^- + Al_2Cl_7^- \rightarrow 2AlCl_4^- \quad (3)$$

with $K_3 = [AlCl_4^-]^2/[Cl^-][Al_2Cl_7^-]$. While insignificant at lower temperatures, $Al_3Cl_{10}^-$ becomes more of a contributor at higher temperatures in very acidic melts.[3,4,24d]

For ZCl = NaCl, the mixtures are liquid over a fair composition range at 225 °C with $K_3 \approx 10^7$,[2] while for ZCl = ImCl, mixtures are liquid for X_{AlCl_3} between 0.33 and 0.67 at ambient temperatures with $K_3 \approx 10^{16}-10^{18}$.[3]

The addition of HCl to Lewis basic $AlCl_3$−ImCl mixtures has been shown to produce Brønsted acidic (but still Lewis

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basic) systems with Hammett acidities close to the range of concentrated hydrochloric acid,[4] while the addition of HCl to Lewis acidic mixtures yields superacidic systems of strength comparable to liquid HF.[5] The acidity of HCl in various neutral buffered melts has also been studied.[6] Mixtures of $AlCl_3$ and pyridinium chloride are Brønsted acidic without HCl addition and appear to be even stronger superacids when $AlCl_3$ is in excess, although quantitative data are lacking at present.[7,8]

We have shown by HCl solubility measurements,[9] ^{1}H NMR spectroscopy,[10] IR spectroscopy,[11] and electrochemistry[9] that the protic species present in $AlCl_3$−ImCl are HCl_2^-, $H_2Cl_3^-$, $H_3Cl_4^-$, and $ClHAlCl_4^-$ in Lewis basic systems, $ClHAlCl_4^-$ in Lewis neutral systems, and $ClHAl_2Cl_7^-$ and $ClHAlCl_4^-$ in Lewis acidic systems. Our evidence points to $ClHAl_2Cl_7^-$ as the superacid.

Although there is ample evidence for the formation of species $H_nCl_{n+1}^-$ in the literature, it is quite spotty.[12] There are precedents for the formation of species XHY^- [13] but not with Y^- = bulky chloroaluminate ion.

To support our experimental observations of these systems, we embarked on a program of calculating the geometries, energies, and vibrational frequencies of the various ions and molecules believed to be involved. Elsewhere we have reported the data for $(HCl)_n$, $(H_nCl_{n+1})^-$, and $(H_{n+1}Cl_n)^+$ [14] and the analogous fluorine species,[15] for which more experimental comparisons were available. Theoretical data have also been obtained for ZCl−BCl_3−HCl and ZF−BF_3−HF systems, but the experimental scope here is limited.[16]

In this paper we present ab initio, density functional, and semiempirical SCF calculations for $AlCl_3$, Al_2Cl_6, $AlCl_4^-$, $Al_2Cl_7^-$, $AlCl_2^+$, $HAlCl_4$, $HAlCl_3^+$, $HAlCl_5^-$ (which will be written as $ClHAlCl_4^-$), and $HAl_2Cl_8^-$ ($ClHAl_2Cl_7^-$). In particular, we discuss the significance of these species to ambient-temperature melt studies in the light of the $\Delta G°$ and K values for key reactions. Energy differences for some of these reactions (often without thermal and zero-point energy corrections) have appeared in the literature (vide infra). However, as we have noted previously, PV work and $T\Delta S$ terms can be significantly important so that ΔG is a much more meaningful parameter in assessing equilibria than the often-reported ΔE or ΔH.[14,15] The extension of these calculations to liquid HCl, molten $NaAlCl_4$, and molten LiCl−KCl temperatures is under way.[17]

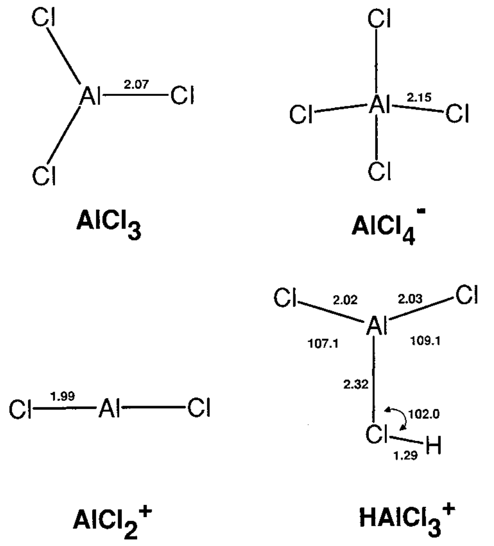

Figure 1. Structures of $AlCl_3$, $AlCl_4^-$, $AlCl_2^+$, and $HAlCl_3^+$ determined by the MP2/6-311+G(d,p) ab initio method. Bond lengths are in angstroms and angles in degrees.

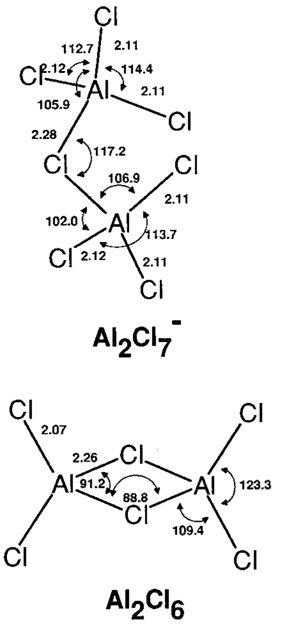

Figure 2. Structures of $Al_2Cl_7^-$ and Al_2Cl_6 determined by the MP2/6-311+G(d,p) ab initio method. Bond lengths are in angstroms and angles in degrees.

Calculations

Ab initio, density functional, and semiempirical calculations were performed using GAUSSIAN 92/DFT and GAUSSIAN 94.[18] Geometries of all species, except for $ClHAl_2Cl_7^-$, were optimized 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 procedures. Optimizations for $ClHAl_2Cl_7^-$ were performed using all methods except MP2/6-311+G(d,p). Vibrational frequencies were also obtained using the same methods and basis sets except (a) MP2/6-311+G(d,p) frequency calculations were not possible for Al_2Cl_6 and $Al_2Cl_7^-$; (b) no post-Hartree−Fock or density functional frequency computations were feasible for $ClHAl_2Cl_7^-$. From these 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 obtain

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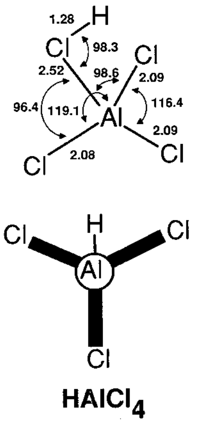

Figure 3. Structure and conformation of $HAlCl_4$ determined by the MP2/6-311+G(d,p) ab initio method. Bond lengths are in angstroms and angles in degrees.

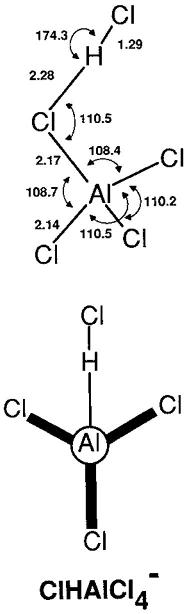

Figure 4. Structure and conformation of $HAlCl_5^-$ ($ClHAlCl_4^-$) determined by the MP2/6-311+G(d,p) ab initio method. Bond lengths are in angstroms and angles in degrees.

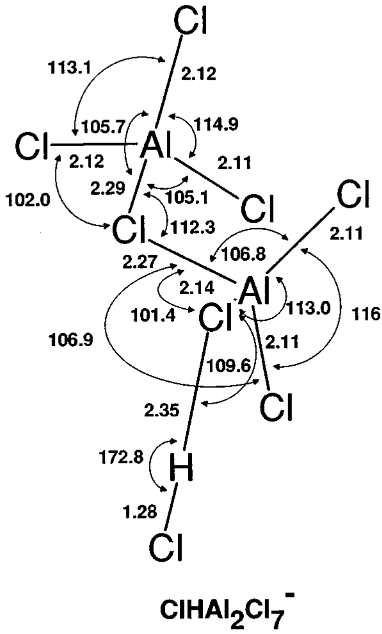

Figure 5. Structure of $ClHAl_2Cl_7^-$ determined by the MP2/3-21+G-(d,p) ab initio method. Bond lengths are in angstroms and angles in degrees.

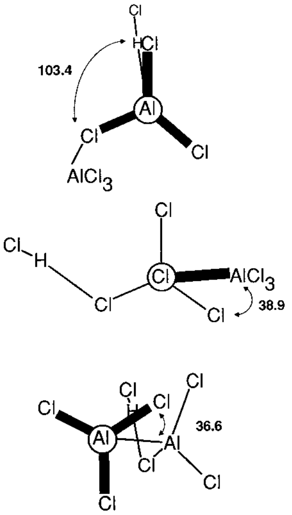

Figure 6. Conformation of $ClHAl_2Cl_7^-$ determined by the MP2/3-21+G(d,p) ab initio method. Dihedral angles are in degrees.

entropies ($S°$) as well as zero-point energies and thermal corrections 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[19] and MP2 values by 0.95[20]), to give U values at 298 K. Reaction internal energies ($\Delta U°$) were converted to reaction enthalpies ($\Delta H°$) by means of eq 4, which assumes ideal-gas behavior for all species.[21] In Gaussian 94 the conversion of U to H values, with thermal corrections, is carried out automatically. $\Delta S°$ values were obtained using $S°$s taken from frequency calculations for polyatomic ions and molecules and employing the Sackur–Tetrode equation for monatomic ions.[21]

$$\Delta H° = \Delta U° + \Delta nRT \tag{4}$$

Results

Figures 1–6 provide the structures and conformations of the species studied as determined from MP2/6-311+G(d,p) optimizations, except for $ClHAl_2Cl_7^-$, where MP2/3-21+G(d,p) was the method used. Structures and energies for $AlCl_3$ (C_{3v}),[22] Al_2Cl_6 (D_{2d}),[22a–b23] $AlCl_4^-$ (T_d),[22a,b,d,23c,24] $Al_2Cl_7^-$ (C_2),[22b,23c,24a–b,d,e,25] $AlCl_2^+$ ($D_{\infty h}$),[22g,23c,26] and $HAlCl_4$ (C_s)[22d] have been reported recently from various calculations, and our results are essentially the same as the most reliable of these. The agreement with experimental data, where available, is exceptionally good in most cases (Table 1). The structures of $ClHAlCl_4^-$ and $ClHAl_2Cl_7^-$, which have not been reported previously, are essentially those of the anions, $AlCl_4^-$ and $Al_2Cl_7^-$, to which HCl has been attached through a "long" H–Cl bond of 2.3 and 2.4 Å, respectively (Figures 4–6). For this reason, the formulas $ClHAlCl_4^-$ and $ClHAl_2Cl_7^-$ have been used to represent these anions. The preferred conformation of $ClHAlCl_4^-$ is "staggered", belonging to the C_s point group; the dihedral angle involving the H, the hydrogen-bonded Cl, Al, and one of the other Cl's is 180°. The Cl–H–Cl–Al dihedral angle is also 180°. Although the lowest energy conformation, it is only of the order of 1 kJ/mol more stable than the "eclipsed" form.

The energy surface of the $ClHAl_2Cl_7^-$ anion is more complex than any of the other species studied, and several structures appear as local minina with energies differing by only 1 kJ/

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Table 1. Comparison of Experimental and Calculated Structures

species	structural parameters[a]			
	parameter	exp	ref	calc[b]
$AlCl_3$ (C_{3v})	Al−Cl	2.068	27	2.067 (2.069)[c]
$AlCl_4^-$ (T_d)	Al−Cl	2.12	28	2.149 (2.149)[c]
		2.127−2.132	29	
		2.09−2.16	22b, 30	
$AlCl_2^+$ ($D_{\infty h}$)	Al−Cl	2.05−2.25	31	1.993
Al_2Cl_6 (D_{2d})	$Al-Cl_t$	2.065	32	2.072
	$Al-Cl_b$	2.252		2.259
	Al−Al	3.102		3.160
	$\angle AlCl_bAl$	89.0		88.8
	$\angle Cl_bAlCl_t$	109.7		109.4
	$\angle Cl_tAlCl_t$	123.4		123.3
$Al_2Cl_7^-$ (C_2)	$Al-Cl_t$	2.97−2.13	33	2.109, 2.113
	$Al-Cl_b$	2.22−2.29		2.122
	$\angle AlCl_bAl$	110.8−115.1		2.279
	$<Cl_bAlCl_t$	102.5−108.2		117.2
	$\angle Cl_tAlCl_t$	111.1−116.5		102.0, 105.9, 106.9 112.7, 113.7, 114.4

[a] All lengths are in Å and angles in degrees. t = terminal; b = bridge. [b] Calculated structures were obtained from MP2/6-311+G(d,p) optimizations unless indicated otherwise. [c] Calculated from CCSD/6-311+G(d,p) optimization.

Table 2. Comparison of Experimental and Calculated Heats of Formation[a]

species	ΔH_f^o(kJ/mol)		
	exp	ref	calc (MNDO, AM1, PM3)
$AlCl_3$	−584.5 ± 2.9	31a	−587, −594, −511
	−585.7 ± 1.8	34	
$AlCl_4^-$	−1117 ± 10	35	−1140, −1100, −1080
$AlCl_2^+$	481 ± 75	31a	498, 436, 520
Al_2Cl_6	−1295.7 ± 3.4	31a	−1240, −1260, −1300
	−1299.0 ± 1.9	34	
$Al_2Cl_7^-$	−1862	35	−1822, −1800, −1840

[a] All values are determined at 298 K except those from ref 35, which are quoted at 0 K.

Table 3. Thermodynamic Data Calculated at 298 K for Reactions Involving $Al_nCl_m^{(-)}$ Species[a]

	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J mol^{-1} K^{-1}	$\Delta G°$/kJ mol^{-1}
$2AlCl_3 \rightarrow Al_2Cl_6$	−132.9	−149.6	−88.3
$2AlCl_3 \rightarrow AlCl_2^+ + AlCl_4^-$	563.2	−11.1	566.5
$Cl^- + AlCl_3 \rightarrow AlCl_4^-$	−331.8	−121.3	−295.7
$HCl + AlCl_3 \rightarrow AlCl_4^- + H^+$	1075.1	−45.6	1088.7
$HCl + AlCl_3 \rightarrow HAlCl_4$	−32.8	−96.6	−4.01
$HCl + AlCl_4^- \rightarrow ClHAlCl_4^-$	−31.3	−71.7	−9.89
$AlCl_3 + AlCl_4^- \rightarrow Al_2Cl_7^-$	−143.4	−117.5	−108.4
$HCl + 2AlCl_3 \rightarrow Al_2Cl_7^- + H^+$	931.7	−163.0	980.3
$HCl + AlCl_2^+ \rightarrow HAlCl_3^+$	−114.4	−111.6	−81.1
$Cl^- + Al_2Cl_7^- \rightarrow 2AlCl_4^-$	−188.4	−3.80	−187.3
$H_2Cl_3^- + 2Al_2Cl_7^- \rightarrow H_2Cl^+ + 4AlCl_4^-$	620.8	174.0	569.0
$2HCl_2^- + 3Al_2Cl_7^- \rightarrow H_2Cl^+ + 6AlCl_4^-$	478.3	182.0	424.0
$3H_2Cl_3^- + 5Al_2Cl_7^- \rightarrow 2H_3Cl_2^+ + 10AlCl_4^-$	1066.5	313.6	973.0
$3HCl_2^- + 4Al_2Cl_7^- \rightarrow H_3Cl_2^+ + 8AlCl_4^-$	319.4	168.7	269.1
$2HCl + 2AlCl_3 \rightarrow H_2Cl^+ + Al_2Cl_7^-$	361.5	−252.6	436.8
$2HCl + AlCl_3 \rightarrow AlCl_4^- + H_2Cl^+$	504.9	−135.1	545.2
$HCl_2^- + AlCl_4^- \rightarrow Cl^- + ClHAlCl_4^-$	72.1	31.9	62.6
$ClHAlCl_4^- + AlCl_4^- \rightarrow HCl_2^- + Al_2Cl_7^-$	116.3	−28.1	124.7
$HCl + Al_2Cl_7^- \rightarrow ClHAl_2Cl_7^-$	−30.4	−64.6	−11.2
$2ClHAl_2Cl_7^- \rightarrow HCl_2^- + 2AlCl_4^- + Al_2Cl_7^-$	716.1	124.3	679.1
$ClHAlCl_4^- + Al_2Cl_7^- \rightarrow AlCl_4^- + ClHAl_2Cl_7^-$	6.62	2.8	5.8
$ClHAl_2Cl_7^- + 2AlCl_4^- \rightarrow HCl_2^- + 2Al_2Cl_7^-$	110.2	−37.0	121.2

[a] All data were obtained using MP2/6-311+G(d,p) optimizations and frequency determinations except for Al_2Cl_6 and $Al_2Cl_7^-$, whose zero-point energies and entropies were obtained from frequency calculations done at the MP2/3-21+G(d,p) level. The last four reactions, producing or requiring $ClHAl_2Cl_7^-$, use energy data from MP2/3-21+G(d,p) optimizations with zero-point energies and entropies taken from HF/3-21+G(d,p) frequency calculations.

mol or less. The lowest energy structure (Figure 5) has the conformation shown in Figure 6 with the H, Cl, Al, bridge Cl dihedral angle equal to 103.4°.

All the calculational methods used in this study predict essentially the same structure for each species investigated and shown in Figures 1−6 with the following four exceptions: (a) For $HAlCl_4$, all find a C_s minimum. However, while the semiempirical methods predict an eclipsed conformation with an HClAlCl dihedral angle of 0°, the result of ab initio and DFT minimizations is a staggered conformation with the dihedral angle equal to 60° (Figure 3). In the case of the HF and MP2/6-311+G(d,p) computations, the eclipsed conformation is a saddle point (transition structure). (b) As noted above, at the MP2/6-311+G(d,p) level, $ClHAlCl_4^-$ adopts a staggered conformation (Figure 4). The same energy minimum is predicted by PM3, but the other computational methods suggest the C_s eclipsed structure to be the lowest energy. Nonetheless, the energy differences between the two conformations is small. (c) For $Al_2Cl_7^-$, all methods but PM3 predict a C_2 structure (Figure 2). From PM3, the optimized structure has C_s symmetry. (d) With the exception of PM3, all methods find the basic conformation of Figure 6 for the lowest energy conformation of $ClHAl_2Cl_7^-$, although there may be other local minima in the energy surface of the ion. For example, at the HF/3-21+G(d,p) level, the lowest energy conformation has the H, Cl, Al, bridge Cl dihedral angle equal to 106°. There are other minima on the potential-energy surface with that dihedral equal to −99°, 6° and 179°. At the HF/6-311+G(d,p) level, there is really only one other minimum, one with the dihedral of around 180°. It is this latter conformation that has the lowest energy for PM3 computations. In addition to these differences, Al−Cl bond lengths are nearly always shorter for AM1 optimizations while MNDO calculates approximately the same bond lengths as the ab initio and DFT methods. PM3 is far less predictable; for example, the PM3 Al−Cl bond length is shorter than that expected for $AlCl_3$ but longer for $AlCl_4^-$, $Al_2Cl_7^-$, and $ClHAl_2Cl_7^-$. In Al_2Cl_6, the terminal Al−Cl lengths are shorter while those involving the bridging Cl's are longer. MNDO predicts longer H−Cl bonds for $ClHAlCl_4^-$ and $ClHAl_2Cl_7^-$, but AM1 and PM3 find the terminal bond longer and the interior H−Cl shorter as the result of a stronger ClH−Cl bond.

Although the structures may be less reliable, $\Delta H_f°$ values, calculated using semiempirical methods, are in reasonable agreement with literature experimental values available for two molecules and three ions (Table 2). In addition to the experimental data shown in Table 2, Petrie, using the G2 level of theory, has calculated the following enthalpies of formation at 0 K: 524 ± 20 kJ/mol for $AlCl_2^+$ and −595 ± 20 kJ/mol for $AlCl_3$.[22g]

The vibrational frequencies we have calculated are in excellent agreement with those reported previously from computations and from Raman or infrared spectroscopy. For example, Ystenes et al. have calculated the frequencies of $AlCl_3$ using a number of basis sets.[22a,e] Their "recommended values" (the experimental ones)[27] of 151, 214, 375, and 616 cm^{-1} compare favorably with our frequencies of 140, 192, 378, and 613 cm^{-1} calculated at the MP2/6-311+G(d,p) level with a 0.95 scaling factor. Another recent theoretical assessment of the frequencies finds values of

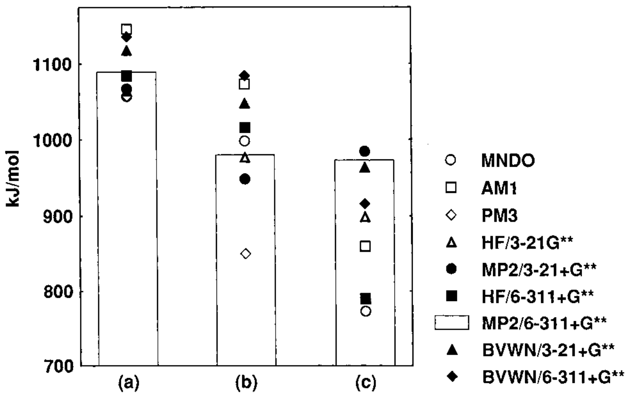

Figure 7. Comparison of $\Delta G°$ values determined by various semiempirical and ab initio methods for (a) $HCl + AlCl_3 \rightarrow AlCl_4^- + H^+$; (b) $HCl + 2AlCl_3 \rightarrow Al_2Cl_7^- + H^+$; (c) $3H_2Cl_3^- + 5Al_2Cl_7^- \rightarrow 2H_3Cl_2^+ + 10AlCl_4^-$.

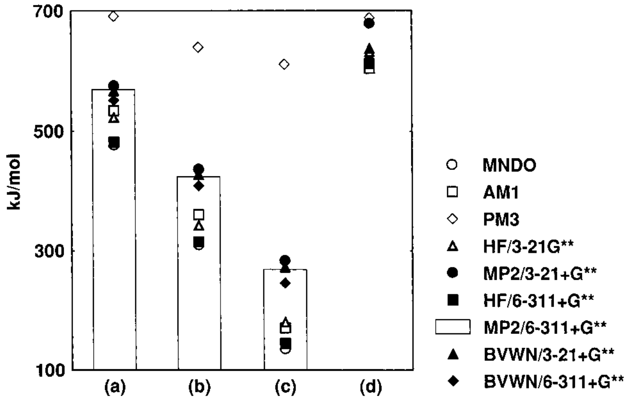

Figure 8. Comparison of $\Delta G°$ values determined by various semiempirical and ab initio methods for (a) $H_2Cl_3^- + 2Al_2Cl_7^- \rightarrow H_2Cl^+ + 4AlCl_4^-$; (b) $2HCl_2^- + 3Al_2Cl_7^- \rightarrow H_2Cl^+ + 6AlCl_4^-$; (c) $3HCl_2^- + 4Al_2Cl_7^- \rightarrow H_3Cl_2^+ + 8AlCl_4^-$; (d) $2ClHAl_2Cl_7^- \rightarrow H_2Cl^+ + 2AlCl_4^- + Al_2Cl_7^-$.

154, 213, 402, and 642 cm^{-1}.[22f] Our corresponding scaled MP2/6-311+G(d,p) frequencies for $AlCl_4^-$ are 109, 171, 337, and 493 cm^{-1} as compared to the best computed values of 117, 179, 339, and 486 cm^{-1} [22a] and the experimental values of 119, 182, 346, and 488 cm^{-1}.[28] For Al_2Cl_6, we obtain scaled frequencies of 20, 68, 95, 118, 125, 133, 141, 167, 176, 215, 290, 319, 338, 430, 483, 522, 613, and 622 cm^{-1}. Ystenes et al. get comparable scaled values of 25 (24), 65, 98 (98), 121, 121 (115), 132 (123), 139 (143), 171 (168), 183 (178), 222 (219), 257 (281), 316 (320), 336 (337), 433 (418), 477 (483), 514 (511), 609 (614), and 620 (626) cm^{-1}.[22a] Frequencies in parentheses are those observed experimentally.[36] Our computed vibrational frequencies noted above for these three species, plotted against the experimental values, give a linear correlation with slope of 1.00 and a correlation coefficient of 0.9995.

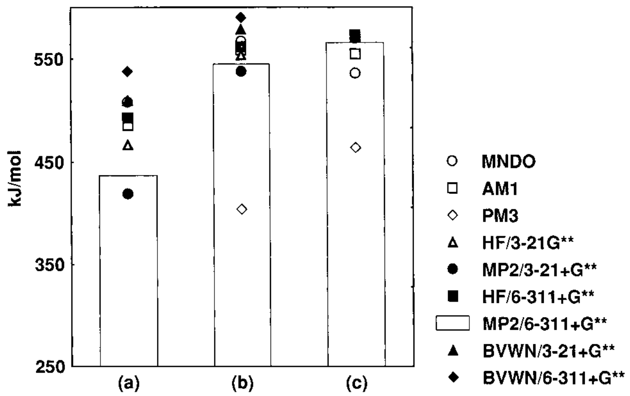

Figure 9. Comparison of $\Delta G°$ values determined by various semiempirical and ab initio methods for (a) $2HCl + 2AlCl_3 \rightarrow H_2Cl^+ + Al_2Cl_7^-$; (b) $2HCl + AlCl_3 \rightarrow H_2Cl^+ + AlCl_4^-$; (c) $2\ AlCl_3 \rightarrow AlCl_2^+ + AlCl_4^-$.

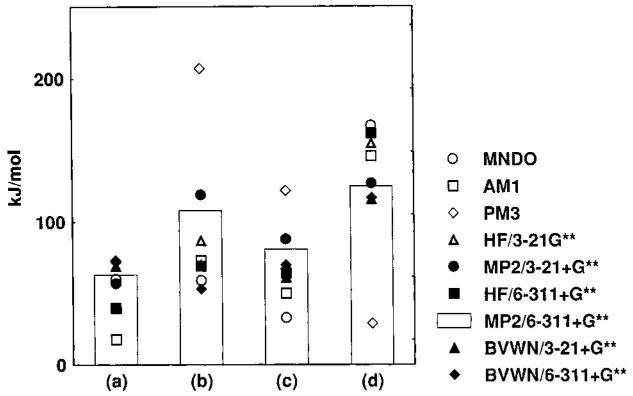

Figure 10. Comparison of $\Delta G°$ values determined by various semiempirical and ab initio methods for (a) $HCl_2^- + AlCl_4^- \rightarrow Cl^- + ClHAlCl_4^-$; (b) $Al_2Cl_7^- \rightarrow AlCl_4^- + AlCl_3$; (c) $HAlCl_3^+ \rightarrow HCl + AlCl_2^+$; (d) $ClHAlCl_4^- + AlCl_4^- \rightarrow HCl_2^- + Al_2Cl_7^-$.

Table 3 lists thermodynamic data ($\Delta H°$, $\Delta S°$, and $\Delta G°$) for 22 reactions, calculated using optimizations and frequency determinations at the MP2/6-311+G(d,p) level wherever possible. The zero-point energies and entropies of Al_2Cl_6 and $Al_2Cl_7^-$ were obtained from MP2/3-21+G(d,p) frequency calculations. The four reactions involving $ClHAl_2Cl_7^-$ use energy data taken from MP2/3-21+G(d,p) optimizations combined with HF/3-21+G(d,p) zero-point energies and entropies. Figures 7–12 display graphical comparisons of the $\Delta G°$ values, obtained from the various semiempirical, ab initio, and density functional computations, for each of these reactions.

For most reactions the methods, with the possible exception of PM3, give qualitatively comparable results; $\Delta G°$ values calculated from PM3 data are noticeably different for 14 of the

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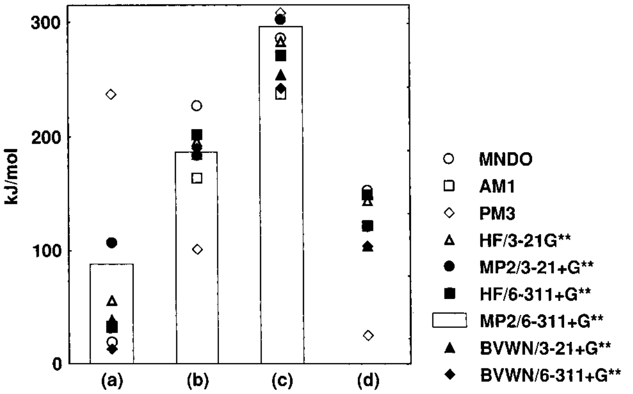

Figure 11. Comparison of $\Delta G°$ values determined by various semiempirical and ab initio methods for (a) $Al_2Cl_6 \rightarrow 2AlCl_3$; (b) $2AlCl_4^- \rightarrow Cl^- + Al_2Cl_7^-$; (c) $AlCl_4^- \rightarrow Cl^- + AlCl_3$; (d) $ClHAl_2Cl_7^- + 2AlCl_4^- \rightarrow HCl_2^- + 2Al_2Cl_7^-$.

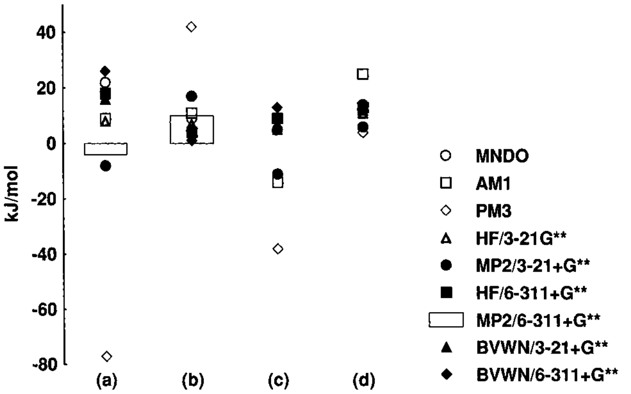

Figure 12. Comparison of $\Delta G°$ values determined by various semiempirical and ab initio methods for (a) $HCl + AlCl_3 \rightarrow HAlCl_4$; (b) $ClHAlCl_4^- \rightarrow HCl + AlCl_4^-$; (c) $HCl + Al_2Cl_7^- \rightarrow ClHAl_2Cl_7^-$; (d) $ClHAlCl_4^- + Al_2Cl_7^- \rightarrow AlCl_4^- + ClHAl_2Cl_7^-$.

22 reactions presented. Interestingly, the MP2 results are remarkably similar regardless of the basis set used, i.e., 3-21+G-(d,p) and 6-311+G(d,p). For six reactions (two from Table 3 and four from the previous paper[14]), we have also obtained $\Delta G°$ using CCSD/6-311+G(d,p) computations. The average difference between the MP2 and CCSD values of $\Delta G°$ is less than 1%. As a result, we feel confident in using MP2 results. Since MP2/6-311+G(d,p) and BVWN/6-311+G(d,p) calculations differ more than the two MP2 calculations, the data of Table 3 use MP2/3-21+G(d,p) calculations for the computationally large anion, $ClHAl_2Cl_7^-$.

The dimerization reaction (reaction 5) has been well studied. Our calculated $\Delta H°$(298 K) value of −132.9 kJ/mol Al_2Cl_6 compares well with previously computed values of −127.4[22b] and −140 kJ/mol[23c] and with the experimental estimates of −121 ± 4[29] and −127 ± 6 kJ/mol.[31a,34] A recently reported computation of −153 kJ/mol for the dimerization "energy" appears to be in line with our estimate.[30] For the same reaction, the $\Delta S°$ of −149.6 J/K mol in Table 3 compares well with experimental values of −154 ± 7[31a] and 155 ± 7 J/K mol.[34] Our reaction enthalpies of −114.4 kJ/mol for reaction 2, −32.8 kJ/mol for reaction 6, and 696.1 kJ/mol for reaction 7, calculated at 298 K, also compare moderately well with previous calculations of −141.71 (ab initio with smaller basis set at 0 K),[22b] −7.97 (ab initio with comparable basis set at 0 K),[22d] and 680 kJ/mol (ionic model),[23c] respectively.

Table 4. Equilibrium Constants Calculated at 298 K for Reactions Involving $Al_nCl_m^{(-)}$ Species[a]

	K (calcd)	K (lit)
$2AlCl_3 \rightarrow Al_2Cl_6$	3.00×10^{15}	1.35×11^{14} [b] 1.67×10^{14} [c] 1.75×10^{14} [d]
$2AlCl_3 \rightarrow AlCl_2^+ + AlCl_4^-$	5.06×10^{-100}	
$Cl^- + AlCl_3 \rightarrow AlCl_4^-$	6.76×10^{51}	1.6×10^{19} [e]
$HCl + AlCl_3 \rightarrow AlCl_4^- + H^+$	1.47×10^{-191}	
$HCl + AlCl_3 \rightarrow HAlCl_4$	5.05	
$HCl + AlCl_4^- \rightarrow ClHAlCl_4^-$	5.41×10	1.33×10^{-1} [f]
$AlCl_3 + AlCl_4^- \rightarrow Al_2Cl_7^-$	1.00×10^{19}	1.6×10^{3} [e]
$HCl + 2AlCl_3 \rightarrow Al_2Cl_7^- + H^+$	4.91×10^{-164}	
$HCl + AlCl_2^+ \rightarrow HAlCl_3^+$	1.64×10^{14}	
$Cl^- + Al_2Cl_7^- \rightarrow 2AlCl_4^-$	6.76×10^{32}	1.0×10^{16} 1.0×10^{18} [e]
$H_2Cl_3^- + 2Al_2Cl_7^- \rightarrow H_2Cl^+ + 4AlCl_4^-$	1.85×10^{-100}	
$2HCl_2^- + 3Al_2Cl_7^- \rightarrow H_2Cl^+ + 6AlCl_4^-$	4.80×10^{-75}	
$3H_2Cl_3^- + 5Al_2Cl_7^- \rightarrow 2H_3Cl_2^+ + 10AlCl_4^-$	2.83×10^{-171}	
$3HCl_2^- + 4Al_2Cl_7^- \rightarrow H_3Cl_2^+ + 8AlCl_4^-$	6.80×10^{-48}	
$2HCl + 2AlCl_3 \rightarrow H_2Cl^+ + Al_2Cl_7^-$	2.74×10^{-77}	
$2HCl + AlCl_3 \rightarrow AlCl_4^- + H_2Cl^+$	2.74×10^{-96}	
$HCl_2^- + AlCl_4^- \rightarrow Cl^- + ClHAlCl_4^-$	1.07×10^{-11}	
$ClHAlCl_4^- + AlCl_4^- \rightarrow HCl_2^- + Al_2Cl_7^-$	1.39×10^{-22}	
$HCl + Al_2Cl_7^- \rightarrow ClHAl_2Cl_7^-$	9.17×10	1.08×10^{-1} [f]
$2ClHAl_2Cl_7^- \rightarrow HCl_2^- + 2AlCl_4^- + Al_2Cl_7^-$	1.07×10^{-119}	
$ClHAlCl_4^- + Al_2Cl_7^- \rightarrow AlCl_4^- + ClHAl_2Cl_7^-$	9.64×10^{-2}	
$ClHAl_2Cl_7^- + 2AlCl_4^- \rightarrow HCl_2^- + 2Al_2Cl_7^-$	5.85×10^{-22}	

[a] All data were obtained using MP2/6-311+G(d,p) optimizations and frequency determinations except for Al_2Cl_6 and $Al_2Cl_7^-$, whose zero-point energies and entropies were obtained from frequency calculations done at the MP2/3-21+G(d,p) level. The last four reactions, producing or requiring $ClHAl_2Cl_7^-$, use energy data from MP2/3-21+G(d,p) optimizations with zero-point energies and entropies taken from HF/3-21+G(d,p) frequency calculations. [b] Calculated using thermodynamic data from ref 31a. [c] Calculated using data from ref 40. [d] Calculated using thermodynamic data from ref 34. [e] Reference 3. [f] Reference 9.

$$2AlCl_3 \rightarrow Al_2Cl_6 \tag{5}$$

$$HCl + AlCl_3 \rightarrow HAlCl_4 \tag{6}$$

$$Al_2Cl_6 \rightarrow AlCl_4^- + AlCl_2^+ \tag{7}$$

Table 4 provides the equilibrium constants calculated from our thermodynamic data and compares them with literature data where that is available. In a mixture of $AlCl_3$−ImCl, equilibria 1, 2, and 5 govern the relative amounts or vapor pressures of the species—$AlCl_3$, $AlCl_4^-$, $Al_2Cl_7^-$, and Al_2Cl_6. Using the equilibrium constants shown in Table 4 for these reactions, it is possible to estimate the amounts of each molecule or ion arising from various initial concentrations of $AlCl_3$ and Cl^-

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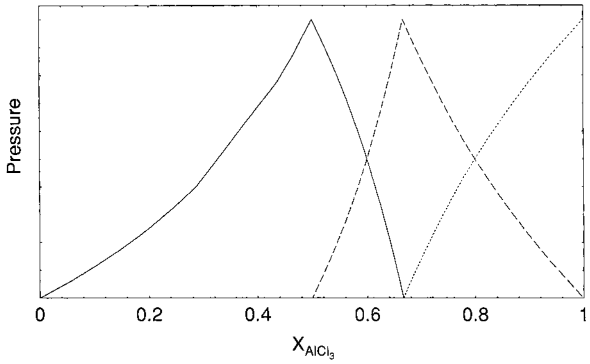

Figure 13. Partial presures (concentrations) of species as a function of the initial X_{AlCl_3} in an $AlCl_3$:Cl^- mixture: (—) $AlCl_4^-$; (- - -) $Al_2Cl_7^-$; (···) Al_2Cl_6.

(Figure 13). These results agree with the host of experimental evidence (vide supra) that under basic conditions, $0 < X_{AlCl3} \leq 0.5$, $AlCl_4^-$ is the predominant aluminum species. As the mixture becomes more acidic ($0.5 \leq X_{AlCl_3} \leq 0.67$), the $AlCl_4^-$ is replaced by $Al_2Cl_7^-$. Above an aluminum chloride mole fraction of 0.8, Al_2Cl_6 becomes the major species.

What happens when HCl is added to a $AlCl_3-Cl^-$ mixture depends on X_{AlCl_3} as well. In basic mixtures, evidence of reactions 8−11 ($\Delta G° = -72.5, -30.2, -21.4$, and -21.2 kJ/mol, respectively)[14] is expected. Under more acidic conditions,

$$HCl + Cl^- \rightarrow HCl_2^- \quad (8)$$

$$HCl + HCl_2^- \rightarrow H_2Cl_3^- \quad (9)$$

$$HCl + H_2Cl_3^- \rightarrow H_3Cl_4^- \quad (10)$$

$$HCl + H_3Cl_4^- \rightarrow H_4Cl_5^- \quad (11)$$

the predominant reactions are expected to include reactions 12 and 13,[9] with $\Delta G° = -9.9$ and -11.2 kJ/mol (Table 3). Using

$$HCl + AlCl_4^- \rightarrow ClHAlCl_4^- \quad (12)$$

$$HCl + Al_2Cl_7^- \rightarrow ClHAl_2Cl_7^- \quad (13)$$

the calculated values of $\Delta G°$ for these six reactions, it is possible to conclude that the strength of the potential bases increases in the order $Al_2Cl_7^- \leq AlCl_4^- < H_3Cl_4^- \cong H_2Cl_3^- < HCl_2^- \ll Cl^-$. Similarly, a comparison of reactions 1 ($\Delta G° = -295.7$ kJ/mol), 8 ($\Delta G° = -72.5$ kJ/mol), and 14 ($\Delta G° = -315.8$ kJ/mol) indicates that Lewis acidity increases in the order $HCl \ll AlCl_3 \leq Al_2Cl_6$.

$$Al_2Cl_6 + Cl^- \rightarrow Al_2Cl_7^- \quad (14)$$

The similarity of reactions 15−18 ($\Delta G° = -62.6, -61.3, -51.1$,[14] and -42.3 kJ/mol,[14] respectively) leads to the conclusion that as leaving groups in a nucleophilic substitution, $HCl_2^- < H_2Cl_3^- < Al_2Cl_7^- \leq AlCl_4^-$, Figures 12 and 13.

$$Cl^- + ClHAlCl_4^- \rightarrow AlCl_4^- + HCl_2^- \quad (15)$$

$$Cl^- + ClHAl_2Cl_7^- \rightarrow Al_2Cl_7^- + HCl_2^- \quad (16)$$

$$Cl^- + H_3Cl_4^- \rightarrow H_2Cl_3^- + HCl_2^- \quad (17)$$

$$Cl^- + H_2Cl_3^- \rightarrow 2HCl_2^- \quad (18)$$

Finally, the data of Tables 3 and 4 suggest, in agreement with the literature, that species such as $AlCl_2^+$ and $HAlCl_3^+$ are unlikely to be found in $AlCl_3$−ImCl mixtures, with or without added HCl. $HAlCl_4$ could exist in quite acidic mixtures but is unlikely if the Cl^- concentration is significant.

Summary

The structures, resulting from semiempirical, ab initio, and DFT energy minimizations, for nine aluminum- and chlorine-containing species agree well with experimental data and previous calculations where they are available. For all but $HAlCl_4$, $ClHAlCl_4^-$, $ClHAl_2Cl_7^-$, and $Al_2Cl_7^-$, the various computational methods predict the same basic structure. In the case of $HAlCl_4$, the optimized structure has a staggered conformation for the ab initio and DFT methods but an eclipsed conformation for the three semiempirical methods. MP2/6-311+G(d,p) and PM3 predict a staggered conformation for $ClHAlCl_4^-$, while the other methods suggest the C_s eclipsed structure to be the lowest energy. Nonetheless, the energy differences between the two conformations is small. With all but PM3, a C_2 minimum is obtained for $Al_2Cl_7^-$ and the conformation of Figure 6 is obtained for $ClHAl_2Cl_7^-$.

From a comparison of the thermodynamic data for 22 reactions involving these aluminum and chlorine species, we have shown that most methods, with the exception of PM3, give qualitatively similar results and that the data agree quite well with reported experimental or computational results. Our calculations confirm the observations for $AlCl_3$−ImCl mixtures, that under basic conditions $AlCl_4^-$ is the predominant aluminum species. As the mixture becomes more acidic, $AlCl_4^-$ is systematically replaced by $Al_2Cl_7^-$. We have also shown that above $X_{AlCl_3} = 0.8$, Al_2Cl_6 is dominant. Coupling the thermodynamic results from this investigation with data from a previous study indicates that in these solutions, base strength increases in the order $Al_2Cl_7^- \leq AlCl_4^- < H_3Cl_4^- \cong H_2Cl_3^- < HCl_2^- \ll Cl^-$. Acidity increases in the order $HCl \ll AlCl_3 \leq Al_2Cl_6$ and as leaving groups in a nucleophilic substitution $HCl_2^- < H_2Cl_3^- < Al_2Cl_7^- \leq AlCl_4^-$. Finally, the evidence from calculations confirms observations that species such as $AlCl_2^+$ and $HAlCl_3^+$ are unlikely to be found in $AlCl_3$−ImCl mixtures, although $HAlCl_4$ could exist in acidic solutions containing HCl.

In this paper we have presented what must be considered as the intrinsic thermodynamics of various equilibria involving aluminum and chlorine species. Work is continuing to show how that these gas-phase results can be applied to molten salts through studies at a variety of pressures and with different solvation models.

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