Thermochemistry of Iron Chlorides and Their Positive and Negative Ions

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The iron chlorides FeCl, $FeCl_2$, and $FeCl_3$ and their ions $FeCl^+$, $FeCl_2^+$, $FeCl^-$, $FeCl_2^-$, and $FeCl_3^-$ were investigated using MP2 and QCISD(T) calculations with double- and triple-ζ basis sets augmented with multiple sets of diffuse and polarization functions. The dissociation enthalpies for FeCl → Fe + Cl, $FeCl_2$ → FeCl + Cl, and $FeCl_3$ → $FeCl_2$ + Cl are predicted to be 82.5, 109.6, and 59.6 kcal/mol at 298.15 K, respectively. The calculated heats of formation of these species in the gas phase at 298.15 K are +45.3 kcal/mol for FeCl, −35.8 kcal/mol for $FeCl_2$, and −66.8 kcal/mol for $FeCl_3$. The calculated heat of formation of FeCl is 15 kcal/mol lower than the estimated value of +60.0 (±20.0) kcal/mol reported in the JANAF tables, but is in reasonably good agreement with a recent experimental determination (+49.5 ± 1.6 kcal/mol). The calculated ionization potential of FeCl is 7.89 eV and that of $FeCl_2$ is 10.10 eV. The electron affinities are 1.54 eV for FeCl, 0.99 eV for $FeCl_2$, and 3.90 eV for $FeCl_3$. Comparison of the bond dissociation enthalpies in $FeCl_n$, $FeCl_n^+$, and $FeCl_n^-$ reveals a preference for iron to exist in the +2 oxidation state (as $FeCl_2$, $FeCl^+$, or $FeCl_3^-$); this preference is also seen when comparing IPs and the EAs of the iron chlorides. We also evaluated the dissociation energies, IPs and EAs of the iron chloride species using the B3LYP version of density functional theory. Comparison to the high-level *ab initio* results shows that density functional theory with the large basis set is accurate to 5−10 kcal/mol for these species.

I. Introduction

The enthalpies, entropies, and free energies of formation of simple binary and ternary compounds are fundamental thermochemical data. The bond dissociation enthalpies (BDEs) and bond dissociation free energies (BDFEs) of these compounds are essential in understanding free radical reactions and other processes. We are particularly interested in the thermochemistry of the transition metals used in metallurgy and chemical processes. Iron is arguably one of the more important of these metals, so we begin with a study of the monomeric chlorides of that metal.

The iron chlorides $FeCl_3$, $FeCl_2$, and FeCl exhibit quite different thermal behaviors. $FeCl_3$ begins to decompose into $FeCl_2$ + Cl_2 at its melting point of 577 K. $FeCl_2$, on the other hand, has a high thermal stability and can be distilled unchanged at its normal boiling point of 1297 K. FeCl, though known spectroscopically[1] and listed in standard thermochemical reference works,[2,3] is unstable toward disproportionation and exists only in dilute gas phase. These facts suggest that as one successively adds chlorine atoms to iron, the first bond formed is relatively weak, the second bond (forming $FeCl_2$) is significantly stronger, and the third bond (forming $FeCl_3$) is again weak. The BDEs and BDFEs derived from published standard thermochemical data[3] are listed in Table 1.

Some theoretical work has been done previously on iron chlorides. Delaval and Schamps[4] have studied the electronic energy levels of FeCl at the SCF level. Bominaar et al.[5] have calculated the electronic energy levels and Mossbauer spectroscopic parameters of $FeCl_2$ at various levels of theory. Mishra et al.[6] have also calculated Mossbauer spectroscopic parameters of $FeCl_2$ at the SCF level, and Chou et al.[7] and Veal et al.[8] have calculated X-ray properties of $FeCl_2$ using density functional theory. Mandich et al.[9] have calculated the bond length and orbital structure of $FeCl^+$ at the SCF level. The species $FeCl_4^-$ has been the subject of several studies. Deeth et al.[10] have calculated its spin density and X-ray properties, Butcher et al.[11] have calculated its orbital structure and photoelectron spectrum, and Oliphant and Bartlett[12] have calculated its electronic energy levels. All three of these studies employed density functional theory to describe the $FeCl_4^-$ ion.

TABLE 1: Experimental Thermochemical Data on $FeCl_n(g)$[a]

species	T	ΔH_f	ΔG_f	BDE[b]	BDFE[c]
FeCl	298.15	+60.00	+51.54	68.29	62.26
	2000	+49.21	+9.93	70.44	22.67
$FeCl_2$	298.15	−33.70	−37.18	122.69	114.14
	2000	−42.73	−51.97	122.30	63.20
$FeCl_3$	298.15	−60.50	−59.24	55.79	47.48
	2000	−69.21	−48.00	56.84	−2.77

[a] From ref 3. Temperatures are in K; energy units are kcal/mol. [b] BDE is ΔH for the reaction $FeCl_n(g) \rightarrow FeCl_{n-1}(g) + Cl(g)$. [c] BDFE is ΔG for the reaction $FeCl_n(g) \rightarrow FeCl_{n-1}(g) + Cl(g)$.

We have performed high-level *ab initio* calculations on the neutral iron chlorides $FeCl_n$ ($n = 1-3$) and the corresponding anions with $n = 1-3$ and cations with $n = 1-2$. Our primary focus is on the bond dissociation enthalpies and free energies and the ionization potentials and electron affinities of these species. We compare the results of the high-level calculations with less-demanding levels of theory, and particularly with density functional theory. A brief description of the electronic structures of each species is given.

II. Methods

For most calculations we used a double-ζ-plus-polarization basis set, which we will refer to as the "WHsf" basis set. For

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TABLE 2: Calculated Electronic Energies in Hartrees

	MP2/WHsf	QCISD/WHsf	DFT/WHext	est-QCISD(T)/WHext//QCISD/WHsf
Fe(^{5}D)	−1262.925 13	−1262.542 99	−1263.640 54	−1262.944 70
Fe^+(^{6}D)	−1262.649 03	−1262.263 26	−1263.348 40	−1262.658 06
Cl	−459.623 16	−459.570 97	−460.186 40	−459.745 58
Cl^-	−459.740 79	−459.684 03	−460.303 71	−459.874 63
Cl_2	−919.310 86	−919.200 02	−920.424 71	−919.582 05
FeCl	−1722.679 20	−1722.237 62	−1723.938 93	−1722.821 58
$FeCl_2$	−2182.470 90	−2181.973 62	−2184.280 79	−2182.742 74
$FeCl_3$	−2642.165 21	−2642.639 62	−2644.531 84	−2642.583 72
$FeCl^+$	−1722.385 73	−1721.951 94	−1723.650 39	−1722.531 62
$FeCl_2^+$	−2182.082 43	−2181.620 15[a]	−2183.906 73	−2182.371 40[b]
$FeCl^-$	−1722.720 48	−1722.289 78	−1724.006 72	−1722.877 99
$FeCl_2^-$	−2182.503 18	−2182.005 51	−2184.316 83	−2182.779 03
$FeCl_3^-$	(−2641.629 48)[c]		−2644.683 67	−2652.727 09[d]

[a] At BD(T)/WHsf. [b] See Methods. [c] At MP3(fc)/WH. [d] At est-QCISD(T)/WHext//MP3(fc)/WH.

iron, this is based on the Wachters primitive basis set[13] (14s11p5d), which was contracted to [8s6p2d]. To this were added the diffuse d function optimized by Hay[14] and the diffuse s and three f functions added by Raghavachari and Trucks,[15] making a basis set of (15s11p6d3f) primitives contracted to [9s6p3d3f]. A basis set using the same primitives (but contracted differently) has been used to reproduce the excitation energy and ionization potential of iron.[15,16] For chlorine, the Dunning−Huzinaga double-ζ basis set[17] was augmented with a set of diffuse s and p functions[18] and a set of polarization d functions.[19] This basis set consists of (13s9p1d) primitives contracted to [7s5p1d]. The WHsf basis set has 63 functions per iron atom and 27 functions per chlorine atom. We occasionally made use a somewhat smaller basis set (WH), which for iron consists of the Wachters primitive basis set, contracted as in WHsf, and the Hay d function; for chlorine the same functions are used as in the WHsf basis set. Some single-point calculations were performed using a larger basis set, which will be referred to as the "WHext" basis set. This consists of the WHsf basis set for iron augmented by two additional diffuse d functions (exponents 0.028 325 and 0.007 081) and the 6-311+G(3df) basis set of chlorine. For iron the WHext basis set is (15s11p8d3f) contracted to [9s6p5d3f], and for chlorine it is (14s11p3d1f) contracted to [7s6p3d1f]. This is 73 basis functions per iron atom and 47 per chlorine atom.

One of the difficulties in studying transition metal species is to determine the proper spin state. According to ligand-field theory, complexes with only a few ligands (and thus having only a weak "ligand field") should have high-spin ground states: quintet for Fe(II) and Fe(0), sextet for Fe(III) and Fe(I). Thus, we have studied $FeCl_2$, $FeCl^{\pm}$, and $FeCl_3^-$ in their quintet states and FeCl, $FeCl_3$, and $FeCl_2^{\pm}$ in their sextet states. $FeCl_2$ has been shown to exist in the $^5\Delta$ state[5] and FeCl in the $^6\Delta$ state.[4] To test the quality of the wave functions, we performed a stability test of each wave function and examined S^2 for signs of spin contamination. Each species proved to have a stable wave function, and with one exception ($FeCl^-$, $S^2 = 6.11$) the S^2 were within ± 0.02 of their proper value of $S(S+1)$, where $2S+1$ is the spin multiplicity of the species.

Calculations were performed using development versions of GAUSSIAN 94.[20] The procedure used for each species was to optimize the geometry and calculate the frequencies at MP2-(full)/WHsf and then to optimize at the QCISD/WHsf level of theory. At the QCISD/WHsf geometry, single-point calculations were performed at QCISD(T)/WHsf and at MP2(full)/WHext. The reaction energy at 0 K is taken to be the QCISD(T)/WHsf reaction energy plus the difference between the MP2/WHext and MP2/WHsf energies, calculated at the QCISD/WHsf geometries. This should be a very good estimate of the QCISD-(T)/WHext//QCISD/WHsf energy since the effect of the larger basis set (WHext vs WHsf) and the effect of the higher correlation method (QCISD(T) vs MP2) are very nearly additive.[21] The ionization potential (IP) of Fe was used as a test of accuracy. At this level of theory (hereafter referred to as est-QCISD(T)/WHext//QCISD/WHsf) the IP is 7.80 eV; applying the relativistic correction of 0.06 eV determined by Martin and Hay[22] gives 7.86 eV, so that the difference between our highest level of theory and the experimental value of 7.90 eV is only 0.04 eV (1 kcal/mol). Electronic energy levels of the molecules and ions of interest are provided in Table 2.

$FeCl_2^+$ received a different treatment since the high NORM-(A) values[23] (in excess of 2.0) in the QCISD calculation indicated that the molecule was not adequately described at this level of theory. Examination of the principal contributions to the QCISD wave function showed that configurations other than the Hartree−Fock ground state are important in $FeCl_2^+$. Since most of the principal non-ground-state configurations were single excitations, it was anticipated that Brueckner doubles (BD)[24] would provide a more adequate description of the ion. The BD wave function is closely related to the QCISD wave function, but differs in that the contribution of single excitations is eliminated by explicit transformation of the orbitals. Hence, in the BD model the orbitals relax in the presence of dynamic correlation through double excitations. We used the BD(T) model, which includes a perturbational correction for triple excitations. The NORM(A) values for the BD(T) calculation of $FeCl_2^+$ were quite reasonable (around 1.1). Therefore, we optimized the geometry of $FeCl_2^+$ numerically at the BD(T)/WHsf level of theory. To evaluate the energies of reactions involving $FeCl_2^+$, we also evaluated the BD(T)/WHsf energy of $FeCl_2$ at the QCISD/WHsf geometry. The est-QCISD(T)/WHext//QCISD/WHsf energy of $FeCl_2^+$, used to calculate energies of all reactions involving this ion, was defined to be (E[$FeCl_2$, QCISD(T)//QCISD/WHsf] + IP[$FeCl_2$, BD(T)/WHsf]) + (E[$FeCl_2^+$, MP2/WHext//BD(T)/WHsf] − E[$FeCl_2^+$, MP2/WHsf//BD(T)/WHsf]). The first term provides an energy of $FeCl_2^+$ which can be compared to the QCISD(T)/WHsf energies of the other species; the second term is the basis set correction. Equivalently, the est-QCISD(T)/WHext//QCISD/WHsf energy of $FeCl_2^+$ can be expressed as E[$FeCl_2$, est-QCISD(T)/WHext//QCISD/WHsf] + IP[$FeCl_2$, BD(T)/WHsf] + (IP[$FeCl_2$, MP2//WHext] − IP[$FeCl_2$, MP2/WHsf]). We also performed BD(T)/WHsf//QCISD/WHsf calculations on Fe and FeCl. The calculated D_e values (kcal/mol) for Fe−Cl (78.2) and FeCl−Cl (105.2) at BD(T)/WHsf//QCISD/WHsf are essentially the same as the D_e values calculated at QCISD(T)/WHsf//QCISD/WHsf (78.5 and 105.6, respectively).

For $FeCl_3^-$ the geometry and frequencies were obtained at MP2(fc)/WH because of the large size of this anion. Single-point QCISD(T)/WHsf and MP2(full)/WHext calculations were then performed at this geometry. For $FeCl^-$ the difference in the bond lengths calculated at MP2(fc)/WH and QCISD/WHsf is 0.09 Å. Since the calculated force constant for the symmetric Fe−Cl stretch in $FeCl_3^-$ is 0.318 32 hartree/Bohr,[2] a similar error in the Fe−Cl bond length in $FeCl_3$ would lead to an error in energy of approximately 0.005 hartree or 3 kcal/mol.

Using the thermal energies and entropies obtained from the unscaled MP2/WHsf frequency calculations, the 0 K energies were converted to enthalpies and free energies at 298.15 and 2000 K. The thermal energies were computed as the sum of translational, rotational, and vibrational (including zero-point energy) contributions; the entropies were computed as the sum of transitional, rotational, vibrational, and electronic contributions. Standard formulas for an ideal gas in the canonical ensemble,[25] using the rigid-rotor and harmonic-oscillator approximations, were employed in the calculations. For monatomic species, the only contribution to the thermal energy is translational; for the entropy, there is a translational contribution and an electronic contribution. Spectroscopically derived electronic energy levels[26] were used in the calculations of the electronic entropy of the open-shell monatomic species. The levels in the ^{5}D (ground, 415.933, 704.003, 888.132, and 978.074 cm^{-1}) and ^{5}F (6928.280, 7376.775, 7728.071, 7985.795, and 8154.725 cm^{-1}) terms of Fe, the ^{6}D (ground, 384.77, 667.64, 862.63, and 977.03 cm^{-1}), ^{4}F (1872.60, 2430.08, 2837.94, and 3117.48 cm^{-1}), and ^{4}D (7955.24, 8392.92, 8680.47, and 8846.76 cm^{-1}) terms of Fe^+, and the ^{3}P (ground, 881 cm^{-1}) term of Cl were included in the entropy calculation. Literature electronic energy levels are also available for FeCl[4] and $FeCl_2$,[27] and these were used in the calculation of the entropy of these species. For FeCl the $^6\Delta$ (ground), $^6\Sigma$ (1211 cm^{-1}), and $^6\Pi$ (2515 cm^{-1}) states were included in the entropy calculation; for $FeCl_2$ the $^5\Delta$ (ground), $^5\Pi$ (4800 cm^{-1}), and $^5\Sigma$ (7140 cm^{-1}) states were included. $FeCl_3$ is not expected to have excited states low enough to contribute significantly to the entropy since the corresponding ion, $^6Fe^{3+}$, has a half-filled (d^5) arrangement. Thus, neglect of the entropy due to electronic excitations should be valid for this molecule. The entropy due to electronic excitations was neglected for the ionic iron halide species as well. The entropies for these species at 298.15 K should be accurate since electronic excitations accounted for 0.02 and <0.01 cal mol^{-1} K^{-1} for FeCl and $FeCl_2$, respectively, at this temperature.[28] At 2000 K electronic excitations still contribute only 1.3 and 0.3 cal mol^{-1} K^{-1} to the entropies of FeCl and $FeCl_2$, respectively, so the entropies of the ionized iron halides should be at worst underestimated by 1−2 cal mol^{-1} K^{-1}.

To determine the performance of density functional theory on these species, we performed calculations using the B3LYP hybrid density functional[29] with the WHext basis set. Density functional methods provide results at a fraction of the cost of explicit electron-correlation methods (for $FeCl^+$ QCISD/WHsf required 166 min per optimization cycle and 745 Mbyte of disk space; B3LYP/WHext required only 19 min per cycle and 128 Mbyte of disk space), but to date only a few key examples of nonlocal density functional theory calculations have been reported for iron compounds.[30] Comparison of density functional theory results to those from higher level calculations will be discussed in the followng section.

III. Results and Discussion

A. Geometries. The bond length in $FeCl_2$ has been measured in the gas phase by Hargittai et al.;[31] our theoretical bond length of 2.144 Å is in good agreement with the experimental value of 2.151 Å. The calculated vibrational frequencies (unscaled) in this molecule (86, 362, and 528 cm^{-1}) are in agreement with the experimentally determined frequencies (88, 350, and 492 cm^{-1}) listed in that work. The calculated geometries for the neutral and ionized iron chlorides are presented in Table 3.[32] The vibrational frequencies, zero-point and thermal energies, and standard entropies at 298.15 and 2000 K for these species are given in Table 4. The number of chlorines attached to the iron has very little effect on the Fe−Cl bond length. This is contrary to what one would expect from an ionic model of the bonding in these compounds, which would predict shorter bond lengths due to increased electrostatic attraction as the charge on the central atom increases. Neutral FeCl is an exception in that it does not have a somewhat longer bond length than $FeCl_2$ and $FeCl_3$. There is, in contrast, a marked dependence of the bond length on the charge of the system: as one goes from $FeCl^-$ to FeCl to $FeCl^+$, the Fe−Cl distances become shorter by approximately 0.1 Å per electron. Although $FeCl_2$ is linear, both $FeCl_2^+$ and $FeCl_2^-$ are significantly distorted from linearity, with a bond angle of 144° for the cation and 110° for the anion. $FeCl_3$ and $FeCl_3^-$ are trigonal planar. The geometries change little on going from MP2/WHsf or B3LYP/WHext to QCISD/WHsf.

TABLE 3: Ground Electronic States and Equilibrium Geometries[a]

	state	symm	R_{Fe-Cl}	$\angle_{Cl-Fe-Cl}$
FeCl	$^6\Delta$	$C_{\infty v}$	2.179[b] (2.168[c] 2.196[d])	
$FeCl_2$	$^5\Delta$	$D_{\infty h}$	2.143[b] (2.129[c] 2.128[d])	180.0
$FeCl_3$	$^6A'_1$	D_{3h}	2.144[b] (2.105[c] 2.144[d])	120.0
$FeCl^+$	$^5\Delta$	$C_{\infty v}$	2.068[b] (2.056[c] 2.063[d])	
$FeCl_2^+$	$^6A_1$	C_{2v}	2.053[e] (2.028[c] 2.074[d])	144.4[e] (149.8[c] 141.4[d])
$FeCl^-$	$^5\Delta$	$C_{\infty v}$	2.266[b] (2.250[c] 2.280[d])	
$FeCl_2^-$	$^6A_1$	C_{2v}	2.272[b] (2.260[c] 2.298[d])	110.4[b] (110.1[c] 110.8[d])
$FeCl_3^-$	$^5A'_1$	D_{3h}	2.272[f]	120.0

[a] Distances are in angstroms, and angles are in degrees. [b] QCISD/WHsf. [c] MP2/WHsf. [d] B3LYP/WHsf. [e] BD(T)/WHsf. [f] MP2(fc)/WH, where "WH" is the Wachters−Hay basis set without the added s and f functions.

TABLE 4: Calculated (MP2/WHsf) Vibrational Frequencies (Unscaled), Zero-Point Energies (ZPEs), Thermal Energies, and Entropies at 298.15 K and at 2000 K[a]

	frequencies	*ZPE*	$E^{th}_{298.15}$	E^{th}_{2000}	$S_{298.15}$	S_{2000}
Fe			0.89	5.96	42.35	53.84
Fe^+			0.89	5.96	42.56	54.20
Cl			0.89	5.96	39.34	49.60
Cl^-			0.89	5.96	36.59	46.04
Cl_2	518	0.66	1.70	13.29	53.34	69.93
FeCl	409	0.58	1.67	13.36	61.50	78.23
$FeCl_2$	86,[b] 362, 528	1.52	2.78	24.39	71.22	98.88
$FeCl_3$	108, 113,[b] 399, 513[b]	2.51	3.59	33.38	81.62	118.24
$FeCl^+$	516	0.74	1.61	13.22	60.56	77.15
$FeCl_2^+$	63, 471, 633	1.67	2.53	22.28	72.96	98.45
$FeCl^-$	292	0.42	1.75	13.51	61.85	78.72
$FeCl_2^-$	116, 321, 350	1.13	2.69	22.76	74.83	100.88
$FeCl_3^-$	95,[b] 123, 283, 370[b]	1.91	3.85	33.93	83.59	120.73

[a] Frequencies are in cm^{-1}, ZPEs and thermal energies are in kcal/mol, and entropies are in cal/(mol K). [b] Doubly degenerate.

B. Bond Energies. The energies required to break the Fe−Cl bonds in the iron chlorides and their ions are displayed in Table 5. Dissociation energies may be measured from the minimum of the potential surface (D_e) or from the ground vibrational state (D_0). D_0 is equal to the bond dissociation enthalpy at 0 K. The BDEs change by less than 1 kcal/mol on going from 0 to 298.15 K and change only by 1−3 kcal/mol on going to 2000 K. The BDE of the Cl−Cl bond (experi-

TABLE 5: Calculated[a] Dissociation Energies (D_e and D_0), Bond Dissociation Enthalpies (BDE), and Bond Dissociation Free Energies (BDFE) for Fe−Cl and Cl−Cl Bonds[b]

bond	D_e	D_0	$BDE_{298.15}$	BDE_{2000}	$BDFE_{298.15}$	$BDFE_{2000}$
Cl−Cl	57.0	56.4	57.1	59.0	49.5	0.8
Fe−Cl	82.4	81.8	82.5	84.4	76.3	36.6
ClFe−Cl	110.2	109.2	109.6	108.2	100.8	48.4
Cl_2Fe−Cl	59.9	58.9	59.6	59.8	50.9	−1.1
Fe^+−Cl	80.3	79.6	80.3	82.3	73.7	27.4
$ClFe^+$−Cl	59.1	58.2	58.7	59.0	50.7	2.6
Fe−Cl^-	36.8	36.4	37.0	38.8	31.7	−3.6
ClFe−Cl^-	52.0	51.4	51.9	53.8	44.9	2.5
Cl_2Fe−Cl^-	68.9	68.5	68.9	68.9	61.7	19.9

[a] At est-QCISD(T)/WHext//QCISD/WHsf, except as noted in Methods. [b] Energy units are kcal/mol.

TABLE 6: Effect of Level of Theory on Dissociation Energies (D_e) of Iron Chlorides and Cl_2

	D_e (kcal/mol)			
	MP2/ WHsf	QCISD/ WHsf	DFT/ WHext	est-QCISD(T)/WHext[a] //QCISD/WHsf
Cl−Cl	40.51	36.93	55.16	57.03
Fe−Cl	82.15	77.84[b]	81.57	82.39
ClFe−Cl	105.76	98.08[b]	108.84	110.18
Cl_2Fe−Cl	44.65	59.34	51.86	59.86
Fe^+−Cl	71.25	74.11	83.83	80.31
$ClFe^+$−Cl	46.15		55.18	59.11[c]
Fe−Cl^-	34.24	39.38	39.20	36.81
ClFe−Cl^-	52.20	52.62	46.55	51.97

[a] E[est-QCISD(T)/WHext] = E[QCISD(T)/WHext] − (E[MP2/ Whext] − E[MP2/WHsf]). [b] At BD(T)/WHst//QCISD/WHsf the D_e of Fe−Cl is 78.22 and the D_e of FeCl−Cl is 105.24. [c] See methods.

mentally 58.0 kcal/mol at 298.15 K and 60.7 kcal/mol at 2000 K)[3] is well produced (calculated 57.1 kcal/mol at 298.15 K and 59.0 kcal/mol at 2000 K). The larger 6−311+G(3df) basis set used in the WHext is required to reproduce this BDE; use of the D95+(d) basis set (WHsf) leads to a gross underestimation of the Cl−Cl dissociation energy (see Table 6). The BDEs of the Fe−Cl bond vary widely, from 37.0 kcal/mol for the bond in $FeCl^-$ to 109.6 kcal/mol for the bond in $FeCl_2$. As implied by the thermal behavior of the iron chlorides, the ClFe−Cl bond is stronger than the Fe−Cl bond, and the Cl_2Fe−Cl bond is much weaker than the ClFe−Cl bond. The calculated D_e's depend strongly on the level of theory used (Table 6). The B3LYP/WHext method actually performs better than QCISD/ WHsf for many of these dissociation energies, showing not only the utility of density functional theory for these species but also the importance of using the larger basis set with multiple polarization functions on these molecules. Even in the worst cases, B3LYP/WHext appears to be accurate to 5−10 kcal/mol. The anions tend to have weak Fe−Cl bonds, reflecting the population of an antibonding orbital by the additional electron; the bonds in the cations are not significantly weakened. Entropy is important at elevated temperatures: at 2000 K many of the species become unbound or nearly so, having BDFEs near or below zero.

C. Ionization Potentials. Adiabatic ionization potentials (IP) and electron affinities (EA) are tabulated in Table 7. The calculated IP of Fe (7.80 eV) deviates from the experimental IP (7.90 eV) by 0.10 eV (2.3 kcal/mol); 0.06 eV of this difference is ascribed to relativistic effects, as described above in the Methods section. The calculated EA of Cl(3.51 eV) differs from the experimental EA (3.61 eV) also by 0.10 eV. We calculate an IP of 7.89 eV for FeCl and an IP of 10.10 eV for $FeCl_2$. Schoonmaker and Porter[33] in their mass spectroscopic study of $FeCl_2$ report an appearance potential of 11.5 ± 0.5 for $FeCl_2^+$ and an appearance potential of 12.8 ± 0.5 for $FeCl^+$.

TABLE 7: Adiabatic Ionization Potentials (IP) and Electron affinities (EA) in eV

	MP2/ WHsf	QCISD/ WHsf	DFT/ WHext	est-QCISD(T)/WHext[a] //QCISD/WHsf	expt
Fe (IP)	7.51	7.61	7.95	7.80	7.90
FeCl (IP)	7.99	7.77	7.85	7.89	≤8.08 ± 0.10[b]
$FeCl_2$ (IP)	10.57		10.18	10.10[c]	≤10.34[d]
FeCl (EA)	1.12	1.42	1.84	1.54	
$FeCl_2$ (EA)	0.88	0.87	0.98	0.99	
$FeCl_3$ (EA)			4.13	3.90[e]	
Cl (EA)	3.20	3.09	3.68	3.51	3.61

[a] E[est-QCISD(T)/WHext] = E[QCISD(T)/WHsf] + (E[MP2/ WHest] − E[MP2/WHsf]). [b] Reference 32. [c] See Methods. [d] Reference 34. [e] Anion at MP2(fc)/WH geometry.

The $FeCl_2^+$ appearance potential is an experimental upper bound for the IP of $FeCl_2$. Since the $FeCl^+$ is formed by the process [$e^- + FeCl_2 \rightarrow FeCl^+ + Cl + 2e^-$], the appearance potential is an upper bound for the ΔE of this reaction, which is equal to D_0(ClFe−Cl) + IP(FeCl). Assuming our calculated D_0(ClFe−Cl) is correct, the upper bound for IP(FeCl) is thus 8.1 ± 0.5 eV. In a more recent mass spectrometric study by Hildenbrand[34] the appearance potential for $FeCl_2^+$ is 10.63 ± 0.10 eV and the appearance potentials for $FeCl^+$ were 12.6 ± 0.03 eV from $FeCl_2$ and 8.08 ± 0.10 eV from FeCl. Using the datum with the smaller uncertainty, we thus have 8.08 ± 0.10 eV as an upper bound for the IP of FeCl. Berkowitz et al.[35] and Lee et al.[36] have independently measured the vertical ionization potential of $FeCl_2$ by photoelectron spectroscopy to be 10.45 and 10.34 eV, respectively; the vertical IP is also an upper bound for the adiabatic IP which we calculate. The positive EAs for FeCl, $FeCl_2$, and $FeCl_3$ indicate that all three of the corresponding anions are bound in the gas phase. The IPs of EAs calculated at MP2/WHsf and QCISD/WHsf are approximately as accurate as the D_e's; that is, they differ from the est-QCISD-(T)/WHext//QCISD/WHsf values by 5−10 kcal/mol or 0.2−0.4 eV. However, MP2/WHsf severely underestimates the EA of FeCl 1.12 vs 1.54 eV at est-QCISD(T)/WHext//QCISD/ WHsf).[37] B3LYP/WHext overestimates the EA of FeCl (1.84 eV), despite its good agreement with est-QCISD(T)/WHext// QCISD/WHsf on the EA of $FeCl_2$ and the IP of FeCl.

D. Thermochemistry. From the calculated BDEs and BDFEs of the iron chlorides and of Cl_2 and the experimental ΔH_{vap} and ΔS_{vap} of iron, which are 99.30 kcal mol^{-1} and 36.62 cal mol^{-1} K^{-1} at 298.15 K and 89.28 kcal mol^{-1} and 28.96 cal mol^{-1} K^{-1} at 2000 K,[3] it is possible to obtain enthalpies and free energies of formation for the iron chlorides using a thermodynamic cycle. The same can be done for the ions provided a standard state for charge can be agreed upon. The thermal electron convention, in which the free electron is taken as a standard state ($\Delta H_f(e^-) = 0$ and $\Delta G_f(e^-) = 0$), is used here.[38] Table 8 shows the heat capacities at constant pressure (C_p), standard entropies (S), heats of formation (ΔH_f), and free energies of formation (ΔG_f) of the iron chlorides at selected temperatures. For the ΔH_{vap} and ΔS_{vap} of iron, the experimental values at each temperature were used. It should be noted that the standard state of iron changes with the temperature: at 298.15 K the solid α phase is the standard state for iron, and at 2000 K the liquid phase is the standard state.

The calculated thermochemical parameters for $FeCl_2$ are in excellent agreement with experiment; the calculated heat of formation of $FeCl_3$ is 5−6 kcal mol^{-1} too low, but the entropy and heat capacity are in good agreement. The discrepancy for FeCl deserves some explanation. Since no accurate thermochemical data were available for FeCl due to its instability, an educated guess of +60.0 ± 20.0 kcal mol^{-1} for the heat of formation of FeCl at 298.15 K was used in the JANAF tables.[2]

TABLE 8: Heat Capacities (C_p), Standard Entropies (S), Heats of Formation (ΔH_f), and Free Energies of Formation (ΔG_f) of Iron Chlorides in the Gas Phase[a] (Experimental Values (Ref 3) Are Given in Parentheses for Comparison)

	T (K)	C_p	S	ΔH_f	ΔG_f
FeCl	298.15	8.41	61.5	+45.3	+36.9
		(9.16)	(61.6)	(+60.0)	(+51.5)
	2000	8.93	79.6	+34.4	−4.9
		(9.60)	(79.6)	(+49.2)	(+9.9)
$FeCl_2$	298.15	13.61	71.2	−35.8	−39.2
		(13.76)	(71.5)	(−33.7)	(−37.2)
	2000	14.87	99.2	−44.2	−52.9
		(15.75)	(99.6)	(−42.7)	(−52.0)
$FeCl_3$	298.15	17.69	81.6	−66.8	−65.3
		(18.56)	(82.3)	(−60.5)	(−59.2)
	2000	19.81	118.2	−74.6	−51.4
		(19.84)	(119.4)	(−69.2)	(−48.0)
$FeCl^+$	298.15	8.17	60.56	+227.3	+219.2
	2000	8.92	77.15	+216.4	+181.9
$FeCl_2^+$	298.15	12.20	72.96	+197.1	+193.2
	2000	13.86	98.18	+186.9	+179.6
$FeCl^-$	298.15	8.64	61.85	+9.8	+1.3
	2000	8.94	78.72	−1.0	−38.6
$FeCl_2^-$	298.15	13.09	74.83	−59.1	−63.5
	2000	13.89	100.88	−69.0	−81.1
$FeCl_3^-$	298.15	18.56	83.59	−157.1	−156.2
	2000	19.84	120.73	−164.6	−146.4

[a] Units are kcal mol^{-1} K^{-1} as appropriate. For ions the thermal electron convention is used.

Subsequent compilations of thermochemical data (e.g. ref 3) have quoted the JANAF values. Our calculations show that this estimate was approximately 15 kcal mol^{-1} too high, and the enthalpies and free energies should be adjusted accordingly. In contrast, the JANAF enthalpic data for $FeCl_2$ and $FeCl_3$ are based on actual experimental measurements, and the experiments are in agreement with each other to ±1 kcal mol^{-1}. Spin−orbit coupling accounts for 1.15 kcal/mol of the difference between experimental and calculated heats of formation of $FeCl_3$(g). The calculated heat of formation is based on the reaction $Fe(g) + {}^3/_2Cl_2(g) \rightarrow FeCl_3(g)$, and spin−orbit coupling lowers the energy of the Fe atom by 1.15 kcal/mol,[39] whereas the spin−orbit coupling energies of Cl_2 and $FeCl_3$ are zero since a molecule in a nondegenerate electronic state has zero orbital angular momentum.[40] The experimental determination of the heat of formation of gas phase $FeCl_3$ is complicated because dimerization and decomposition to $FeCl_2$ must be taken into account. The difference between the calculated and experimental heat of formation of $FeCl_3$ may reflect these difficulties.

It is of interest to compare the *average* bond strengths of the iron chlorides. This is the ΔH for the reaction $[FeCl_n(g) \rightarrow Fe(g) + nCl(g)]$, divided by n. The average bond strengths (at 298.15 K) are 82.5 kcal mol^{-1} for FeCl, 96.1 kcal mol^{-1} for $FeCl_2$, and 83.8 kcal mol^{-1} for $FeCl_3$. The bonds in $FeCl_3$ and FeCl have essentially the same strength; the bonds in $FeCl_2$ are significantly stronger. Thus, the low BDE for Cl_2Fe-Cl is due not to the third Fe−Cl bond being particularly weak but to the gain in strength in the two remaining Fe−Cl bonds. Weakening of bonds on going from 2- to 3-coordination has been observed in anionic and cationic iron carbonyls;[41] there it is attributed to the loss of sd hybridization, which lessens the repulsion between the σ-bonding and unpaired Fe electrons, on going from the 2-coordinate to the 3-coodinate species. With the carbonyl complexes, however, the bond strengths in the 1-coordinate and 2-coordinate species are nearly equal. Moreover, the BDE in $FeCl_3^-$ (68.9 kcal/mol) is *greater* than in $FeCl_2^-$ (51.9 kcal/mol), indicating a *strengthening* of the bonds on going from 2- to 3-coordination. It is clear that the oxidation state of the iron (which is kept constant in the iron carbonyl series) is a more important factor in determining bond strenghts to iron. The strongest Fe−Cl bonds in the cation series are in $FeCl^+$ (80.3 vs 69.5 for $FeCl_2^+$), and the strongest Fe−Cl bonds in the anion series are in $FeCl_3^-$, both of which like $FeCl_2$ contain an Fe(II).

E. Electronic Structure. The electronic structures of the iron chlorides also show the influence of the oxidation state. The ground electron configurations of Fe, Fe^+, Fe^{2+}, and Fe^{3+} are s^2d^6, s^1d^6, s^0d^6, and s^0d^5, respectively.[26] The polar covalent bond in FeCl is primarily formed from the 4s orbital of Fe—the orbital that loses an electron on ionization to Fe^+—and the $3p_z$ orbital of Cl. Since the Fe 4s orbital has double occupancy and the Cl 3p has single occupancy, a two-center three-electron bond is formed (Figure 1). The Fe 3d orbitals participate little in the bonding since they are much lower in energy than the Fe 4s and Cl 3p orbitals and much higher in energy than the Cl 3s orbital. In forming the ions $FeCl^+$ and $FeCl^-$, it is the 4s−3p antibonding orbital that gains or loses an electron, just as the 4s orbital is the one changing in occupancy on going from Fe^+ to Fe or Fe^{2+}. Thus, $FeCl^+$ has a "normal" two-electron bond, and there is little covalent bonding in $FeCl^-$. This is in accord with the vibrational frequencies (516, 409, and 292 cm^{-1}) in $FeCl^+$, FeCl, and $FeCl^-$, and with the low BDE of $FeCl^-$. However, despite the higher bond order in $FeCl^+$ and the ion/induced dipole attraction that should contribute to the binding energy of $FeCl^+$, the D_0 of $FeCl^+$ is approximately the same as that of FeCl. This again shows the preference of iron for the +2 oxidation state. In all three of these species the single Fe spin-β 3d electron is in a δ orbital.

The dichloride, $FeCl_2$, has an electronic structure similar to FeCl. The Fe 4s and the symmetric combination of the Cl $3p_z$ orbitals form one bond, which is now a two-electron bond since the two $3p_z$ electrons of the Cl atoms go into the antisymmetric combination of the orbitals (Figure 1). $FeCl_2$ has stronger bonds than FeCl because unlike in FeCl the antibonding orbital in $FeCl_2$ is unoccupied. The Fe spin-β 3d electron is in a δ orbital. $FeCl_2^+$ is not well described by a single-reference wave function. The principal configurations are obtained by removing an electron from either the 3dδ orbital on Fe or one of the lone-pair orbitals on Cl. In $FeCl_2^-$, the added electron goes into a diffuse orbital with antibonding character. The Fe spin-β 3d electron occupies an orbital of a_1 symmetry. In $FeCl_3$ three two-center two-electron bonds are formed using the Fe 4s and Cl 3p orbitals. Two of the six electrons come from the 4s orbital of the iron atom, three come from the chlorine atoms, and the remaining electron has been promoted from the iron 3d block. The Cl_2Fe-Cl bond is presumably weakened due to the energetic cost of this promotion. On reduction of $FeCl_3^-$, the additional electron goes back into the iron d block, more specifically into the spin-β $3d_0$ orbital. The energy of promoting the electron from the Fe 3d orbital is thus partially regained, and as a result, the EA of $FeCl_3$ (3.90 eV) is greater than those of $FeCl_2$ (0.99 eV) and FeCl (1.54 eV).

IV. Conclusion

The geometries, electronic structures, and thermochemistry of iron chlorides and the corresponding cations and anions were calculated using a high-level *ab initio* procedure. The calculated bond dissociation energies (82.5 kcal/mol for $FeCl \rightarrow Fe + Cl$, 109.6 kcal/mol for $FeCl_2 \rightarrow FeCl + Cl$, and 59.6 kcal/mol for $FeCl_3 \rightarrow FeCl_2 + Cl$ at 298.15 K) are in accord with the thermal behavior of these compounds. Although the heat of formation of $FeCl_2$ is in good agreement with experiment, the ΔH_f of FeCl is 15 kcal/mol lower than the value found in standard reference works. Since the reference value was based on an estimate rather than on precise experimental measurements, we believe

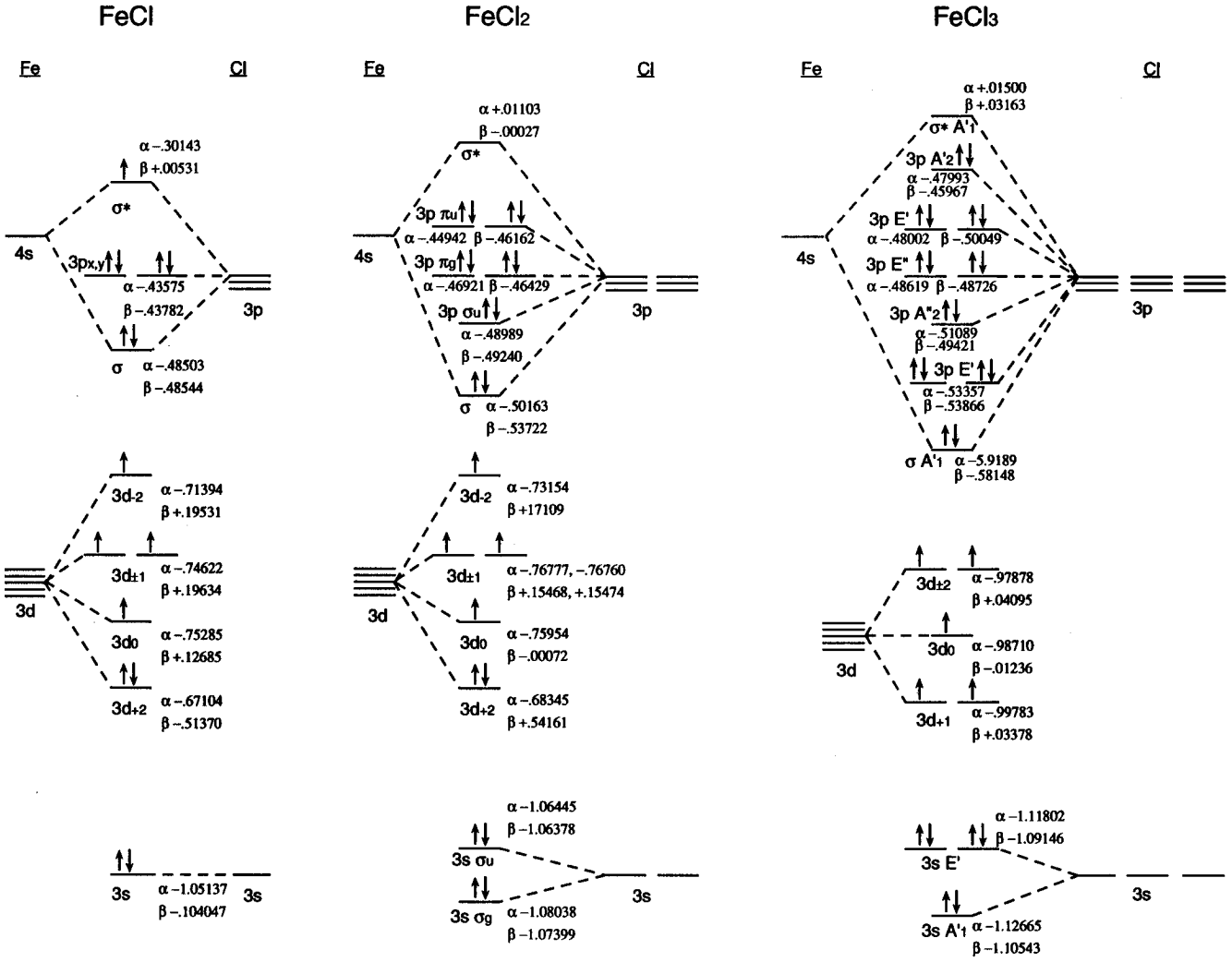

Figure 1. Orbital diagrams for FeCl, $FeCl_2$, and $FeCl_3$. UHF/WHsf orbital energies (hartrees) are given for the α and β orbitals.

that our computationally derived ΔH_f (+45.3 kcal/mol at 298.15 K) is close to the correct value.

Oxidation number appears to be an important factor in the thermochemistry of iron halides. Reactions (such as a bond dissociation or an ionization) in which iron enters a +2 oxidation state are more favorable than corresponding reactions in which iron enters a +3, +1, or 0 oxidation state. For example, the EA of $FeCl_3$ is 3.90 eV, whereas the EAs of $FeCl_2$ and FeCl are 0.99 and 1.54 eV, respectively. In comparison of bond dissociation energies of neutral ligands such as CO, the coordination number (hybridization) has been found to be important, especially on going from two to three ligands.[37] We were unable to observe a significant coordination-number effect in the iron chloride system because the oxidation-state effect is much stronger. Examination of the Hartree−Fock wave function reveals that in the Fe(I) and Fe(0) species at least one electron is placed in an antibonding orbital, whereas in the Fe(II) species all electrons are placed in bonding or nonbonding orbitals. In the Fe(III) species an electron has been promoted from the relatively low-lying iron 3d block, which results in an increase in energy.

We have examined the performance of lower levels of theory in comparison to the QCISD(T) method used for the thermochemical calculations. It was found that the MP2 geometries were quite similar to the QCISD geometries, so that little error would be introduced in evaluating the energies at the MP2 geometries. Density functional theory performed well with the iron chloride species: the B3LYP geometries were also similar to the QCISD geometries, and the energies (using the largest basis set) were accurate at least to 5−10 kcal/mol (0.2−0.4 eV). Use of the larger chlorine basis set (6-311++G(3df) instead of D95+(d)) was found to be important in evaluating Fe−Cl as well as Cl−Cl bond energies. Although $FeCl_2^+$ is poorly described by MP*n* and QCI calculations, the Brueckner doubles method gives a good description of this ion. The B3LYP method was found to be accurate to 5−10 kcal/mol even for reactions involving this cation. It thus appears that modern density functional techniques hold promise for the modeling of more complex iron systems.

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