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Gas-Phase Properties and Fragmentation Behavior of Cationic, Dinuclear Iron Chloride Clusters $Fe_2Cl_n^+$ ($n = 1-6$)[‡]

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Sector-field mass spectrometry is used to probe the fragmentation patterns of cationic dinuclear iron chloride clusters $Fe_2Cl_n^+$ ($n = 1-6$). For the chlorine-rich, high-valent $Fe_2Cl_n^+$ ions ($n = 4-6$), losses of atomic and molecular chlorine prevail in the unimolecular and collision-induced dissociation patterns. Instead, the chlorine deficient, formally low-valent $Fe_2Cl_n^+$ clusters ($n = 1-3$) preferentially undergo unimolecular degradation to mononuclear $FeCl_m^+$ ions. In addition, photoionization is used to determine $IE(Fe_2Cl_6) = 10.85 \pm 0.05$ eV along with appearance energy measurements for the production of $Fe_2Cl_5^+$ and $Fe_2Cl_4^+$ cations from iron(III) chloride vapor. The combination of the experimental results allows an evaluation of some of the thermochemical properties of the dinuclear $Fe_2Cl_n^+$ cations: e.g., $\Delta_fH(Fe_2Cl^+) = 232 \pm 15$ kcal/mol, $\Delta_fH(Fe_2Cl_2^+) = 167 \pm 4$ kcal/mol, $\Delta_fH(Fe_2Cl_3^+) = 139 \pm 4$ kcal/mol, $\Delta_fH(Fe_2Cl_4^+) = 113 \pm 4$ kcal/mol, $\Delta_fH(Fe_2Cl_5^+) = 79 \pm 5$ kcal/mol, and $\Delta_fH(Fe_2Cl_6^+) = 93 \pm 2$ kcal/mol. The analysis of the data suggests that structural effects are more important than the formal valency of iron as far as the Fe−Cl bond strengths in the $Fe_2Cl_n^+$ ions are concerned.

1. Introduction

Despite numerous publications on gaseous metal clusters,[1] most studies on mixed transition-metal cluster ions still lack comprehensive interpretations; this is in equal parts because of the enormous structural complexity and because of the often significant experimental difficulties associated with probing the gas-phase features of clusters. While entering this area of research, we wish to map out first some characteristics of mixed transition-metal clusters by systematically examining their spontaneous and collision-induced fragmentation patterns by mass spectrometric means.[2]

Here, we address the cationic, dinuclear iron chloride clusters $Fe_2Cl_n^+$ ($n = 1-6$). To a first approximation, the electron-withdrawing chlorine ligand can be considered to act as a one-electron acceptor in a chemical sense. Hence, the number of chlorine atoms can be correlated with the average formal valency of iron in the $Fe_2Cl_n^+$ ions; note that the positive charge is also counted as a valency. According to this formalism, both iron atoms in Fe_2Cl^+ can be assigned as Fe^{I}, $Fe_2Cl_2^+$ contains one Fe^{I} and one Fe^{II}, $Fe_2Cl_3^+$ consists of two Fe^{II}, $Fe_2Cl_4^+$ has one Fe^{II} and one Fe^{III}, $Fe_2Cl_5^+$ consists of two Fe^{III}, and the molecular ion $Fe_2Cl_6^+$ corresponds to Fe^{III}/Fe^{IV}. The latter cluster thus contains one formal iron(IV) center; while this oxidation state is not inaccessible for iron, it is less favored energetically. Analysis of the fragmentation patterns and the underlying energetics may enable one to probe whether or not such a relationship between the chlorine content and the formal valency is appropriate.

2. Experimental Methods

In analogy to our previous study of the redox chemistry of mononuclear iron chlorides in the gas phase,[3] most of the experiments were performed with a modified VG ZAB/HF/AMD 604 four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sector) which has been described elsewhere.[4] Briefly, $Fe_2Cl_n^+$ cations ($n = 1-6$) were generated by electron ionization (EI) of anhydrous iron(III) chloride which was heated to 180−220 °C in the solid probe. Under these conditions, a mixture of the monomers and dimers is present as neutrals in the gas phase, i.e., $FeCl_3$ and Fe_2Cl_6 along with some Cl_2 due to thermolysis of the solid.[5] Note that usage of iron(III) chloride is associated with contamination of the ion source resulting in a notable decrease of the instrument performance. After acceleration to a kinetic energy of 8 keV, the ions were mass-selected and subjected to metastable ion (MI) and collisional activation (CA) studies. Due to natural isotope abundances, the spectra of mass-selected $^{56}Fe_2{}^{35}Cl_n^+$ species always contain contributions of $^{54}Fe^{56}Fe^{37}Cl^{35}Cl_{(n-1)}^+$, which gives rise to signals for the losses of ^{37}Cl, $^{54}FeCl_n$, etc. Other isobaric interferences were negligible, and all $Fe_2Cl_n^+$ species ($n = 1-6$) under study showed the expected isotope patterns.[7]

MI spectra of B(1)/E(1) mass-selected $Fe_2Cl_n^+$ ions were recorded by detection of the charged fragments formed unimolecularly in the field-free region between E(1) and B(2) by scanning the latter sector. CA spectra were recorded in the same manner using helium (80% transmission, T) as a collision gas. In addition, the neutrals formed upon fragmentation of the molecular ion $Fe_2Cl_6^+$ were probed by neutral fragment reionization (N_fR) according to Polce et al.[8] In this variant of neutralization−reionization (NR)[9] experiments, helium (80% T) is

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[‡] This paper is dedicated to Professor D. K. Bohme, FRSC, on the occasion of his 60th birthday.

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(1) See, for example: Armentrout, P. B.; Griffin, J. B.; Conceição, J. In *Progress in Physics of Clusters*; Chuev, G. N., Lakhno, V. D., Nefedov, A. P., Eds.; World Scientific: Singapore, 1999; p 198.

(2) Schröder, D.; Jackson, P.; Schwarz, H. *Eur. J. Inorg. Chem.* **2000**, 1171.

(3) Schröder, D.; Bärsch, S.; Schwarz, H. *Int. J. Mass Spectrom.* **1999**, *192*, 125.

(4) Schalley, C. A.; Schröder, D.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1996**, *153*, 173.

(5) See the discussion for Fe_2Cl_6 in ref 6, p 903.

(6) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1 (JANAF Tables).

(7) See: http://www.shef.ac.uk/chemistry/chemputer/, copyright Mark Winter, University of Sheffield.

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used as a first collision gas in order to afford intense fragmentation of the ionic projectile, while minimizing the occurrence of neutralization processes because of the high ionization energy (IE) of helium (IE = 24.59 eV).[10] Next, the remaining ions are removed from the beam by means of a deflector electrode, and the beam of fast neutrals is subsequently reionized with oxygen as collision gas (80% T) and detected by scanning the next sector. On sensitivity grounds, this spectrum was acquired with B(1) mass-selected ions only by scanning E(1). In order to estimate IE(Fe_2Cl_4), also the MI spectra of a few complexes of $Fe_2Cl_4^+$ with arene ligands L were examined. To this end, the corresponding ions were generated by addition of L to iron(III) chloride vapor in a chemical ionization source (repeller voltage ca. 0 V). Due to coincidental mass overlaps, deuterated arenes were used in some cases (see below).

Photoionization studies of iron(III) chloride were performed in the CERISES apparatus[11] which was installed on the beam line SA63 of the synchrotron radiation source SuperACO at LURE (Orsay, France). This beam line is a normal incidence monochromator which provides monochromatic light in the range of 7−30 eV photon energy. Slits were at all time opened to 1 mm, which provides a photon-energy resolution in the range of 500 (i.e., 20 meV at 10 eV). The accuracy of the photon energy was verified by measuring the ionization energy of argon within 2 meV of its nominal value. For the actual experiments, a small oven made from copper was filled with a glass tube containing several milligrams of anhydrous iron(III) chloride and adapted to the source. Sufficient vapor pressure of the neutral was achieved at a nominal oven temperature of 225 ± 3 °C. The neutral species were photoionized, and the cations formed were extracted by a field of 1 V/cm toward an octopole ion guide and then a quadrupole mass spectrometer (Nermag 350 mm), where mass selection was performed. Ions were detected by a multichannel plate operated in the counting mode. Unfortunately, the deterioration of the ion source by iron(III) chloride is even more severe in the CERISES apparatus than in the sector MS. Further, cleaning of the ion source consumed a whole day of the rare beam time at SuperACO. Hence, instead of aiming at a comprehensive survey, the investigation had to be limited to a few key aspects within a single series of experiments conducted during 2 days. Subsequent cleaning required complete disassembly of the ion source as well as the front-end lenses of CERISES. Inter alia, these contaminations led to a rapid failure of the electron detector mounted on CERISES, such that coincidence measurements were impossible. In addition to a decrease in performance, the presence of iron(III) chloride vapor led to several signals which are attributed to reactions of iron(III) chloride with background contaminations. The most intense contaminations (of unknown composition) appeared at m/z = 207 and 242 amu for which the isotope patterns indicate incorporations of two and three chlorine atoms, respectively. Assignment of these signals as contaminations is supported by their continuous increase, relative to the $Fe_2Cl_n^+$ ions, with time evolution as well as their persistence at photon energies ≤10.5 eV at which no $Fe_mCl_n^+$ signals were observed at all.

3. Results

Figure 1 shows a representative photoionization (PI) mass spectrum of iron(III) chloride vapor at a photon energy of 16 eV. Under these conditions, the major ions above $m/z = 100$ amu are due to $Fe_2Cl_n^+$ with $n = 4-6$. The assignment of these signals to $Fe_2Cl_n^+$ is further confirmed by the characteristic isotope patterns obtained in separate scans at enhanced mass resolutions. The only mononuclear iron chloride signal that is clearly discernible in the spectrum corresponds to the $FeCl_2^+$ cation. This behavior is consistent with the composition of iron(III) chloride vapor at a temperature of ca. 200 °C where the dimer Fe_2Cl_6 prevails over the monomer.[5] Below 120 amu, atomic and molecular chlorine ions as well as several signals stemming from background contaminations are observed; however, these signals do not interfere with the ions of interest. Instead, it is noteworthy that also a peak above the molecular ion $Fe_2Cl_6^+$ is observed which formally corresponds to an $Fe_2Cl_7^+$ species of unknown origin. As mentioned in the experimental section, the photoionization spectra changed during the experiments in that several signals due to impurities increased continuously. Thus, after 24 h, the most intense peak above 120 amu switched from $Fe_2Cl_4^+$ in Figure 1 to an ion of unknown origin at mass 207 amu which contains only two chlorine atoms. Increase of this interference is accompanied by a general loss of instrument performance.

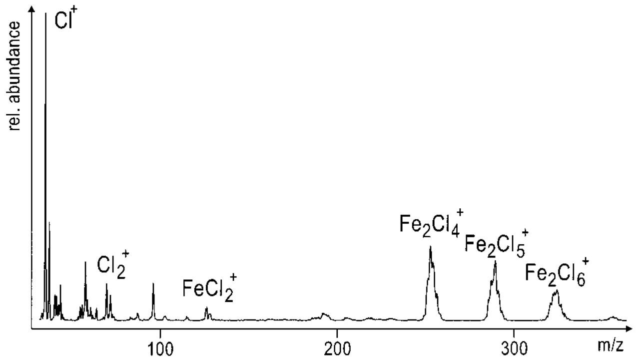

Figure 1. PI mass spectrum of iron(III) chloride vapor at a photon energy of 16 eV. Note part of the unassigned background signals is due to a residual amount of 3-methyl-[4-D_1]-valeramide which was present in the machine from previous experiments conducted a day before.

The only experiments which could be performed before dismounting the source for cleaning were appearance spectra for the $Fe_2Cl_n^+$ ions with $n = 4-6$. In these measurements, the intensity of an ion of interest is monitored as a function of photon energy. Figure 2a−c shows the separate ion profiles. A summary of the results for these three ions in terms of a qualitative breakdown diagram is given in Figure 2d. The data in Figure 2a−c presents the experimental results after correction for the signals present already below the appearance energies, which are due to the nontotal extinction of higher-order photons. This contribution is inherent to grating monochromators and could not be removed by means of cutoff filters due to the high photon energies involved. The higher-order contaminations had maxima between 10 and 11 eV photon energy, and their relative intensities did not exceed 10% of the ion intensities at 16 eV. For the three $Fe_2Cl_n^+$ cations considered here, the appearance energies were determined by linear extrapolation of the straight increase of ion yield (visible about 0.02 eV above the first point departing from the noise level) to the baseline. We recognize that more accurate thresholds might be obtained by fitting the experimental curvature of ion yield to simulate the internal energy distribution. However, the difficulties due to contamination of the ion source, awareness of the fact that the effective temperature of the iron(III) chloride vapor in the experiment must not necessarily correspond to the oven temperature, and uncertainties in the choice of the parameters for modeling dissociative photoionization led us to refrain from such a detailed analysis. Instead, the more robust linear extrapolation to the baseline is applied in conjunction with conservative error estimates. The photon energy dependencies of the traces for

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(8) Polce, M. J.; Beranová, Š.; Nold, M. J.; Wesdemiotis, C. *J. Mass Spectrom.* **1996**, *31*, 1073.

(9) Review: Schalley, C. A.; Hornung, G.; Schröder, D.; Schwarz, H. *Chem. Soc. Rev.* **1998**, *27*, 91.

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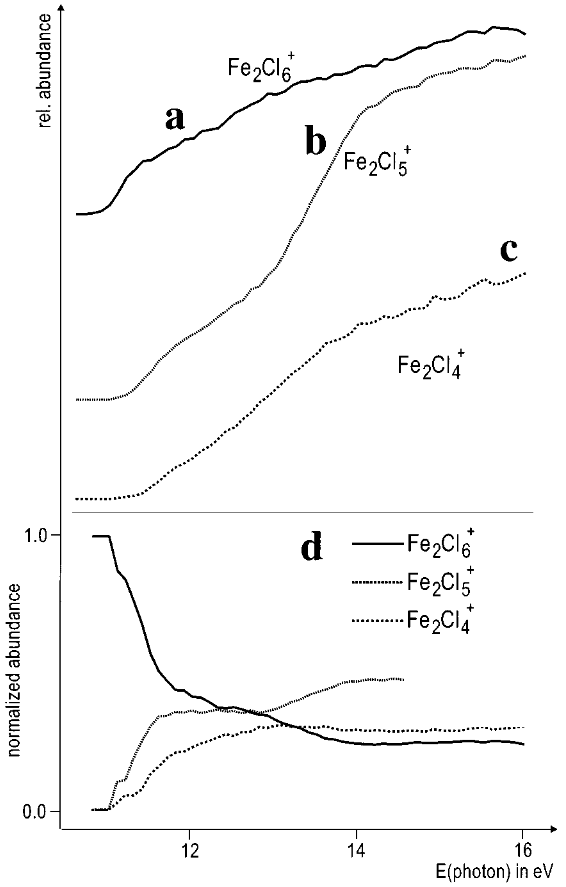

Figure 2. (a) Single-ion monitoring of $Fe_2Cl_6^+$ as a function of photon energy (in eV). (b) Single-ion monitoring of $Fe_2Cl_5^+$ as a function of photon energy. (c) Single-ion monitoring of $Fe_2Cl_4^+$ as a function of photon energy. (d) Schematic threshold diagram for $Fe_2Cl_n^+$ ($n = 4-6$) as a function of photon energy (in eV).

$Fe_2Cl_n^+$ are consistent with photoionization of Fe_2Cl_6 present as the major neutral component in the ion source.[5] The $Fe_2Cl_6^+$ curve rises sharply at a threshold of 10.85 ± 0.05 eV (Figure 2a) being in line with formation of the molecular ion. In comparison, the curves for $Fe_2Cl_5^+$ and $Fe_2Cl_4^+$ increase more smoothly (Figure 2b,c), suggesting that these ions represent primary photofragments of the dissociative photoionization of Fe_2Cl_6. Extrapolation of the onsets to the baseline provides the corresponding appearance energies, $\mathrm{AE}(Fe_2Cl_5^+) = 11.13 \pm 0.1$ eV and $\mathrm{AE}(Fe_2Cl_4^+) = 11.28 \pm 0.1$ eV, respectively. Quite remarkable are the apparently rather low energy demands (ΔE) for the losses of atomic ($\Delta E = 0.28$ eV) and molecular chlorine ($\Delta E = 0.43$ eV) from the molecular ion.

The sector-field experiments include the metastable ion (MI) and collisional activation (CA) mass spectra of $Fe_2Cl_n^+$ ions ($n = 1-6$) generated by electron ionization of gaseous iron(III) chloride (Table 1). In the present context, the major use of the CA spectra is the confirmation of the anticipated elemental compositions of the mass-selected ions. The clean fragmentation patterns obtained for the different $Fe_2Cl_n^+$ ions indeed disprove any significant interferences by isobaric ions which might contaminate the ion beams. Specifically, the ions undergo sequential losses of chlorine to yield the corresponding $Fe_2Cl_{(n-m)}^+$ fragments ($m = 1, 2$) as well as cluster cleavages to afford two mononuclear species, i.e., cationic $FeCl_{(n-m)}^+$ concomitant with neutral $FeCl_m$ ($m, n = 0-3$). Neither ionized atomic nor molecular chlorine was observed in notable amounts, consistent with their high ionization energies, IE(Cl) = 12.97 eV and IE(Cl_2) = 11.48 eV.[10] As far as fragmentation patterns are concerned, some trends are obvious in the CA spectra, but the quantitative analysis is much more straightforward for the MI spectra. This is because ion dissociation induced in high-energy collisions (here, 8 keV) is heavily influenced by dynamic as well as instrumental effects which obscure the underlying intrinsic properties. Specifically, losses of heavy neutrals (and hence detection of light fragment ions) are discriminated against heavy fragment ions. As a consequence, losses of atomic chlorine predominate in most CA spectra. The analysis of the MI spectra is much more instructive. Metastable ion dissociation occurs with ions having an internal energy content sufficient to promote unimolecular decay in the instrumental time window (here, microsecond regime). Qualitatively, this condition restricts the amount of internal energy (E_{int}) of the metastable ions. On the one hand, E_{int} must exceed the required dissociation energy associated with the metastable ion decays observed experimentally; on the other hand, it cannot be much higher than the dissociation asymptote, because the simple bond cleavages observed in the experiments as well as the small size of the molecules limit metastability to the microsecond regime. Therefore, comparing the MI spectra of the $Fe_2Cl_n^+$ clusters may reveal some trends along this series. Let us analyze the data in Table 1 in this particular respect.

$$Fe_2Cl_6^+ \rightarrow Fe_2Cl_5^+ + Cl \quad (1a)$$

$$\rightarrow Fe_2Cl_4^+ + \text{“}Cl_2\text{”} \quad (1b)$$

$$Fe_2Cl_5^+ \rightarrow Fe_2Cl_4^+ + Cl \quad (2a)$$

$$\rightarrow Fe_2Cl_3^+ + \text{“}Cl_2\text{”} \quad (2b)$$

$$\rightarrow FeCl_2^+ + FeCl_3 \quad (2c)$$

$$Fe_2Cl_4^+ \rightarrow Fe_2Cl_3^+ + Cl \quad (3a)$$

$$\rightarrow FeCl_2^+ + FeCl_2 \quad (3b)$$

$$\rightarrow FeCl^+ + FeCl_3 \quad (3c)$$

$$Fe_2Cl_3^+ \rightarrow Fe_2Cl_2^+ + Cl \quad (4a)$$

$$\rightarrow FeCl^+ + FeCl_2 \quad (4b)$$

$$Fe_2Cl_2^+ \rightarrow Fe^+ + FeCl_2 \quad (5)$$

$$Fe_2Cl^+ \rightarrow FeCl^+ + Fe \quad (6a)$$

$$\rightarrow Fe^+ + FeCl \quad (6b)$$

The major fragment in the MI spectrum of the molecular ion $Fe_2Cl_6^+$ corresponds to $Fe_2Cl_5^+$ concomitant with loss of a chlorine atom (reaction 1a). While cluster degradation to mononuclear species (e.g., $FeCl_3^+ + FeCl_3$) is not observed at all for metastable $Fe_2Cl_6^+$, also $Fe_2Cl_4^+$ is formed unimolecularly according to reaction 1b, for which the nature of the neutral is discussed in more detail further below. While losses of Cl and “Cl_2” (reactions 2a and 2b) also occur for the diiron pentachloride cation $Fe_2Cl_5^+$, the base peak of the MI spectrum shifts to cluster cleavage according to reaction 2c. A similar competition of chlorine loss (reaction 3a) and cluster degradations (reactions 3b and 3c) occurs with $Fe_2Cl_4^+$. With decreasing chlorine content, cluster cleavage gains in importance, while

Table 1. Ion Intensities[a−d] Observed in the MI and CA Mass Spectra of B(1)/E(1) Mass-Selected $Fe_2Cl_n^+$ Ions ($n = 1-6$)[e]

	spectrum	$Fe_2Cl_5^+$	$Fe_2Cl_4^+$	$Fe_2Cl_3^+$	$Fe_2Cl_2^+$	Fe_2Cl^+	Fe_2^+	$FeCl_3^+$	$FeCl_2^+$	$FeCl^+$	Fe^+
$Fe_2Cl_6^+$	MI	100	15								
	CA	100	25	5				<1	2	<1	
$Fe_2Cl_5^+$	MI	*f*	20	1					100		
	CA	*f*	100	20	<1			<1	40	4	1
$Fe_2Cl_4^+$	MI		*f*	20					100	4	
	CA		*f*	100	2	1	<1		40	15	2
$Fe_2Cl_3^+$	MI			*f*	2					100	
	CA			*f*	60	7	3		2	100	15
$Fe_2Cl_2^+$	MI				*f*						100
	CA				*f*	45	6			25	100
Fe_2Cl^+	MI					*f*				60	100
	CA					*f*	25			30	100

[a] Given relative to the base peak (100%). [b] Averages of at least two independent experiments, relative error ±30%. [c] Contributions of ^{54}Fe and ^{37}Cl isotopes are neglected. [d] The MI data already include the correction for mass discrimination according to ref 12 (parameters: wide β-slit, KER = 20 meV). [e] For the corresponding data of mononuclear $FeCl_n^+$ cations, see ref 3. [f] This entry corresponds to the mass-selected parent ion.

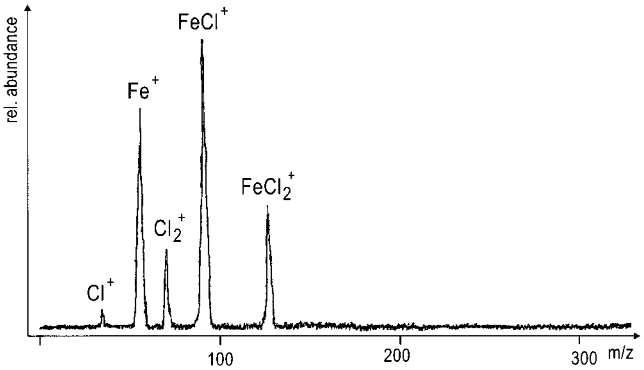

Figure 3. Neutral fragment reionization (N_fR) spectrum of $Fe_2Cl_6^+$.

loss of Cl diminishes for $Fe_2Cl_3^+$ and vanishes in the noise level for the $Fe_2Cl_2^+$ and Fe_2Cl^+ ions. Comparison of the fragment ion yields as a function of *n* reveals clear-cut trends: cluster degradation predominates for the chlorine-deficient, low-valent clusters, while Fe−Cl bond cleavages gain in importance for the chlorine-rich, high-valent ions.

A particular aspect in the MI spectrum of $Fe_2Cl_6^+$ concerns the nature of the neutral "Cl_2" formed in reaction 1b. While loss of one chlorine atom according to reaction 1a is straightforward for metastable $Fe_2Cl_6^+$, sequential losses of two chlorine atoms are difficult to rationalize in the MI spectra. Thus, an excited molecular ion $Fe_2Cl_6^{+*}$ having enough internal energy to expel two chlorine atoms would dissociate much more rapidly and is therefore unlikely to exist as a metastable species with a lifetime of the order of microseconds. Instead, reaction 1b finds a rationale if molecular chlorine is lost as a neutral because the formation of a Cl−Cl bond would provide an additional driving force for dechlorination. Further, the similar appearance energies of $Fe_2Cl_5^+$ and $Fe_2Cl_4^+$ in the PI experiments disfavor sequential losses of atomic chlorine. These arguments are, however, at best educated guesses, rather than convincing evidence for Cl_2 formation. In order to gain more direct insight, the nature of the neutral species formed from $Fe_2Cl_6^+$ was probed in an N_fR experiment.[8] To this end, $Fe_2Cl_6^+$ was subjected to a high-energy collision with helium as a target gas, thereby minimizing the propensity of electron-transfer processes while favoring prompt dissociations of the precursor ion. Subsequent to this collision and removal of all ionic particles from the beam, the fast moving neutral fragments of ion dissociation are ionized in a second collision with oxygen which is well-suited for electron transfer in keV collisions. In addition to the fragment ions $FeCl_n^+$ ($n = 0-2$) expected in this experiment, the resulting N_fR spectrum (Figure 3) shows a distinct signal for Cl_2^+ which is considered as direct experimental evidence for the formation of molecular chlorine in reaction 1b upon collisional activation. Accordingly, the formation of $Fe_2Cl_4^+$ in the photoionization experiments is assigned to dissociative ionization of Fe_2Cl_6 under liberation of molecular chlorine, rather than subsequent losses of two chlorine atoms.

Table 2. Neutrals Losses Observed in the MI Mass Spectra of $(L)Fe_2Cl_4^+$ Complexes with Arene Ligands L[a]

L	IE(L) in eV[b]	−L	$-FeCl_3$	$-Fe_2Cl_4$
C_6D_5Cl	9.07 ± 0.02[c]		100	60
C_6H_6	9.24378		100	
C_6D_6	9.251 ± 0.002		100	
C_6H_5CN[d]	9.73 ± 0.01		100	
C_6F_6	9.90 ± 0.04	100	10	

[a] Relative to the base peak (100%). [b] Taken from the following: http://webbook.nist.gov/chemistry/. [c] Value for C_6H_5Cl. [d] In addition, loss of neutral $FeCl_2$ is observed (10%).

Some additional experiments were performed with complexes of arene ligands L with $Fe_2Cl_4^+$ which were generated by chemical ionization of iron(III) chloride in the presence of L. In the MI spectra of the resulting $(L)Fe_2Cl_4^+$ cations, three major reaction channels are observed (Table 2): (i) loss of the arene ligand L (reaction 7a), (ii) cluster rearrangement and expulsion of neutral $FeCl_3$ (reaction 7b), and loss of neutral Fe_2Cl_4 (reaction 7c).

$$(L)Fe_2Cl_4^+ \rightarrow Fe_2Cl_4^+ + L \tag{7a}$$

$$\rightarrow (L)FeCl^+ + FeCl_3 \tag{7b}$$

$$\rightarrow L^+ + Fe_2Cl_4 \tag{7c}$$

As anticipated, the abundancies of the fragmentation routes correlate with the IEs of the arenes. More specifically, the occurrence of reaction 7a, while 7c is absent with $L = C_6F_6$, implies $IE(Fe_2Cl_4) < IE(C_6F_6) = 9.90$ eV as an upper bound. Likewise, generation of the ionized arene for $L = C_6H_5Cl$ implies $IE(Fe_2Cl_4) > IE(C_6H_5Cl) = 9.07$ eV as a lower limit. In all cases, reaction 7b competes and occurs exclusively for $L = C_6X_6$ (X = H, D) and C_6H_5CN having intermediate IEs. Taking this competing reaction into account, a conservative estimate of $IE(Fe_2Cl_4) = 9.5 \pm 0.4$ eV is derived. While this figure is right at the lower limit of $IE(Fe_2Cl_4) = 10.5 \pm 1.0$ eV derived from earlier appearance energy measurements,[13] this is no reason to worry, in that in this particular study also a value

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(12) Rumpf, B. A.; Allison, C. E.; Derrick, P. J. *Org. Mass. Spectrom.* **1986**, *21*, 295.

(13) Schoonmaker, R. C.; Porter, R. F. *J. Chem. Phys.* **1958**, *29*, 116.

Table 3. Heats of Formation at 0 K (in kcal/mol) of Neutral and Ionic Fe_mCl_n Species ($m = 1, 2$; $n = 1-6$) and Ionization Energies (in eV) Used in the Data Analysis

	$\Delta_fH°_{neutral}$	IE	$\Delta_fH°_{ion}$
Fe	98.0 ± 2[a]	7.9024[b]	280.2 ± 1.8[a]
FeCl	47 ± 3[c]	7.9 ± 0.1[c]	229 ± 2[c]
$FeCl_2$	−33.8 ± 0.5[a]	10.28 ± 0.15[c]	203.3 ± 3.5[c]
$FeCl_3$	−60.5 ± 1.2[a]	(10.93)[d]	(191.5)[e]
Fe_2Cl_4	−103.7 ± 1.0[a]		
Fe_2Cl_6	−157.3 ± 2.0[a]	10.85 ± 0.05[f]	92.9 ± 2.3[e]
Cl	28.571[a]		
Cl_2	0		
Fe_2			314.1 ± 3[g]

[a] Taken from ref 6. [b] See: physics.nist.gov/atomic. [c] See Appendix I. [d] Theoretical estimate, see ref 3. [e] Derived from $\Delta_fH°_{neutral}$ and IE. [f] Photoionization threshold, this work. [g] Derived from $D_0(Fe^+-Fe) = 2.78 \pm 0.09$ eV (ref 14).

of $IE(FeCl_2) = 11.5 \pm 0.5$ eV has been reported which is more than 1 eV above $IE(FeCl_2) = 10.28 \pm 0.15$ eV used here.

4. Discussion

The following analysis is based on some thermochemical data used as anchoring references. These data as well as their error margins are evaluated from various literature values (Appendix I) and are compiled in Table 3.

At first, we assign the sharp rise of the $Fe_2Cl_6^+$ signal in the PI experiments to a genuine photoionization of the neutral precursor molecule. Given the characteristics of the onset, it is further assumed that the appearance energy corresponds to the adiabatic ionization energy, that is, $IE(Fe_2Cl_6^+) = 10.85 \pm 0.05$ eV. Combination with $\Delta_fH(Fe_2Cl_6) = -157.3 \pm 2.0$ kcal/mol for the neutral compound yields $\Delta_fH(Fe_2Cl_6^+) = 92.9 \pm 2.3$ kcal/mol for the molecular ion. Further, the appearance energies $AE(Fe_2Cl_5^+) = 11.13 \pm 0.1$ eV and $AE(Fe_2Cl_4^+) = 11.28 \pm 0.1$ eV can be used to estimate the heats of formation of the resulting cations. There exists some ambiguity in this conversion, however, because the appearance energies are sensitive to two different effects operating in opposite directions. (i) In general, appearance energies for dissociative ionization experience kinetic shifts which depend on the ion dissociation rates and the ions' lifetimes sampled in the experiments. For example, a large polyatomic molecule with strong bonds needs to contain a considerable amount of excess internal energy before yielding a detectable fraction of fragments in a given instrument. This kinetic effect shifts the appearance energies to values larger than the thermochemical thresholds. The dissociations 1a and 1b sampled in the present photoionization experiments are, however, unlikely to be subject to pronounced kinetic shifts because the ions are relatively small and specifically liberation of Cl and Cl_2 from $Fe_2Cl_6^+$ is obviously facile (see above). (ii) The second factor to be considered is the internal energy of the precursor. Specifically, at a temperature of about 225 °C, which is required to establish a sufficient vapor pressure in the PI experiments, the internal energy content of neutral Fe_2Cl_6 amounts to about 0.72 eV.[6] This contribution of internal energy is substantial and might cause the fragments' appearance energies to be shifted below the thermodynamic thresholds at 0 K. In particular, the obvious weakness of the $Cl_5Fe_2^+-Cl$ bond in the molecular ion $Fe_2Cl_6^+$ suggests that the appearance of the $Fe_2Cl_5^+$ benefits from the finite temperature of the precursor. In a first approximation, these arguments suggest neglect of the kinetic shifts while the appearance energies are lowered by half of the internal energy content. Within conservative error estimates, the corrected appearance energies $AE_{corr}(Fe_2Cl_5^+) = 11.49 \pm 0.4$ eV and $AE_{corr}(Fe_2Cl_4^+) = 11.64 \pm 0.4$ eV are obtained. With $\Delta_fH(Fe_2Cl_6) = -157.3 \pm 2.0$ kcal/mol, these values translate to $\Delta_fH(Fe_2Cl_5^+) = 79.1 \pm 9.4$ kcal/mol and $\Delta_fH(Fe_2Cl_4^+) = 111.1 \pm 9.4$ kcal/mol, respectively. Also note the assumption that the formation of the $Fe_2Cl_4^+/Cl_2$ couple according to reaction 1b has no barrier in excess of endothermicity.

In this fortunate case, the metastable ion spectra can be used to extract valuable thermochemical information for the $Fe_2Cl_n^+$ clusters. Specifically, the kinetic method developed by Cooks and co-workers[15] is applied to quantitatively analyze the fragmentation data. The central assumption of the kinetic method is that the branching ratio for ion dissociation via two competing channels A and B is determined by the difference of the free energies of the two routes according to $\Delta\Delta G(T_{eff}) = RT_{eff}\ln(I_A/I_B)$, where T_{eff} is an effective ion temperature and I_A and I_B are the fragments' relative intensities. By definition, the kinetic method can only provide relative energies, and anchoring to reference values is required when absolute quantities are to be derived. While there is an ongoing debate in the literature about the theoretical foundations of the kinetic method,[16] it has found many, often extremely valuable applications. Without entering this discussion in any detail, an obviously crucial parameter in the kinetic method is the choice of the effective temperature T_{eff}. For the sake of simplicity, let us first assume $T_{eff} = 473$ K, i.e., the sample temperature of 200 ± 20 °C used in the sector experiments; the choice of this estimate is justified further below. The fortunate circumstances in the present case are (i) that most ions undergo competing fragmentations leading to Fe−Cl bond cleavages and cluster degradation of mononuclear iron chlorides, and particularly (ii) that the thermochemistry of neutral and cationic $FeCl_n$ is settled reasonably well (Table 3).

In the analysis of the MI data of the $Fe_2Cl_n^+$ cations in terms of the kinetic method, two types of corrections are applied. At first, instrumental discrimination effects are accounted for by a weighting procedure[12] which results in slightly enhanced intensities of the low-mass ions compared to the raw data. The second correction is more subtle. In general, one may neglect thermal effects on $\Delta\Delta G$ in competitive ion dissociations by assuming that $\Delta\Delta G(T_{eff})$ is roughly equal to $\Delta\Delta H$ at 0 K, unless major conformational changes take place upon dissociation (e.g., for chelating ligands); of course, all dissociations are assumed to only yield two fragments. Neglect of thermal corrections is particularly justified if absolute thermochemical data are of interest, considering the error margins of the kinetic method and the underlying assumptions as well as the uncertainties of the references values. Moreover, two recent theoretical studies of gaseous iron compounds suggest that thermal corrections are of minor importance at ambient temperatures.[17,18] If, however, a polyatomic molecule can dissociate into either two molecular fragments or one polyatomic and one atomic fragment, the latter pathway experiences a significant discrimination due to entropy effects. As outlined in Appendix II, the corresponding correction term is estimated as 3 ± 1 kcal/mol and is applied to all fragmentations in which pathways also yielding atoms compete with others in which only molecules are formed.

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Table 4. Analysis of the MI Spectra of the $Fe_2Cl_n^+$ Cations in Terms of the Kinetic Method at Several Effective Temperatures (T_{eff} in K) and Quantities Derived Accordingly

reactants	products	$\sum\Delta_fH_{products}$ (known)	intensity	$\Delta\Delta G$ for T_{eff} (K)				ΔE_{corr} [a]	$\sum\Delta_fH_{products}$ (unknown)[b]	derived quantity
				298	473	673	1000			
$Fe_2Cl_6^+$	$Fe_2Cl_5^+ + Cl$	107.7	100	*0.0*	*0.0*	*0.0*	*0.0*			
	$Fe_2Cl_4^+ + Cl_2$		15	1.1	1.8	2.5	3.8	+3	112.4	$\Delta_fH(Fe_2Cl_4^+) = 112 \pm 10$ kcal/mol
	$FeCl_3^+ + FeCl_3$	131.0	S/N[c]	3.2	5.0	7.1	10.6	+3	>116	
$Fe_2Cl_5^+$	$Fe_2Cl_4^+ + Cl$		20	1.0	1.5	2.2	3.2	−3	141.3	$\Delta_fH(Fe_2Cl_4^+) = 113 \pm 4$ kcal/mol
	$Fe_2Cl_3^+ + Cl_2$		1	2.7	4.3	6.2	9.2	0	147.1	$\Delta_fH(Fe_2Cl_3^+) = 147 \pm 5$ kcal/mol
	$FeCl_2^+ + FeCl_3$	142.8	100	*0.0*	*0.0*	*0.0*	*0.0*			
$Fe_2Cl_4^+$	$Fe_2Cl_3^+ + Cl$		20	1.0	1.5	2.2	3.2	−3	168.0	$\Delta_fH(Fe_2Cl_3^+) = 139 \pm 4$ kcal/mol
	$FeCl_2^+ + FeCl_2$	169.5	100	*0.0*	*0.0*	*0.0*	*0.0*			
	$FeCl^+ + FeCl_3$	168.5	4	1.9	3.0	4.3	6.4	0	172.5	
$Fe_2Cl_3^+$	$Fe_2Cl_2^+ + Cl$		2	2.3	3.7	5.2	7.8	−3	195.9	$\Delta_fH(Fe_2Cl_2^+) = 167 \pm 4$ kcal/mol
	$FeCl^+ + FeCl_2$	195.2	100	*0.0*	*0.0*	*0.0*	*0.0*			
$Fe_2Cl_2^+$	$Fe_2Cl^+ + Cl$		S/N[c]	3.2	5.0	7.1	10.6	−3	>248	$\Delta_fH(Fe_2Cl^+) > 220$ kcal/mol
	$Fe^+ + FeCl_2$	246.4	100	*0.0*	*0.0*	*0.0*	*0.0*			
Fe_2Cl^+	$Fe_2^+ + Cl$	342.7	S/N[c]	3.2	5.0	7.1	10.6	0	>332	
	$FeCl^+ + Fe$	327.2	60	0.3	0.5	0.7	1.0	0	327.5	
	$Fe^+ + FeCl$	327.2	100	*0.0*	*0.0*	*0.0*	*0.0*			

[a] Correction term to account for finite thermal effects when atoms are formed, see Appendix II. [b] $T_{eff} = 473$ is used in this column. [c] Noise level (<0.5) used in calculation.

The molecular ion $Fe_2Cl_6^+$ does not undergo degradation to mononuclear fragments of known thermochemistry. Hence, the kinetic method only yields the relative stabilities of $Fe_2Cl_5^+$ and $Fe_2Cl_4^+$ (Table 4). Assuming that reactions 1a and 1b lack barriers in excess of the reactions' endothermicities, the difference of 4.8 kcal/mol at $T_{eff} = 473$ K agrees reasonably well with the difference of 0.15 eV (3.5 kcal/mol) of the corresponding thresholds for dissociative photoionization. Relative to $\Delta_fH(Fe_2Cl_5^+) = 79 \pm 9$ kcal/mol derived from the PI experiments, $\Delta_fH(Fe_2Cl_4^+) = 112 \pm 10$ kcal/mol is obtained. Both fragmentation channels are thus well below $\sum\Delta_fH(FeCl_3^+ + FeCl_3) = 131$ kcal/mol, consistent with the absence of formal Fe−Fe cleavage products in the MI spectrum of $Fe_2Cl_6^+$. The dissociation of metastable $Fe_2Cl_5^+$ to afford $FeCl_2^+$ and neutral $FeCl_3$ provides an anchor for the analysis of the competing channels yielding $Fe_2Cl_4^+$ and $Fe_2Cl_3^+$. $\Delta_fH(Fe_2Cl_4^+) = 113 \pm 4$ kcal/mol and $\Delta_fH(Fe_2Cl_3^+) = 147 \pm 5$ kcal/mol are obtained accordingly; note that formation of $Fe_2Cl_3^+$ is assumed to be accompanied by that of molecular chlorine without any barrier being operative. An independent value of $\Delta_fH(Fe_2Cl_4^+) = 115 \pm 9$ kcal/mol can be derived by combining the heat of formation of the neutral compound with the IE derived from the MI spectra of the $(L)Fe_2Cl_4^+$ complexes. The three independent values derived for $Fe_2Cl_4^+$ are in good agreement with each other. Using the most precise one, $\Delta_fH(Fe_2Cl_4^+) = 113 \pm 4$ kcal/mol derived from reaction 2, as a reference for reaction 1, we can further refine $\Delta_fH(Fe_2Cl_5^+)$ to 79 ± 5 kcal/mol. Next, the competition of Fe−Fe and Fe−Cl cleavages for metastable $Fe_2Cl_4^+$ suggests $\Delta_fH(Fe_2Cl_3^+) = 139 \pm 4$ kcal/mol. Note, however, that the formally isoenergetic reactions 3b and 3c do not occur with equal intensities, although the difference is within the uncertainty of the reference data. Both values for $Fe_2Cl_3^+$ are consistent with $\Delta_fH(Fe_2Cl_3^+) = 144 \pm 23$ kcal/mol derived from appearance measurements by Schoonmaker and Porter.[13,19] In the further analysis, we prefer $\Delta_fH(Fe_2Cl_3^+) = 139 \pm 4$ kcal/mol derived from reaction 3a, because kinetic control of the loss of molecular chlorine appears to become more likely with decreasing chlorine content of the cluster and might cause the slightly larger value derived from reaction 2b. While an analogous treatment of the fragmentation of metastable $Fe_2Cl_3^+$ leads to $\Delta_fH(Fe_2Cl_2^+) = 167 \pm 4$ kcal/mol, the absence of Cl losses for metastable $Fe_2Cl_2^+$ and Fe_2Cl^+ only provides a lower limit of $\Delta_fH(Fe_2Cl^+) > 220 \pm 4$ kcal/mol. However, $\Delta_fH(Fe_2Cl_2^+) = 167 \pm 4$ kcal/mol together with the known heat of formation of the Fe_2^+ cation[14] implies a sum of 204 ± 5 kcal/mol for the sequential bond energies $D_0(ClFe_2^+{-}Cl)$ and $D_0(Fe_2^+{-}Cl)$. As a first approximation, we assume that the partitioning of the sequential bond strengths of the two bridging chlorine ligands correlates with that found for the related oxygen clusters. Thus, the bond-dissociation energies $D_0(Fe_2O^+{-}O) = 99.2 \pm 7.7$ kcal/mol[20] and $D_0(Fe_2^+{-}O) = 117.6 \pm 4.6$ kcal/mol[21] imply that the first chlorine ligand is ca. 20% more strongly bound than the second. A rough estimate of $\Delta_fH(Fe_2Cl^+) = 232 \pm 15$ kcal/mol is obtained accordingly.

After having made this analysis, let us return to the choice of the effective temperature in the sector-field experiments. Inspection of Table 4 and particularly of the error margins of the values derived shows that the choice of T_{eff} is not too critical because the resulting errors in $\Delta\Delta_fH$ are small compared to the uncertainties of the absolute heats of formation used as references (Table 3). Within the set of data available, the most reliable information is the comparison of reactions 1a and 1b for which the value derived from the kinetic method and difference of the respective PI thresholds agree well with T_{eff} assumed as 473 K but also fit for 298 and 673 K, leading to $T_{eff} = 473 \pm 200$ K as an empirical estimate. With respect to other applications of the kinetic method, it is important to note that some of the CA data do not match the derived values whatever temperature is chosen because the base peaks change, e.g., from $FeCl_2^+$ to $Fe_2Cl_4^+$ in the MI and CA spectra of $Fe_2Cl_5^+$, respectively. This is not to say that competing reactions in collisional activation experiments cannot be described in terms of the kinetic method; rather, it highlights the relevance of size effects as well as instrumental aspects. For example, a large polyatomic proton-bound dimer $[A{-}H^+{-}B]$ may well fragment quasi-adiabatically upon collisional activation in the keV regime. Likewise, ion dissociation upon gradual increase of internal energy in low-energy collisions may be governed by thermochemical effects. In high-energy CA of a small molecule, however, dynamic effects and collection efficiencies may

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(19) The good agreement between the data in ref 13 and the present results may be due to the proximity of the appearance energy for $Fe_2Cl_3^+$ to that of water which was used as a reference in that study.

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Table 5. Summarized Heats of Formation of the $Fe_2Cl_n^+$ Cations and Bond Dissociation Energies Derived Accordingly (All Values in kcal/mol)

	$\Delta_f H$	D_0(Fe−Cl)	D_0(Fe−Fe)
Fe_2^+	314.1[a]		64[a]
Fe_2Cl^+	232 ± 15	111	95
$Fe_2Cl_2^+$	167 ± 4	93	79
$Fe_2Cl_3^+$	139 ± 4	56	56
$Fe_2Cl_4^+$	113 ± 4	55	57
$Fe_2Cl_5^+$	79 ± 5	62	63
$Fe_2Cl_6^+$	93 ± 2	15	38

[a] Derived from $D_0(Fe^+{-}Fe) = 2.78 \pm 0.09$ eV (ref 14).

obscure the underlying intrinsic thermochemical properties of the species under investigation.

While the above analysis is based on some assumptions and approximations, these are all included in the error bar estimates. Therefore, the data provide a survey of the thermochemical properties of gaseous $Fe_mCl_n^+$ species which is chemically insightful. Table 5 collects this information and the bond energies derived accordingly. Interestingly, instead of correlating with the chlorine content of the cluster (viz., the formal valence of the metal), the Fe−Cl bond strengths are best described to decrease in a stepwise manner (Figure 4). The two first Fe−Cl bond energies are much larger than the next three which are on the order of 60 kcal/mol, and a sharp decrease to $D_0(Cl_5Fe_2^+{-}Cl) = 15$ kcal/mol occurs with the sixth chlorine ligand. Rather than correlating directly with the formal valency, these trends seem to reflect structural effects predominantly. Thus, we assign the two first, large bond strengths to the bridging chlorines, the three intermediate values to terminal chlorine ligands, and the low value for the sixth ligand to the unfavorable oxidation state Fe^{IV} required in the molecular ion (termed as “hypervalent” chlorine in Figure 4). In contrast to the Fe−Cl bonds, the changes in the corresponding Fe−Fe bonds proceed more smoothly along the series, ranging from a minimum for the molecular ion to the largest value for Fe_2Cl^+. The marked decrease of the Fe−Fe bond strength from $D_0(Fe{-}FeCl^+) =$ 95 kcal/mol to $D_0(Fe{-}Fe^+) = 64$ kcal/mol lends further support to the bridging character of chlorine in Fe_2Cl^+. In close analogy to the structures of neutral Fe_2Cl_4 and Fe_2Cl_6, the results suggest the bridging chlorine ligands as a key element of all $Fe_2Cl_n^+$ ions examined here, and probably the same holds true for the neutral counterparts Fe_2Cl_n ($n = 1{-}3, 5$).

A final facet of the ion chemistry of iron chloride can be derived from the competition of reactions 7b and 7c for (L)-$Fe_2Cl_4^+$ with L = chlorobenzene, which suggests that these exit channels are more or less isoenergetic. The corresponding energy balances are

$$\sum \Delta_f H(7b) = \Delta_f H(C_6H_5Cl) + \Delta_f H(FeCl^+) - D_0(C_6H_5Cl{-}FeCl^+) + \Delta_f H(FeCl_3)$$

$$\sum \Delta_f H(7c) = \Delta_f H(C_6H_5Cl) + IE(C_6H_5Cl) + \Delta_f H(Fe_2Cl_4)$$

As all other quantities are known, the kinetic method can be applied to the (L)$FeCl^+/L^+$ ratio in order to estimate the bond strength of the arene complex $(C_6H_5Cl)FeCl^+$ as $D_0(C_6H_5Cl{-}FeCl^+) = 63 \pm 4$ kcal/mol. This value is significantly larger than the bond strength of the bare metal cation to benzene, $D_0(C_6H_6{-}Fe^+) = 49.6 \pm 2.2$ kcal/mol.[22] Comparison with the related (L)Cr^+ and (L)Co^+ complexes for L = C_6H_6 and C_6H_5Cl implies that the chlorine substituent on the ring even seems to reduce metal−arene binding by about 4 kcal/mol.[23] Hence, the chlorine ligand on Fe increases the metal−arene binding energy by ca. 17 kcal/mol, which corresponds to about one-third of the total binding energy. This result confirms our previous suggestion that coordination of a covalent, electronegative ligand—such as chlorine—to the metal center increases the interaction energies with neutral, coordinative ligands.[24] It is intersting to note in this context that, despite the apparently larger binding energies of neutral ligands to $FeCl^+$ compared to Fe^+, the former cation is much less reactive than the bare metal cation.[25] This conclusion reiterates the time-honored—but often neglected—fact that interaction strengths and activation parameters may have nothing in common.

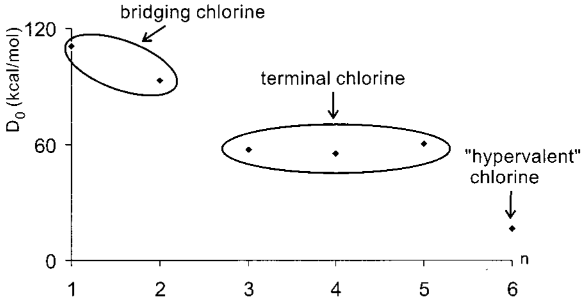

Figure 4. Fe−Cl bond energies of $Fe_2Cl_n^+$ ions as a function of the number of chlorine ligands n.

5. Conclusions

Photoionization experiments and sector-field mass spectrometry provide valuable information about the properties of $Fe_2Cl_n^+$ clusters in the gas phase. As far as the Fe−Cl bond strengths are concerned, structural effects seem to be more relevant than formal valency. From a thermochemical point of view, the dissociation energies derived in this work suggest that the low-valent clusters Fe_2^+ and Fe_2Cl^+ are able to cleave C−Cl bonds in typical organic molecules, while the Fe−Cl bond energies of the $Fe_2Cl_n^+$ cluster with $n = 3{-}5$ are about 20 kcal/mol weaker than C−Cl bonds. A particular role of formal valency is, however, apparent in the ease of dissociation of the molecular ion $Fe_2Cl_6^+$ which can be ascribed to the required presence of an Fe^{IV} center.

Among other aspects, the present work provides two references for future ab initio studies aimed at benchmarking the computational description of coordinatively unsaturated, open-shell transition-metal compounds: (i) the sequence of Fe−Cl and Fe−Fe bond energies of $Fe_2Cl_n^+$ and (ii) the differential ligation of benzene by Fe^+ and $FeCl^+$, respectively. Both properties pose nontrivial challenges to ab initio theory, i.e., the description of spin−spin coupling in $Fe_2Cl_n^+$ clusters and the effect of net charge and formal valency in (L)$FeCl_n^+$ ions ($n = 0, 1$).

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Table 6. Thermochemical Data (in kcal/mol) of Neutral and Ionic Fe_mCl_n Species ($m = 1, 2$; $n = 1-6$) and Ionization Energies (in eV) Available in the Literature

	$\Delta_f H^\circ_{neutral}$	IE	$\Delta_f H^\circ_{ion}$
Fe	98.0 ± 2^{a}	7.9024^{b}	280.2 ± 1.8^{a}
FeCl	$49.2 \pm 1.6^{c,d}$	$\leq 8.08^{c}$	$\leq 229 \pm 2^{e}$
	59.7 ± 20^{a}	7.89^{f}	$229.2^{d,f,g}$
	$45.0^{d,f,g}$	7.90^{h}	$227.0^{f,d}$
	$43.9^{i,g}$	7.93^{i}	$229.0^{g,h}$
	$45.2^{j,g}$	7.91^{j}	$231^{g,i}$
	$47.0^{g,h}$		$233^{g,j}$
$FeCl_2$	$-32.9 \pm 1.0^{c,d}$	10.10^{f}	207
	-33.8 ± 0.5^{a}	$10.23^{k,l}$	$197.0^{d,f,g}$
		$10.34^{l,m}$	
		10.29^{h}	
$FeCl_3$	-60.5 ± 1.2^{a}	10.93^{h}	191.5^{n}
Fe_2Cl_4	-103.7 ± 1.0^{a}	10.5 ± 1.0^{o}	138.4 ± 23.1^{n}
Fe_2Cl_6	-157.3 ± 2.0^{a}		

[a] Reference 6. [b] See: physics.nist.gov/atomic. [c] Experiment, ref 26. [d] Converted to 0 K using the values for neutral Fe_mCl_n in ref 6. [e] Experimental bracket, see text. [f] QCISD(T) calculations, ref 31. [g] Calculated using the bond energy given in the literature. [h] B3LYP calculations, ref 3. [i] CCSD(T) calculations, ref 30. [j] MCPF calculations, ref 30. [k] Photoelectron spectroscopy, ref 32b. [l] Corrected for $\Delta IE_{v/a} = 0.11$ eV, ref 3. [m] Photoelectron spectroscopy, ref 32b. [n] Value derived from $\Delta_f H^\circ{}_{neutral}$ and IE. [o] Appearance energy measurement, ref 13.

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Appendix I

The gas-phase properties of iron chlorides have been studied quite extensively by experimental and theoretical methods (Table 6). Except for the data adopted from the JANAF tables,[6] the thermochemistry was evaluated as follows.

FeCl. The key piece of information for the thermochemistry of FeCl is the ionization energy of the neutral species. Theoretical predictions of 7.91 ± 0.02 eV are consistent with an appearance energy measurement of Hildenbrand.[26] The cationic species $FeCl^+$ is known to be formed upon interaction of bare Fe^+ with methyl chloride according to reaction I.1.[27]

$$Fe^+ + CH_3Cl \rightarrow FeCl^+ + CH_3 \qquad (I.1)$$

The cross section for the reaction of ground state Fe^+ (^6D) at thermal energy is only about 2% of the collisional cross section. This is confirmed by a rate constant $k_r = (1.6 \pm 0.5) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} as determined by ICR experiments;[28] the collision rate constant amounts to $k_c = 1.7 \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1}. However, the energy dependence of reaction I.1 reported in ref 27 shows no indications for a thermochemical control, and hence, we attribute the low reaction efficiency to the operation of a kinetic barrier. Occurrence of reaction I.1 at thermal energy thus implies $\Delta\Delta G_{298} \leq 0 \pm 2$ kcal/mol. As an atom is involved, reaction I.1 shows a significant thermal correction of 2.4 ± 1 kcal/mol (see Appendix II). In conjunction with $D_0(CH_3-Cl) = 81.9$ kcal/mol,[10,29] we arrive at $D_0(Fe^+-Cl) \geq 79.5 \pm 2$ kcal/mol or $\Delta_f H(FeCl^+) \leq 229 \pm 2$ kcal/mol. This value is in good agreement with recent theoretical predictions at various levels of theory.[3,30,31] Thus, reaction I.1 is assigned to be thermoneutral at 298 K. Combined with IE(FeCl), we arrive at $\Delta_f H(FeCl) \leq 47 \pm 3$ kcal/mol, which is consistent with the experimental data for the neutral compound, though slightly lower than the value given by Hildenbrand.[26] Further, note that the figure given in JANAF tables is significantly larger though still within the error limits. Combining this information, we assign the values $\Delta_f H(FeCl) = 47 \pm 3$ kcal/mol, IE(FeCl) = 7.9 ± 0.1 eV, and $\Delta_f H(FeCl^+) = 229 \pm 3$ kcal/mol.

$FeCl_2$. The JANAF value $\Delta_f H(FeCl_2) = 33.8 \pm 0.5$ kcal/mol is consistent with recent results of Hildenbrand[26] and used as such. The heat of formation of the cation can thus be derived from the IE of neutral $FeCl_2$. Two photoelectron spectroscopic studies[32] yield an average of 10.39 ± 0.1 eV for the vertical IE_v to which we apply the calculated[3] difference of $\Delta IE_{v/a} = 0.11$ eV between the vertical and adiabatic ionization energies of $FeCl_2$ to arrive at $IE(FeCl_2) = 10.28 \pm 0.15$ eV. Hence, $\Delta_f H(FeCl_2{}^+) = 203.3 \pm 3.5$ kcal/mol is obtained. While ab initio calculations predict slightly lower values,[3,31] we rely on this estimate because the neutral reference seems to be settled well and the photoelectron spectra are hard to defeat.

$FeCl_3$ and Fe_2Cl_4. For both neutral compounds, the JANAF values are adopted. Surprisingly, the ionization energy of $FeCl_3$ has not been measured. Thus, we must rely on a single value from ab initio studies[3] and derive $\Delta_f H(FeCl_3{}^+)$ accordingly. An earlier appearance energy measurement for $IE(Fe_2Cl_4{}^+)$[13] is questioned, however, and not used in the analysis (see text).

Appendix II

Consider the competitive dissociation of a tetra-atomic system ABCD according to reactions II.1 and II.2 (Chart 1) and attribute the corresponding degrees of freedom (ABC is assumed to be bent).

The formation of two molecular fragments in reaction II.1 is associated with a gain of one rotational degree of freedom to be compared with loss of one vibrational mode relative to the formation of an atom in reaction II.2. Given that vibrations are usually more difficult to excite than rotations, the density of states is larger for reaction II.1 at ambient temperature. Hence, when both reactions are in competition, reaction II.1 is favored over reaction II.2 due to entropic effects. While this is an almost trivial, merely qualitative deduction, let us try to estimate the relevance of this thermal effect in competitive fragmentation by reference to several other systems studied in our laboratory.

$$Fe(Xe)^+ + N_2 \rightarrow Fe(N_2)^+ + Xe \qquad (II.3)$$

The relevance of entropic effects when atoms are involved was first recognized in a study of the ligand-exchange reaction (II.3) of the $Fe(Xe)^+$ cation with weakly coordinating ligands such as dinitrogen. According to ab initio calculations, the left-hand side (two molecules) of reaction II.3 is favored by about $\Delta E_{corr} = \Delta\Delta G_{298} - \Delta\Delta G_0 = 1.9 \pm 0.3$ kcal/mol at 298 K.[33] Given the accuracy of equilibrium measurements (usually a few

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Chart 1

ABCD →	AB +	CD (II.1)	versus ABC +	D (II.2)	Δ
translation	3	3	3	3	0
rotation	2	2	3	0	+1
vibration	1	1	3	0	- 1

tenths of a kilocalorie per mole), this correction term is indeed quite substantial. After becoming aware of this effect, we recognized that several other reactions show significant entropic effects between 0 and 298 K whenever an atom is formed, e.g., 3.4 kcal/mol for $Au(Xe)^+/C_6F_6$,[34] 1.7−2.7 kcal/mol for several $VO_mH_n^+$ compounds,[35] and 2.4 kcal/mol for Fe^+/CH_3Cl.[28]

$$FeCl_3 \rightarrow FeCl_2 + Cl \qquad (II.4)$$

$$FeCl_3 \rightarrow FeCl + Cl_2 \qquad (II.5)$$

Another estimate with particular relevance to the present study is provided by analysis of the hypothetical dissociations of neutral $FeCl_3$ according to reactions II.4 and II.5. Again, the data given in ref 6 suggest thermal corrections of 2.0 and 2.7 kcal/mol at 298 and 473 K, respectively, in favor of reaction II.5 yielding two molecular fragments compared to formation of an atom in reaction II.4.

Resuming all examples discussed in this appendix, an empirically estimated average of $\Delta E_{corr} = 3 \pm 1$ kcal/mol at $T_{eff} = 473$ K is used in the evaluation of the MI data according to the kinetic method.

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