Journal of Organometallic Chemistry, 391 (1990) 209–218
Elsevier Sequoia S.A., Lausanne
JOM 20862

A mass spectrometric investigation of chloro-, bromo- and methyl-ferrocenes by electron and photon impact ionisation

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(Received January 10th, 1990)

Abstract

Various ferrocenes $Fe(C_5H_{5-n}Cl_n)_2$ ($n = 1$–5), $Fe(C_5H_4Br)_2$, $Fe(C_5H_{5-n}(CH_3)_n)_2$ ($n = 1$–5) have been investigated by electron and photon impact mass spectroscopy. Ionisation and appearance potentials (IP/AP) have been measured and we have characterized the influence of substitutions of CH_3, Cl, or Br at the cyclopentadienyl rings upon the IPs, APs, and the fragmentation pathways. In addition, some bond energies are derived.

Introduction

There is considerable theoretical interest in the ferrocene molecule, and as a consequence it has been investigated by many authors and methods [1–11]. Structure, bonding, bond lengths etc. of the unsubstituted bis(η^5-cyclopentadienyl)iron, (i.e. ferrocene), are all well known. Nonetheless, the data for substituted ferrocenes remains sparse, although a description for synthesizing substituted ferrocenes was given by Kovar, Rausch, Rosenberg and Hedberg in 1971 and 1973 [12,13]. Optical absorption studies have shown that even symmetric substitutions will affect the Cp-metal bonding [14].

0022-328X/90/$03.50

With the advent of new thin film technologies such as OMVPE (organometallic vapor phase epitaxy) or MOCVD (metal-organic chemical vapor depositions), organometallics like metallocenes have been regarded as candidates for these technologies [15–17]. In this paper we have examined how the physical and chemical properties of ferrocene are changed when the hydrogen atoms at the cyclopentadienyl ring are substituted by chlorine or bromine atoms or methyl groups. We investigated in the gas phase, 1,1-dichloroferrocene, 1,1′,2,2′-tetrachloroferrocene, 1,1′,2,2′,3,3′-hexachloroferrocene, 1,1′,2,2′,3,3′,4,4′-octachloroferrocene, 1,1′,2,2′,3,3′,4,4′,5,5′-decachloroferrocene; 1,1′-dibromoferrocene; 1,1′-dimethylferrocene, and 1,1′,2,2′,3,3′,4,4′,5,5′-decamethylferrocene by electron and photon impact mass spectroscopy.

Experimental

Gas phase species are generated by vaporization of solid compounds in a Knudsen cell. The beam of the molecules to be investigated cross the beam of synchrotron radiation in the ionization region of a quadrupole mass spectrometer (QMS), Fig. 1. The ion yield detected in the QMS is recorded as the dependence on photon energy (ion yield or ion efficiency curve = IEC) in the range from 5–25 eV. From these curves ionization potentials (IP) and appearance potentials (AP) are obtained.

Electron impact ionization (EI) could be attained at 70 and 30 eV or less. The apparatus for EI measurements, described previously [18], was nearly the same as for photoionization (PI), which is shown in Fig. 1. The impact energy of both EI and PI could be run from 5 to 25 eV, so that IPs and APs could be derived from ion efficiency curves.

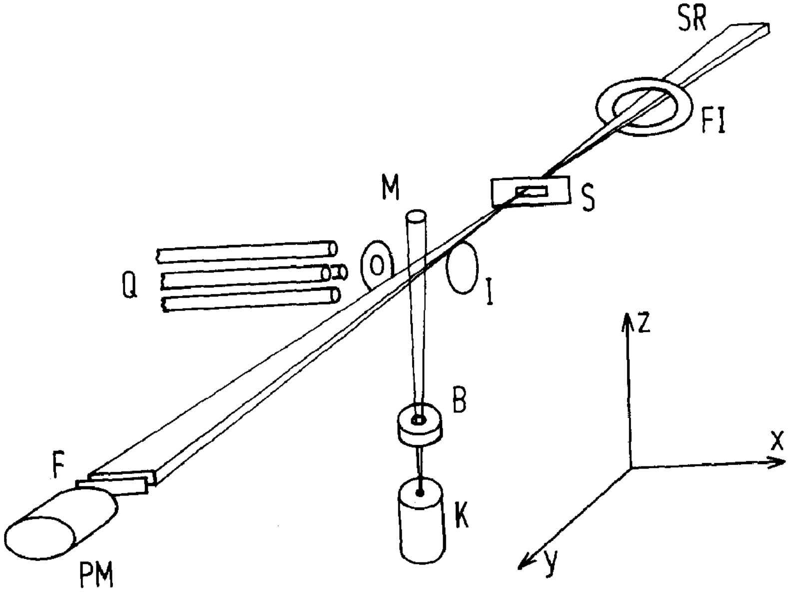


Fig. 1. Schematic experimental set-up (PM: photomultiplier; Q: quadrupole mass analyzer; I: ionisation chamber; S: slit; SR: synchrotron radiation; F: Na-salicylate window; K: Knudsen cell; M: molecular beam; FI: LiF window).

Results and discussion

In Fig. 2 EI and PI mass spectra of the ferrocenes are shown, the upper ones are EI at 70 eV those below are PI at 25 eV. It is immediately clear from Fig. 2 that the methylferrocene photoionization spectra are the less complicated ones. Neglecting abstraction of single or multiple hydrogen, the same is also true (though not as dramatically) for the EI spectra. When the impact energy is diminished, as shown in Fig. 3, the spectra simplify, as expected.

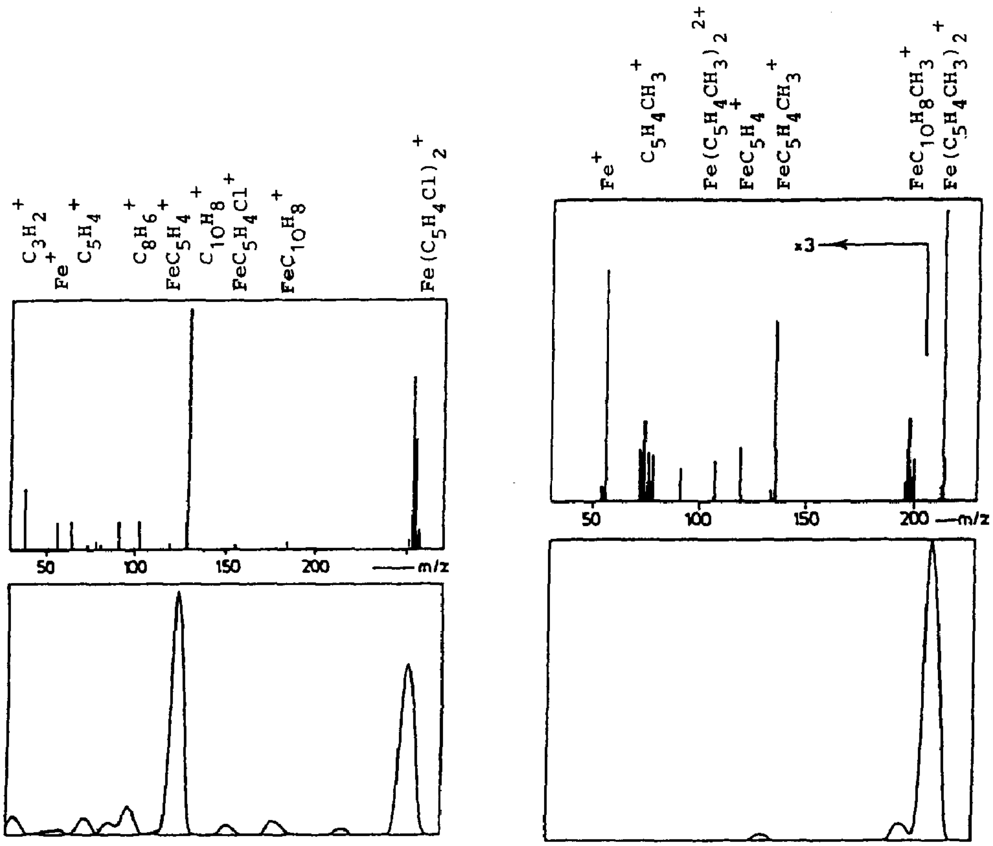
To elucidate the fundamental ionization and fragmentation processes, ionization efficiency curves (IECs-see for instance Fig. 9) have been taken of all parent and fragment ions with both the EI and PI methods. From these IECs the fragment appearance potentials (AP) and the parent ionization potentials (IP) can be derived [18]. These values are compiled in Tables 1 and 2 for the bromo-, chloro-, methyl-and unsubstituted ferrocene. The ionization potentials for ferrocene (PI = 6.61 ± 0.08 eV, EI = 6.9 ± 0.2 eV), dibromoferrocene (PI = 7.0 ± 0.05 eV, EI = 7.5 ± 0.1 eV), dichloroferrocene (PI = 6.97 ± 0.05 eV, EI = 7.1 ± 0.1 eV) and dimethylferrocene (PI = 6.5 ± 0.1 eV, EI = 6.6 ± 0.2 eV) are in good agreement with the photoemission (PES) results of 6.9 eV [19–25], 7.17 eV [21], 7.1 [19,21,22] and 6.72 eV [19,22] respectively.

In Fig. 4 and 5 the IPs of these compounds are shown to demonstrate the dependence on substitution. Both the number and type of substituents are important for the energy value of the IP of a particular ferrocene. The highest occupied molecular orbitals (HOMO) of the molecule have mainly metal *d*-orbital character, thus changes in the metallocene metal have a greater influence upon the first IP than substitutions to the cyclopentadienyl ligand. For example, the IP of cobaltocene is 5.7 eV, that of magnesocene is 8.0 eV as compared to 6.9 eV for ferrocene [23]. We note that all IPs derived from EI measurements are somewhat higher than those from PI. In general, data derived from PI measurements are much more reliable than those from EI, particularly at small energies because of the far better resolution inherent in PI measurements and the greater accuracy attainable in calibrating energies.

The methyl substituents on the cyclopentadienyl ring increase the electron density of the π-orbital system, so that the bonds with the central iron atom in our sandwich structure are stabilized. This can be seen from Fig. 2 where the mass spectra of methylferrocenes show less fragmentation than the chlorinated ferrocenes spectra. Chlorine substitution opens possibilities for fragmentation pathways which do not readily occur with methyl substitution.

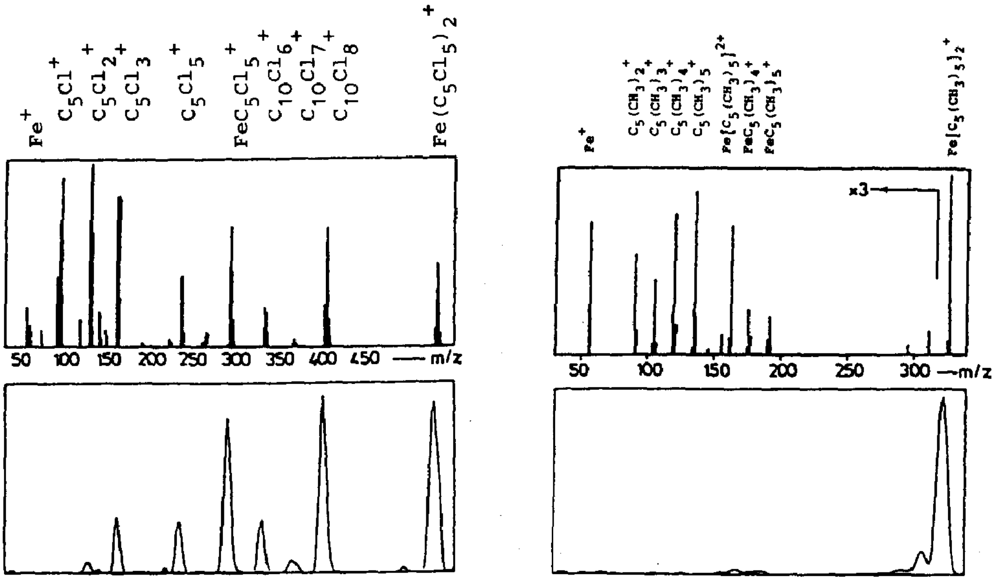
As shown in Fig. 6, the $FeCl_2$ abstraction as a neutral dominates the fragmentation pathway. In all chloroferrocene spectra $C_{10}H_{10-2n}Cl_{2n-2}^+$ $(n = 1–5)$ is one of the abundant fragment ions. Furthermore, formation of $FeCl_2$ also occurs when other fragment ions are created by production of $C_5H_{5-n}Cl_n$ (e.g. formation of $FeC_5H_{5-n}Cl_n^+$) to form $C_5H_{5-n}Cl_{n-2}^+$.

Schematically shown in Fig. 7 are the APs of the halogen substituted ferrocene fragment ions, $C_{10}H_{10-2n}Cl_{2n-2}^+$ and $FeC_5Cl_n^+$, which are created by abstraction of $FeCl_2$ and by abstraction of one cyclopentadienyl ring, respectively. The AP of $C_{10}H_{10-2n}Cl_{2n-2}^+$ fragment ions (obtained by abstraction of $FeCl_2$ from chloroferrocenes) remains stable at about 12 eV, independent of the number of chlorine substitutions to the Cp-ring of the parent ions. The ion ($C_{10}H_{10}^+$) is also found in



1,1'dichloroferrocene

1,1'dimethylferrocene



decachloroferrocene

decamethylferrocene

Fig. 2. EI (upper ones) 70 eV and PI 25 eV mass spectra of four different ferrocenes.

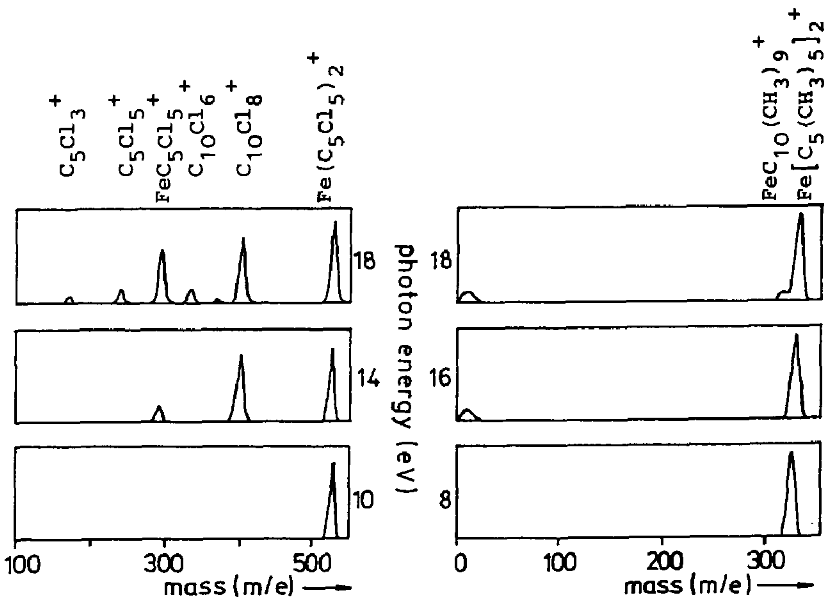


Fig. 3. PI mass spectra of decachloro- and decamethylferrocene at different photon energies.

the mass spectrum of non-substituted ferrocene, though its AP, however, is markedly higher, i.e. 14 eV. We postulate that this ion is the fulvalene ion since we believe that C_5H_5 and $C_5H_5^+$ rings are stable. This indicates that the abstraction of $FeCl_2$ due to the formation of chlorofulvalenes follows a synchronous mechanism so that at the same time the iron-ring and chlorine-carbon bonds are broken, iron-chlorine bonds are formed. Energy arguments favor such a mechanism for the substituted ferrocenes. On the other had the dissociation of the iron-ring bond of the ferrocene molecule itself requires less energy. The substitution with chlorine atoms leads to a pronounced increase of the APs of the $FeC_5H_{5-n}Cl_n^+$. This effect of stabilization is reverted, to a certain extent, with an increasing number of chlorine substituents at the Cp-ring (Fig. 7). Decisive for this is the energy, required for dissociating $Fe(C_5H_{5-n}Cl_n)_2^+$, forming $FeC_5H_{5-n}Cl_n^+$ and $C_5H_{5-n}Cl_n$. The energy for this dissociation, calculated from the AP data, is shown in Table 3.

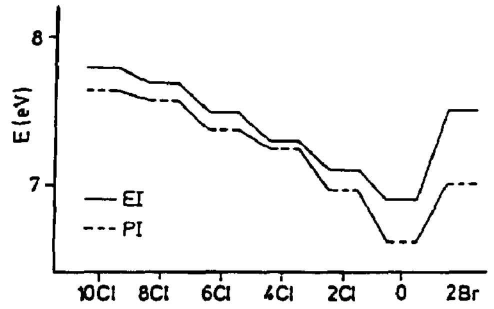


Fig. 4. Ionization potentials of halogenoferrocenes EI and PI derived.

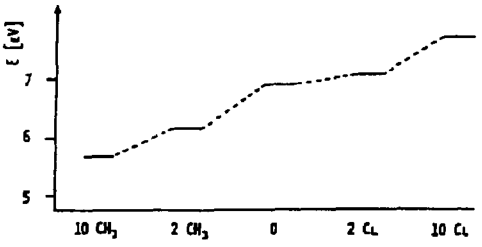


Fig. 5. Ionization potentials of methyl and chloroferrocenes PI derived.

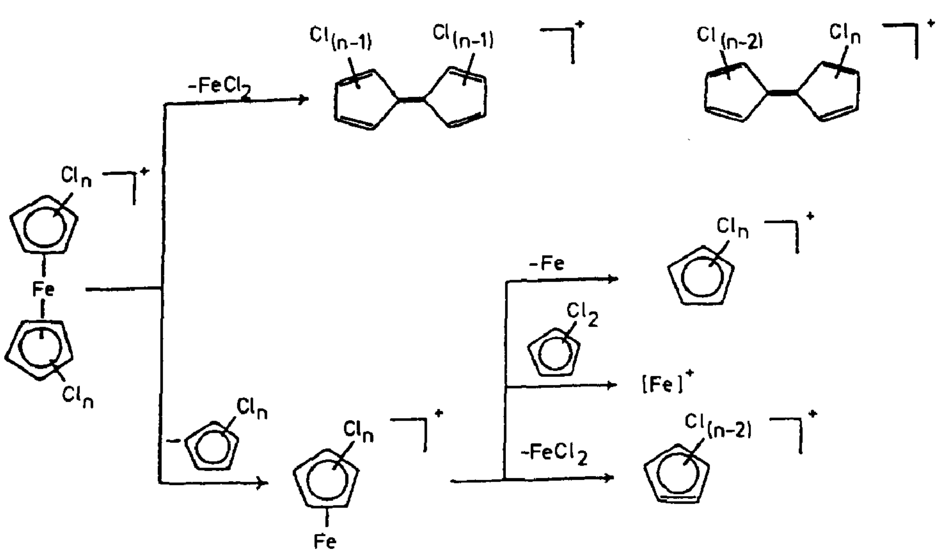


Fig. 6. Main fragmentation pathway of halogenoferrocenes [29].

Various bond strengths can be calculated from the data in Tables 1 and 2 using additional literature data and the thermodynamic cycle shown in Fig. 8. However, one has to be careful in using these cycles for calculating bond energies as the fragmentation process considered must be well defined energetically. One example is the formation of the iron ion Fe$^+$ from unsubstituted ferrocene. A simultaneous

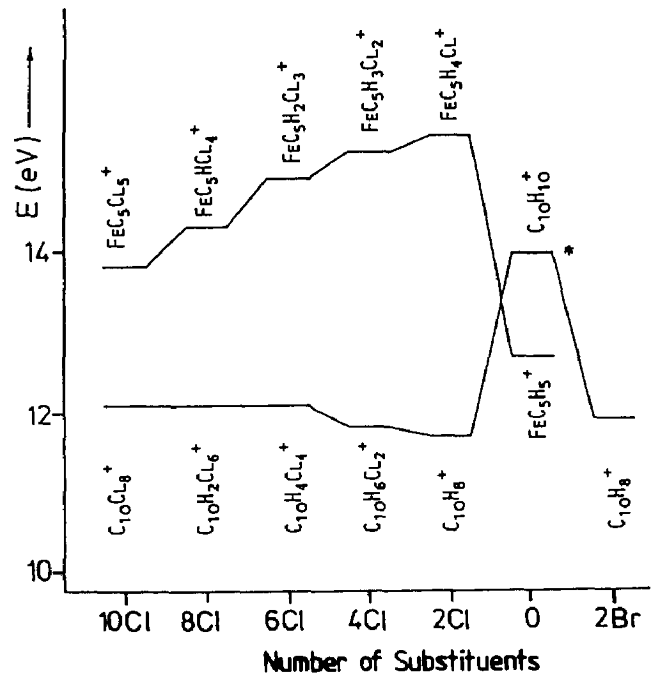


Fig. 7. APs fragment ions formed by abstraction of FeCl$_2$ (12 eV) and by abstraction of one cyclopentadienyl (upper) versus number of substituents.

Table 1

Ionisation and appearance potentials (eV) of substituted ferrocenes derived from ionization effciency curves (IECs) by electron impact (EI) and photoionization (PI)

	EI	PI		EI	PI
decachloroferrocene			octachloroferrocene		
$Fe(C_5Cl_5)_2^+$	7.8±0.1	7.65±0.08	$Fe(C_5HCl_4)_2^+$	7.7±0.1	7.58±0.07
$C_{10}Cl_8^+$	12.1±0.2	11.8 ±0.1	$C_{10}H_2Cl_6^+$	12.1±0.2	11.4 ±0.1
$C_{10}Cl_6^+$	14.2±0.3		$C_{10}H_2Cl_5^+$	14.1±0.3	13.3 ±0.2
$FeC_5Cl_5^+$	13.8±0.2	12.8 ±0.1	$C_{10}H_2Cl_4^+$	14.8±0.3	
$C_5Cl_5^+$	13.9±0.3	13.1 ±0.1	$FeC_5HCl_4^+$	14.3±0.2	13.2 ±0.1
$C_5Cl_3^+$	16.8±0.3		$C_5HCl_4^+$	14.5±0.3	14.0 ±0.1
$C_5Cl_2^+$	19.7±0.3		$C_5HCl_2^+$	16.8±0.3	15.7 ±0.2
			C_5HCl^+	20.1±0.3	
hexachloroferrocene			tetrachloroferrocene		
$Fe(C_5H_2Cl_3)_2^+$	7.5±0.1	7.38±0.05	$Fe(C_5H_3Cl_2)_2^+$	7.3±0.3	7.25±0.05
$C_{10}H_4Cl_4^+$	12.1±0.2	11.1 ±0.3	$C_{10}H_6Cl_2^+$	11.8±0.2	11.0 ±0.3
$C_{10}H_4Cl_3^+$	13.8±0.2	12.6 ±0.1	$C_{10}H_6Cl^+$	14.2±0.2	13.3 ±0.1
$C_{10}H_4Cl_2^+$	15.6±0.3	13.2 ±0.1	$C_{10}H_6^+$		14.6 ±0.1
$FeC_5H_2Cl_3^+$	14.9±0.3	13.9 ±0.1	$FeC_5H_3Cl_2^+$	15.2±0.3	14.5 ±0.1
$C_5H_2Cl_3^+$	15.3±0.3	14.4 ±0.1	$C_5H_3Cl_2^+$		14.4 ±0.2
$C_5H_2Cl^+$	17.1±0.3	16.1 ±0.1	$C_5H_3^+$	17.5±0.2	16.4 ±0.1
$C_5H_2^+$	21.0±0.3				
dichloroferrocene			dibromoferrocene		
$Fe(C_5H_4Cl)_2^+$	7.1±0.1	6.97±0.05	$Fe(C_5H_4Br)_2^+$	7.5±0.1	7.0 ±0.05
$FeC_{10}H_8^+$	12.2±0.3	12.7 ±0.1	$FeC_{10}H_8^+$		12.5 ±0.2
$C_{10}H_8^+$	11.7±0.2	<11.2	$C_{10}H_8^+$	11.9±0.2	12.2 ±0.1
$FeC_5H_4Cl^+$	15.4±0.3	13.7 ±0.1	$C_8H_6^+$	15.0±0.2	13.9 ±0.2
$FeC_5H_4^+$	18.3±0.3				
$C_8H_6^+$	15.5±0.3	13.6 0.1			
$C_5H_4^+$	19.1±0.3				
Fe^+	15.4±0.3	13.7 ±0.1			
decamethylferrocene			dimethylferrocene		
$Fe(C_5(CH_3)_5)_2^+$	6.2±0.1	5.8 ±0.1	$Fe(C_5H_4CH_3)_2^+$	6.6±0.2	6.5 ±0.1
$FeC_{10}(CH_3)_9^+$	9.1±0.2		$FeC_{10}H_8CH_3^+$	7.1±0.3	6.6 ±0.1
$FeC_{19}H_{26}^+$	15.8±0.2	14.8 ±0.1	$FeC_6H_6^+$	13.5±0.3	13.2 ±0.2
$Fe(C_5(CH_3)_5)_2^{2+}$	20.5±0.3		$FeC_5H_5^+$	14.5±0.3	13.9 ±0.2
			$Fe(C_5H_4CH_3)_2^{2+}$	20.6±0.3	
			$C_5H_4CH_3^+$	17.7±0.3	17.7 ±0.3
			Fe^+	16.7±0.3	14.9 ±0.3

(Fig. 9a) as well as a successive (Fig. 9b) abstraction of the ligands occurs, giving rise to two values of the AP of Fe^+ (see Table 2). As can be taken from Fig. 9a (left-hand arrow and insert) the energy requirement for the simultaneous abstraction of both ligands to form Fe^+ amounts to 14.3 eV.

The APs for Fe^+ and the IPs for the molecular ion are compiled for dichloro-, dimethyl- and unsubstituted ferrocene in Table 4. Using these data and the IP of iron in the gas phase (7.87 eV [26]) we are able to calculate – on the basis of the thermodynamic cycle (Fig. 8) – the dissociation energies of FeL_2 and FeL_2^+ corresponding to the simultaneous abstraction of both ligands (L).

Table 2

IPs and APs of ferrocene, comparison of our photoionization data (PI) with literature values

$Fe(C_5H_5)_2^+$	$FeC_8H_8^+$	$FeC_5H_5^+$	$FeC_3H_3^+$	$C_{10}H_{10}^+$	Fe^+	Ref.
7.05 ±0.1		14.38 ±0.3			17.1 ±0.9	3
7.15 ±0.1	13.27±0.1	13.78 ±0.1	18.9 ±0.1		14.4 ±0.5	2
6.9 ±0.1		13.9 ±0.2			12.0 ±1.5	1
6.77 ±0.02		13.93 ±0.08	18.06±0.1	13.96±0.1	13.96 ±0.05	5
6.747±0.009		13.162±0.035			13.506±0.037	11
6.61 ±0.08	13.2 ±0.1	13.3 ±0.1	17.5 ±0.3	13.5 ±0.1	14.3 ±0.2	PI this work

Table 3

Dissociation energy (DE) of the iron–ring bond of the molecular ion in eV (*n*: number of Cl-atoms at one ring)

	$AP(FeC_5H_{5-n}Cl_n^+)$		$IP(Fe(C_5H_{5-n}Cl_n)_2^+)$		$DE(LFe-L)^+$	
	EI	PI	EI	PI	EI	PI
$n=0$	12.7	13.3	6.9	6.61	5.8±0.5 6.63 [2]	6.7 6.4 [11]
$n=1$	15.4	–	7.1	–	8.3	
$n=2$	15.2	14.5	7.3	7.25	7.9	7.3
$n=3$	14.9	13.9	7.5	7.38	7.4	6.5
$n=4$	14.3	13.2	7.7	7.52	6.6	5.6
$n=5$	13.8	12.8	7.8	7.65	6.0	5.2

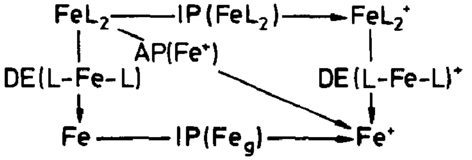


Fig. 8. Thermodynamic cycle for ferrocene ionization/decomposition (L: ligand (substitutent), DE: dissociation energy).

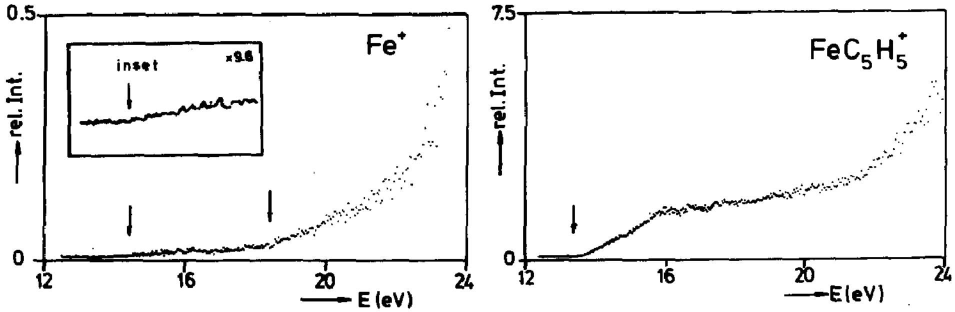


Fig. 9. Ionization efficiency curves (IECs) of ferrocene (PI) for Fe^+ and $FeC_5H_5^+$.

Table 4

Dissociation energies (DE) calculated from IPs/APs (eV)

Molecule	IP	AP Fe^+	DE (L–Fe–L)	DE $(L–Fe–L)^+$
$Fe(C_5H_4Cl)_2$	7.0	13.7	5.8	6.7
$Fe(C_5H_5)_2$	6.6	14.3	6.4	7.7
$Fe(C_5H_4CH_3)_2$	6.5	14.9	7.0	8.4
$Fe_{(g)}$	7.87 [26]	–	–	–

The values included in Table 4 indicate an increasing stabilization in the sequence dichloro-unsubstituted-dimethyl-ferrocene, as well for the neutral molecule as for the molecular ion. Inspection of Table 4 furthermore reveals that the molecular ion has stronger metal to ligand bonds than the neutral molecule (comparison of columns 3 and 4 in Table 4). The removal of an electron from a non-bonding orbital and the electronic relaxation around the positive hole obviously induces a stabilization of the system. Increased positive charge on the metal appears to increase the ligand-metal hybridization, consistent with optical studies [14].

Successive abstraction of ligands from ferrocene, i.e. formation of FeL^+ ($= FeC_5H_5^+$), has a much higher probability than the simultaneous abstraction, as revealed by the comparison of relative intensities in Figs. 9b and 9a. The IEC of Fe^+ (Fig. 9a) exhibits a marked increase in slope at 18.3 eV (marked with an arrow) which is the AP of the formation of Fe^+ from $Fe(C_5H_5)_2$.

Flesch et al [5] arrived at values of 14.4 and 18.9 for the simultaneous and successive processes, respectively, by metastable ion measurements, in good agreement with our data. The large energy of about 4 eV in the successive process, must be correlated with a different final state compared to the simultaneous process, i.e. different products of different energy.

Conclusions

The energy required for the simultaneous abstraction of both cyclopentadienyl rings from the central iron atom, DE(L–Fe–L), was determined for dichloroferrocene, ferrocene and dimethylferrocene. The dissociation energy increases in the given sequence, i.e. from chloro- to dimethylferrocene, as shown in Table 4.

This dissociation energy cannot be determined for all other substituted ferrocenes since, due to competitive fragmentation pathways, the Fe^+ ion intensities are in most cases too small to record IECs. Stabilization of the investigated ferrocene molecules by ionization was also observed.

For possible metal deposition from the vapor of organometallics (MOCVD) one can conclude for substituted ferrocenes: methyl substitution increases the energy necessary for the dissociation of the iron–ring bonds, thus metal deposition becomes less favorable. Furthermore, rearrangements can occur in the excited fragment leading to stabilization and consequently more carbon impurities in thin film production. For dichloroferrocene the required dissociation energy is lower than for unsubstituted ferrocene, but as shown above, the number of competitive fragmentation pathways increases with increasing number of chlorine substitutions. Light- or plasma-induced processes will not lead to metal films as clean as from the unsubstituted molecule.

Unsubstituted complexes such as nickelocene and other organometallic compounds like allylcyclopentadienyl palladium do appear to be suitable source compounds for the deposition of clean metal films [16,27,28].

Acknowledgement

This work has been funded by the German Federal Minister of Research and Technology (BMFT) under the contract number 05 313 FX B3 TP1.

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