Journal of Organometallic Chemistry, 241 (1983) 375–383
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

A REINVESTIGATION OF THE MASS SPECTRA OF SUBSTITUTED FERROCENES: ACCURATE FRAGMENTATION PATHWAYS AND IONIC STRUCTURES BY ANALYSIS OF METASTABLE ION SPECTRA

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(Received August 3rd, 1982)

Summary

The mass spectra of substituted ferrocenes have been reinvestigated making intensive use of the metastable ions. The observed primary fragmentations of the molecular ions are different in some respects from those previously postulated. The study of the metastable ions characteristics of the ions at m/z 186 and m/z 121 indicates that their structures are independent of their precursor ions.

Introduction

Ferrocene and its derivatives have been studied by mass spectrometry since 1955 [1]; since then much information on the mass spectra has been reported and several fragmentation routes have been proposed [2] but these are not always supported by the appropriate metastable transitions.

The mass spectra of this class of compounds are in fact, very simple, generally showing a small number of ions with overwhelming relative abundance; this led to the assumption of very simple fragmentation pathways, and arguments [3] about the substituent effect on the dissociation energy of the bond between the iron atom and the ring have been advanced on the basis of those oversimplifications.

We have reinvestigated the behaviour of some substituted ferrocenes under electron impact and have carefully examined proposed fragmentation schemes using the metastable transitions. Some ionic structures are tentatively discussed on the basis of metastable ion characteristics.

Experimental

Ferrocene derivatives were prepared by literature methods [4]. Mass spectra were

0022-328X/83/0000–0000/$03.00

recorded on a Finnigan-MAT 112S mass spectrometer at 70 eV. The ion source temperature was fixed at 200°C while the sample inlet temperature was varied between 20 and 70°C according to volatility of the relevant compound.

The mean kinetic energy released in metastable transitions was evaluated in the usual way [5]. The collision-induced metastable ions were studied on a VG ZAB 2F mass spectrometer, with air as the collision gas.

The mass spectra were found to be in good agreement with those previously reported; the minor differences observed can be attributed to the different experimental conditions, and a complete listing of the data would be superfluous.

Results and discussion

In spite of the presence of relatively few ions in the mass spectra of the ferrocene derivatives, the fragmentation schemes are quite complex. The scheme for η-C_5H_5Fe-η-$C_5H_4CH_2N(CH_3)_2$ shown in Fig. 1, is representative of the general behaviour of these compounds. The subsequent discussion will be limited to the reactions of the molecular ions and of their direct daughter ions; each of the

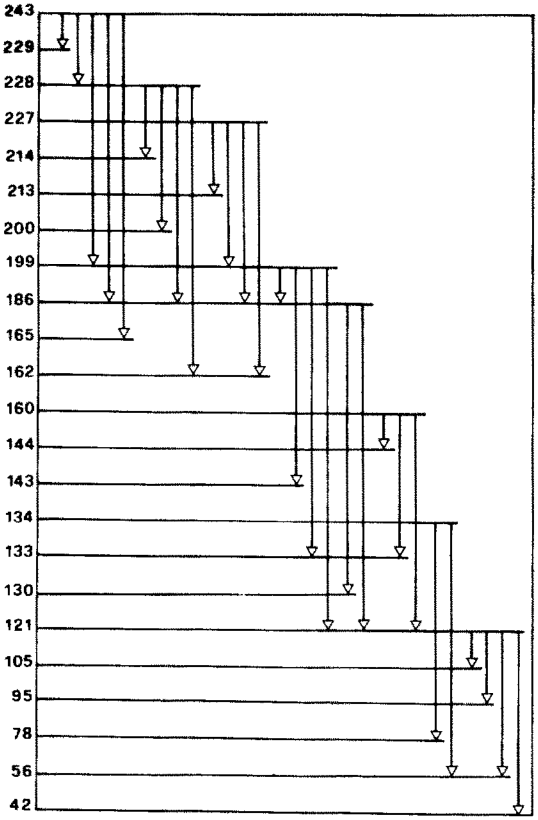
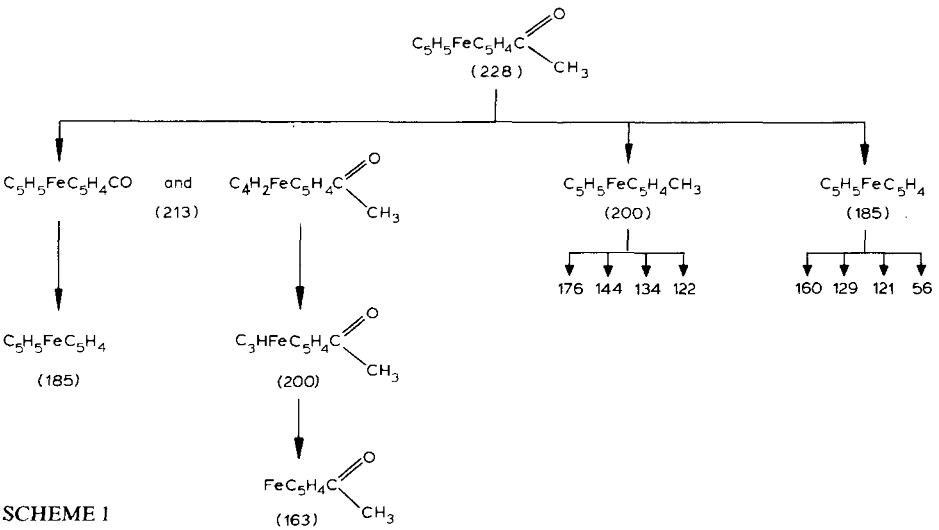


Fig. 1. Fragmentation scheme for η-C_5H_5Fe-η-$C_5H_4CH_2N(CH_3)_2$.



SCHEME 1

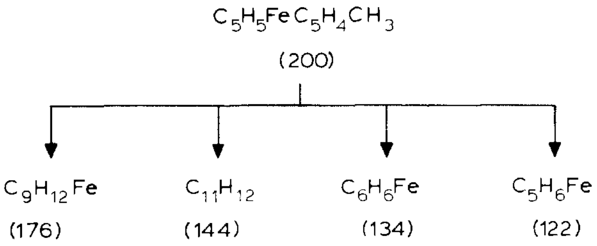
reactions is confirmed by the presence of a metastable transition, observed mainly in the second field free region.

η-C_5H_5Fe-η-$C_5H_4COCH_3$ (I)

The molecular ion undergoes three parallel fragmentation reactions (several have been previously postulated [6]) with the loss of 15, 28 and 43 a.m.u.; the first process is the most favoured in the second field free region, the relative intensities of the associated metastable ions being 100/1/3. Scheme 1 shows some of the observed fragmentations. To rationalize this scheme it is necessary to postulate two different routes to the ion at *m/z* 213, namely (1) loss of the ketonic methyl group (the resulting ion can be formulated as $C_5H_5FeC_5H_4CO$ (1a)) and (2) loss of a methyl group from the cyclopentadiene ring in a reaction found for ferrocene itself (the resulting ion can be formulated as $C_4H_2FeC_5H_4COCH_3$ (1b)). The ion 1a fragments by loss of CO to give $C_5H_5FeC_5H_4$ (*m/z* 185) and the ion 1b loses a ·CH group to give an ion at *m/z* 200, which has a different structure (it can be formulated as $C_3HFeC_5H_4COCH_3$) from that of the ion of the same mass obtained in a single step from the molecular ion. This interpretation is based on two observations: (a) the ion at *m/z* 200 loses 37 a.m.u.; this type of reaction has never been observed in ions with intact cyclopentadiene rings but it becomes very evident after the destruction of the ring; (b) among the fragmentations of the molecular ion of methylferrocene (see compound II later) there is no process giving rise to an ion at *m/z* 163.

η-C_5H_5Fe-η-$C_5H_4CH_3$ (II)

The most probable decomposition reaction of this molecular ion in the metastable region is that leading to the ion at *m/z* 134 (C_6H_6Fe), which is also the base peak in the normal mass spectrum. Other fragmentations (see Scheme 2) lead to the ions at *m/z* 176 (loss of 24 a.m.u.), 144 (loss of an iron atom) and 122 (loss of a benzene molecule). In conflict with a previous report [7], we did not observe single step formation of the ions at *m/z* 121 and 56 from the molecular ion; however, this does not invalidate previous hypotheses about the ionic structures [7].



SCHEME 2

η-C_5H_5Fe-η-C_5H_4CHO (III)

The 70 eV spectrum of this compound is presented in Table 1, since to our knowledge, it has not been previously published, even though this compound is one of the most accessible ferrocene derivatives. The molecular ion undergoes only one fragmentation to ferrocene ion; this must be due to the stability of the ferrocene structure and to the ease of loss of CO; a small shoulder in the metastable peak suggests the loss of a HCHO molecule also, with formation of the ion at *m/z* 184. All the subsequent fragmentations are identical to those of ferrocene itself.

η-C_5H_5Fe-η-C_5H_4COOH (IV)

The mass spectrum of this compound has been previously discussed [6]. The metastable ion spectrum (see Scheme 3) confirms the high probability of formation of the ion at *m/z* 138 (C_5H_5FeOH) due to a rearrangement typical of the ferrocene derivatives bearing oxygen or nitrogen atoms (see also compounds V and VII). In contrast to the previous statement, we did not find evidence for the formation of an ion at *m/z* 121 from the molecular ion; the breaking of an iron–ring bond leads to the ion at *m/z* 165, to which the structure FeC_5H_4COOH can be assigned, in agreement with its subsequent reactions which gave the ions at *m/z* 137 (CO loss) and 73 (FeOH).

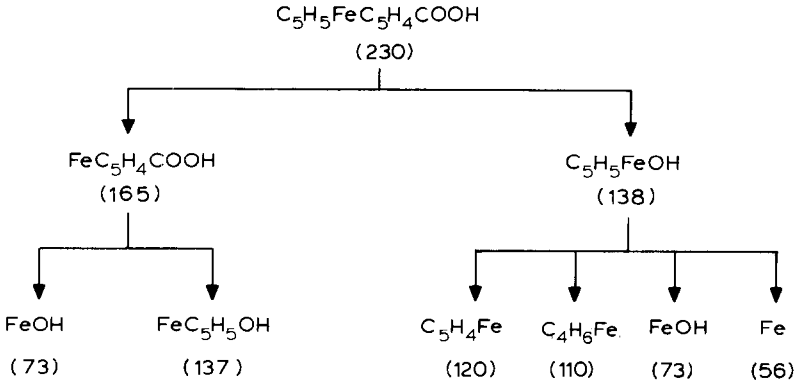
η-C_5H_5Fe-η-$C_5H_4CH_2OH$ (V)

This molecular ion loses H_2O (resulting ion *m/z* 198) in a reaction typical of the alcohols; this reaction competes effectively in the energy range in which metastable ions are formed with formation of the C_5H_5FeOH ion (*m/z* 138). The subsequent

TABLE 1

70 eV MASS SPECTRUM of η-C_5H_5Fe-η-C_5H_4CHO.

m/z	*I*	*m/z*	*I*
214	100	122	8.3
212	5.5	121	93.5
186	93.5	120	13.8
185	5.5	95	11.0
184	17.0	94	11.0
129	11.0	93	2.8
128	11.0	77	2.2

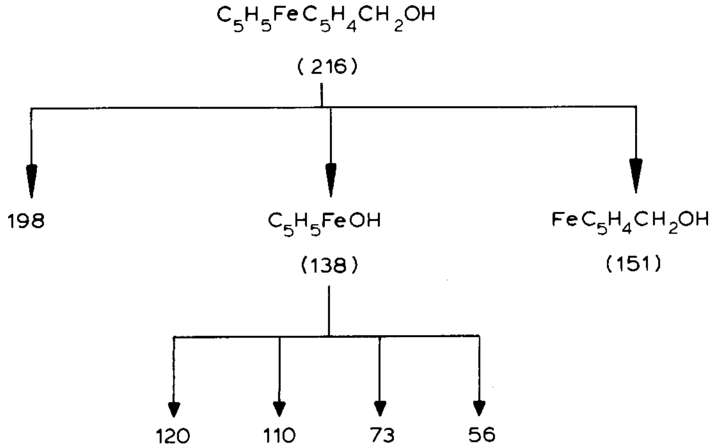


SCHEME 3

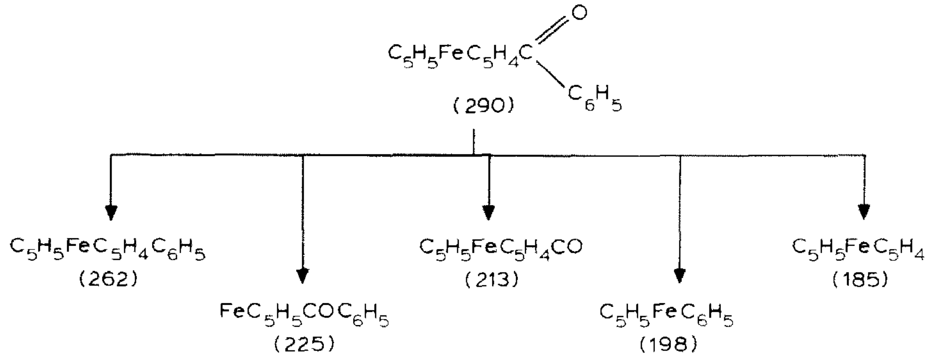
fragmentations of this ion are identical with those found for compound IV, so suggesting a common structure. Scheme 4 summarizes the observed fragmentations, which differ in part from those previously reported [8]. In the second field free region of the spectrometer we did not observe any reaction involving the breaking of the iron–ring bond; but, a search of the decomposition in the first field free region produced some evidence for the formation of the $FeC_5H_4CH_2OH$ ion (m/z 151) from the molecular ion.

η-C_5H_5Fe-η-$C_5H_4COC_6H_5$ *(VI)*

The mass spectrum of this compound differs from that previously reported [6] in respect of the presence of an abundant ion at m/z 262 corresponding to the loss of carbon monoxide from the molecular ion. Furthermore, the observed fragmentations of the molecular ion (see Scheme 5) are different from those previously assumed [6], since formation of $[C_5H_5Fe]^+$ and $[Fe]^+$ from the molecular ion is not observed.



SCHEME 4



SCHEME 5

η-C_5H_5Fe-η-$C_5H_4CH_2N(CH_3)_2$ (VII)

The major feature of the fragmentation [9] of this molecular ion is the high mobility of the $N(CH_3)_2$ group which can migrate to the iron atom, in a process common for this class of compounds, or can be eliminated to give the ion at *m/z* 199, whose formation may be favoured by the possible expansion of the ring from cyclopentadienyl to benzene.

Precursors and structure of the ions at m/z 186

In some of the mass spectra of the above compounds, an ion at *m/z* 186, corresponding to the mass of ferrocene, is present in fairly high relative abundance. This ion has a variety of precursors. Observation of the appropriate metastable transitions showed that it comes; (a) solely from the molecular ion in compound III; (b) mainly from the ion at *m/z* 214 in compound V, in which there is also a very small metastable ion due to the process $M^+ \rightarrow [186]^+$; (c) from the molecular ion from the ion at *m/z* 228 $[M - CH_3]^+$ in compound VII. An ion at *m/z* 186 was found also for compounds VI and II; in these two cases we were not able to find any metastable ion which could account for its generation; this casts some doubt on the origin of this ion, which could be due to contamination by ferrocene or to a pyrolysis reaction in the ion source.

To gain information on the structure of the ions at 186 we compared their

TABLE 2

METASTABLE ION SPECTRA OF *m/z* 186 IONS FROM SUBSTITUTED FERROCENES (The numbers in brackets refer to kinetic energy releases (meV)).

Compound	186 → 171	186 → 160	186 → 130	186 → 121	186 → 56
Ferrocene	9.0(119)	5.0(53)	6.8(59)	100.0(42)	1.1
III	7.8(103)	5.3(78)	8.3(51)	100.0(44)	0.9
V	40.0(103)	6.5(50)	33.5(45)	100.0(43)	1.5
VII [a]		4.2	27.0	100.0(36)	3.4(60)

[a] Interference signals prevented intensity and kinetic energy release measurements (K.E.) for some peaks.

TABLE 3

COLLISION INDUCED METASTABLE ION SPECTRA FROM THE m/z 186 ION

m/z	Compound			
	Ferrocene	III	V	VII
171	4.9	7.2	3.2	1.8
167	2.0	1.5	1.4	1.2
160	4.9	5.9	2.8	1.8
151	7.4	4.2	3.2	7.6
148	2.9	3.0	1.4	3.5
133	2.0	2.5	2.1	4.0
128	6.6	4.6	7.0	2.9
121	56.5	70.0	60.1	36.2
118	7.8	7.2	7.8	12.9
112	24.4	21.6	19.6	34.1
102	100.0	100.0	100.0	100.0
79	3.9	3.8	2.5	3.5
68	10.8	10.6	9.8	11.4
51	7.0	7.6	9.5	7.3

metastable characteristics with those of the same ion from ferrocene. The data are presented in Table 2. While there are some differences in the relative intensities, it is evident that the kinetic energy release does not depend on the nature of precursors of the m/z 186 ions, thus indicating a common structure for all these ions. To get information on the m/z 186 ions which have internal energy below the fragmentation threshold, their collision induced metastable ions were studied. These metastable spectra, reported in Table 3, again point toward a common structure for the non decomposing m/z 186 ions.

Precursors and structure of the ions at m/z 121

The ion at m/z 121, corresponding to C_5H_5Fe, is present in generally high relative abundance in the spectra of monosubstituted ferrocenes. It also has a variety of precursors, and only for compound VII does it originate directly from the

TABLE 4

METASTABLE ION CHARACTERISTICS OF THE m/z 121 IONS FROM SUBSTITUTED FERROCENES

Compound	K.E. (meV) $121 \rightarrow 56$	$(I_{95}/I_{56}) \times 100$
Ferrocene	43	4.3
I	45	19.4
III	43	4.8
V	44	16.5
VI	51	9.9
VII	46	13.9

TABLE 5

COLLISION INDUCED METASTABLE ION SPECTRA FROM THE *m/z* 121 ION

m/z	Compound					
	Ferrocene	I	III	V	VI	VII
95	18.5	22.9	17.5	19.8	20.0	17.0
93	9.8	15.7	8.3	9.8	7.7	8.8
87	83.1	78.3	84.3	93.1	93.1	80.9
86	100.0	100.0	100.0	100.0	100.0	100.0
85	21.5	19.3	19.8	19.6	21.5	20.6
69	27.7	31.3	25.3	34.3	30.8	29.4
56	22.5	24.1	18.3	22.1	25.3	17.7
37	90.5	75.9	75.3	87.0	95.4	83.8

molecular ion. When the *m/z* 186 ion is present (compounds III, V and VII) there is further fragmentation to *m/z* 121; for compound I *m/z* 121 originates from the *m/z* 185 ion and for compound VI from the *m/z* 262 ion. In some cases it has more than one precursor; besides to the transitions already mentioned, metastable ions are present for the reactions 199 ($C_6H_6FeC_5H_5$) → 121 for VII and 198 ($C_6H_5FeC_5H_5$) → 121 for V.

The metastable ion characteristics of the successive fragmentation of the *m/z* 121 ions strongly suggest a common structure for these ions. In Table 4 we list the data for the kinetic energy release in the process $C_5H_5Fe \rightarrow Fe$ and the intensity ratios for the formation of the ions at *m/z* 95 and 56. The collision-induced metastable spectra (see Table 5) again indicate a common structure.

A number of cyclopentadienyliron dicarbonyl compounds also have abundant *m/z* 121 ions in their mass spectra; once again, in spite of different structures of the precursors and of the the different fragmentation processes leading to the C_5H_5Fe ion, the metastable ion characteristics (see Table 6) suggest a common structure. The above experimental results lead to conclusions somewhat different from those previously presented. Thus it was suggested that the intensity ratio of the iron–ring

TABLE 6

METASTABLE ION CHARACTERISTICS OF THE *m/z* 121 IONS FROM η-$C_5H_5Fe(CO)_2X$ COMPOUNDS

X	K.E. (meV)	$(I_{95}/I_{56})\times 100$
Cl	39	8.7
I	39	5.4
$(CH_3)_3Si$	39	11.0
$(C_6H_5)_3Si$	41	[a]
$(C_6H_5)_3Ge$	42	15.6
$(CH_3)_3Sn$	44	5.8
Cl_3Sn	42	[a]

[a] The intensity of the *m/z* 95 ion was too low to be measured.

and iron–substituted ring ions in the mass spectrum of a substituted ferrocene is a measure of the relative dissociation energies of the two iron–ring bonds [3]. This suggestion requires that the two fragment ions originate from the same precursor, namely the molecular ion but our data clearly indicate that the molecular ions of the substituted ferrocenes do not undergo competitive fragmentations to the two ions of interest, and that the ion C_5H_5Fe is not a primary fragment ion (the only exception being in compound VII). On the other hand, the molecular ions of compounds IV, VI and possibly V, fragment to ions of the type [iron–substituted ring]$^+$, and for these compounds there could be a lower dissociation energy for the bond between the iron atom and the cyclopentadienyl ring than for that between iron and the substituted ring, contrary to an earlier suggestion [3]. However, the correlation between ionic abundance and bond dissociation energy of neutral species is not soundly based; it is well known that the stability of ionic species is important in controlling the fragmentation; in this respect, it seems significant that after ionization the fragmentation process leaves the charge in that part of the molecule (the iron–substituted ring fragment) in which a greater charge delocalization is possible.

From the above discussion it is clear that the substituted ferrocenes do not fragment in the same way as ferrocene. This can be understood in terms of the available appearance potential data for the principal ions of the ferrocene mass spectrum. The ionization energy of ferrocene is near to 7.0 eV [10], while the appearance potential of C_5H_5Fe is at least 12.8 eV [11] and that of $C_5H_5FeC_3H_3$ is about 13.3 eV [12]. This means that the fragmentations of ferrocene require a very high activation energy. The presence of substituents in the ring makes possible other fragmentation pathways, requiring lower activation energies, so that the typical ferrocene ion reactions are less important; such an effect has been already noted in the case of organic molecules [13]. In conclusion, we wish to emphasize that the similarity of the metastable ion characteristics of ions of the same empirical composition suggests common structures for these ions; but this does not give any indication of their actual structures, which may even be different from those deduced from structures of the corresponding neutral molecules.

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