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FERROCENE COMPOUNDS

XVI *. MASS-ANALYZED ION KINETIC ENERGY (MIKE) SPECTRA OF SOME MONOSUBSTITUTED FERROCENE DERIVATIVES

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Summary

The mass-analyzed ion kinetic energy (MIKE) spectra of some monosubstituted ferrocenes having an unsaturated moiety in the α- or β-position to the cyclopentadienyl ring and β-phenyl-γ-ferrocenoylbutyric acid are presented and discussed.

Introduction

Ion kinetic energy spectrometry allows the study of unimolecular reactions and is a unique source of information on thermochemistry, molecular structure, isotopic quantitation and reaction dynamics [1].

In this paper we have concentrated on the MIKE spectra of compounds **1–9** with the objective of increasing knowledge of the effects of substituents on the fragmentation processes. The investigation was directed towards assessing the similarities and differences between compounds **1–9**, which we synthesized in order to study their chemical reactions, structures and spectrometric characteristics. The formulae and names of the compounds studied are given in Table 1.

Experimental

Compounds **1–9** were synthesized as described in refs. 2, 3 and 4. The measurements were made on a CEC 21-110B mass spectrometer at 70 eV with an accelerat-

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* For Part XV see V. Rapić and N. Filipović-Marinić, Org. Mass Spectrom., submitted.

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TABLE 1

FORMULAE AND NAMES OF THE COMPOUNDS STUDIED [a]

	R	R¹	R²	
$\mathrm{FcCOCH{=}CRR^1}$				
1	H	Ph		β-Ferrocenoylstyrene
2	NH_2	$CONHNH_2$		α-Amino-β-ferrocenoylacrylic acid hydrazide
3	NH_2	CO_2Et		Ethyl α-amino-β-ferrocenoylacrylate
4	NHPh	CO_2Et		Ethyl α(*N*-phenylamino)-β-ferrocenoylacrylate
$\mathrm{FcCR{=}CR^1R^2}$				
5	CH_3	H	H	1-Isopropenylferrocene
6	H	CO_2Et	$(CH_2)_2CO_2H$	(*E*)-1-Ethyl hydrogen 2-ferrocenylmethyleneglutarate
7	H	CO_2H	CH_2CO_2H	(*E*)-2-Ferrocenylmethylenesuccinic acid
8	H	CO_2H	$(CH_2)_2CO_2H$	(*E*)-2-Ferrocenylmethyleneglutaric acid
9 $\mathrm{FcCOCH_2CH(Ph)CH_2CO_2H}$				β-Phenyl-γ-ferrocenoylbutyric acid

[a] $\mathrm{Fc = C_5H_5FeC_5H_4}$.

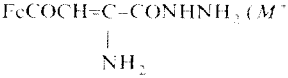
ing voltage of 6 kV. The samples were introduced from a heated inlet at ca. 10^{-4} Pa. The unimolecular MIKE spectra indicated decomposition of molecular ions in the third field-free region between the magnetic analyser and the second electrostatic

TABLE 2

MIKE SPECTRA OF COMPOUNDS 1-4

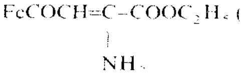
1 $\mathrm{FcCOCH{=}CHPh}$ ($M^{+\cdot} = 316$)

m_2^*: 298 ($M - H_2O$), 287 ($M - CHO$), 272 ($M - H_2O - C_2H_2$), 251 ($M - C_5H_5$), 223 ($M - C_5H_5 - CO$), 213 ($FcCO^+$), 186 (Fc^+), 185 ($C_{10}H_9Fe^+$), 178 ($C_5H_5COCH{=}CHPh^+ - H_2O$), 165 ($C_{13}H_9^+$)

2  ($M^{+\cdot} = 313$)

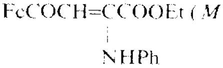
$\mathrm{FcCOCH{=}\underset{NH_2}{C}{-}CONHNH_2}$

m_2^*: 295 ($M - H_2O$), 282 ($M - NHNH_2$), 253 ($M - HCONHNH_2$), 248 ($M - C_5H_5$), 230 ($M - C_5H_5 - H_2O$), 213 ($FcCO^+$), 186 (Fc^+), 185 ($C_{10}H_9Fe^+$)

3  ($M^{+\cdot} = 327$)

$\mathrm{FcCOCH{=}\underset{NH_2}{C}{-}COOC_2H_5}$

m_2^*: 309 ($M - H_2O$), 298 ($M - CHO$), 281 ($M - EtOH$), 262 ($M - C_5H_5$), 253 ($M - HCOOEt$), 234 ($M - C_5H_5 - CO$), 233 ($M - C_5H_5 - CHO$), 227 ($M - C_5H_5 - OEt$), 213 ($FcCO^+$), 186 (Fc^+), 185 ($C_{10}H_9Fe^+$)

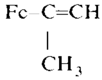
4  ($M^{+\cdot} = 403$)

$\mathrm{FcCOCH{=}\underset{NHPh}{C}COOEt}$

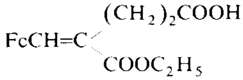
m_2^*: 385 ($M - H_2O$), 374 ($M - CHO$), 357 ($M - EtOH$), 338 ($M - C_5H_5$), 329 ($M - HCOOEt$), 313 ($M - C_5H_5 - CO$), 299 ($M - C_5H_5 - OEt$), 281, 264 ($M - C_5H_5 - HCOOEt$), 235 ($M - C_5H_5 - HCOOEt - HCO$), 213 ($FcCO^+$)

TABLE 3

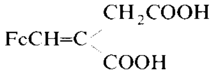
MIKE SPECTRA OF COMPOUNDS **5**–**9**

5 
$\mathrm{Fc{-}C(CH_3){=}CH_2}$ ($M^{+\cdot} = 226$)

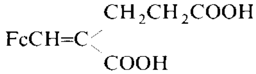
m_2^{+}: 210 ($M-\mathrm{CH_4}$), 200 ($M-\mathrm{C_2H_2}$), 199 ($M-\mathrm{C_2H_3}$), 198 ($M-\mathrm{C_2H_4}$), 197 ($M-\mathrm{C_2H_5}$), 186 ($\mathrm{Fc^+}$), 161 ($M-\mathrm{C_5H_5}$), 153, 145 ($M-\mathrm{C_5H_5}-\mathrm{CH_4}$), 133 ($M-\mathrm{C_5H_5}-\mathrm{C_2H_4}$), 121 ($M-\mathrm{C_5H_5}-\mathrm{C_3H_4}$)

6 
$\mathrm{FcCH{=}C(CH_2)_2COOH(COOC_2H_5)}$ ($M^{+\cdot} = 356$)

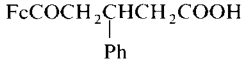
m_2^{+}: 338 ($M-\mathrm{H_2O}$), 328 ($M-\mathrm{C_2H_4}$), 310 ($M-\mathrm{HCOOH}-\mathrm{EtOH}$), 296 ($M-\mathrm{CH_3COOH}$), 291 ($M-\mathrm{C_5H_5}$), 282 ($M-\mathrm{HCOOEt}$), 273 ($M-\mathrm{C_5H_5}-\mathrm{H_2O}$), 268 ($M-\mathrm{CH_3COOEt}$), 262, 251, 245 ($M-\mathrm{C_5H_5}-\mathrm{EtOH}$)

7 
$\mathrm{FcCH{=}C(CH_2COOH)(COOH)}$ ($M^{+\cdot} = 314$)

m_2^{+}: 296 ($M-\mathrm{H_2O}$), 270 ($M-\mathrm{CO_2}$), 249 ($M-\mathrm{C_5H_5}$), 231 ($M-\mathrm{C_5H_5}-\mathrm{H_2O}$), 224 ($M-\mathrm{HCOOH}-\mathrm{CO_2}$), 204 ($M-\mathrm{C_5H_5}-\mathrm{COOH}$), 185 ($\mathrm{C_{10}H_9Fe^+}$)

8 
$\mathrm{FcCH{=}C(CH_2CH_2COOH)(COOH)}$ ($M^{+\cdot} = 328$)

m_2^{+}: 310 ($M-\mathrm{H_2O}$), 290, 284 ($M-\mathrm{CO_2}$), 282 ($M-\mathrm{HCOOH}$), 268 ($M-\mathrm{CH_3COOH}$), 263 ($M-\mathrm{C_5H_5}$), 245 ($M-\mathrm{C_5H_5}-\mathrm{H_2O}$), 233, 218 ($M-\mathrm{C_5H_5}-\mathrm{COOH}$), 199 ($\mathrm{FcCH_2}^+$), 171

9 
$\mathrm{FcCOCH_2CH(Ph)CH_2COOH}$ ($M^{+\cdot} = 376$)

m_2^{+}: 358 ($M-\mathrm{H_2O}$), 330 ($M-\mathrm{HCOOH}$), 316 ($M-\mathrm{CH_3COOH}$), 311 ($M-\mathrm{C_5H_5}$), 293 ($M-\mathrm{C_5H_5}-\mathrm{H_2O}$), 283 ($M-\mathrm{C_5H_5}-\mathrm{CO}$), 265 ($M-\mathrm{C_5H_5}-\mathrm{HCOOH}$), 228 ($\mathrm{FcCOCH_3}^+$), 213 ($\mathrm{FcCO^+}$), 199 ($\mathrm{FcCH_2}^+$), 185 ($\mathrm{C_{10}H_9Fe^+}$)

analyser. The voltage applied to the second electrostatic analyser was scanned in a range from $E = E_0$ to $E = 0$. When a selected ion $[M]^{+\cdot}$ passes through the third field-free region of the above mass spectrometer it may unimolecularly fragment; scanning the electric sector voltage downwards from the value which transmits $[M]^{+\cdot}$ ($E = E_0$) produces the well-known ion kinetic energy spectrum. We consider only ions which undergo exclusively metastable dissociations.

$$m_1{}^{+\cdot}\,[M^{+\cdot}] \rightarrow m_2{}^{+} + m_3$$

The MIKE spectra for the molecular ions of compounds **1**–**9** are shown in Tables 2 and 3; the suggested compositions of the m_3 fragments lost from $[M^{+\cdot}]$ are shown in parentheses in this case.

Results and discussion

Cais et al. [5] have reported the EI mass spectra of some derivatives of ferrocenylacrylic acid but there has been no previous report on the MIKE spectra of this type of compound.

Some obvious conclusions can be drawn from the data in Tables 2 and 3. Firstly, fragmentation leads mainly to the formation of $[M-H_2O]^{+\cdot}$ ions for all the compounds, except for compound **6**, which does not contain oxygen. It is suggested that the presence of a carboxyl group facilitates elimination of an H_2O molecule, formed from a carboxylic OH group and a hydrogen atom originating from the side-chain or the cyclopentadienyl ring. Second, the appearance of the fragment $[M-C_5H_5]^+$ indicates the occurrence in all cases of a simple cleavage resulting in the loss of an unsubstituted cyclopentadienyl group from the molecular ion. This is to some extent in accord with previous studies by Innorta et al. [6], who found that the dissociation energy for the bond between the iron atom and the cyclopentadienyl ring could be lower than for that between iron and the substituted ring. Additionally, in all the spectra some characteristic fragmentation patterns, originating from the ferrocene moiety are observed: 185 $[C_5H_5FeC_5H_4]^+$, 186 $[C_5H_5FeC_5H_5]^+$, 171 $[C_5H_5FeC_4H_2]^+$, 121 $[C_5H_5Fe]^+$.

Another decompositions of metastable $M^{+\cdot}$ ions involves the cleavage in the ligands adjacent to the ferrocenyl group. In the compounds containing the carboxylic group eliminations of HCOOH, CH_3COOH, etc. are observed. On the other hand, in compounds with ligands containing two carboxylic groups decarboxylation $[M-CO_2]^{+\cdot}$ and the combined loss $[M-CO_2-HCOOH]^{+\cdot}$ are favoured. The elimination of EtOH, HCOOEt, or CH_3COOEt takes place in compounds containing carboxylate groups.

The relative intensities of the above mentioned ions for compound **1**–**9** vary from 10^{-2} to 10^{-4} with respect to the intensity of $M^{+\cdot}$ in each case. The MIKE spectra of the molecular ions of **1**–**9** show some peaks which were not seen in the EI mass spectra or appeared only in very low abundance ($\approx 1\%$).

*Compounds **1**–**4***

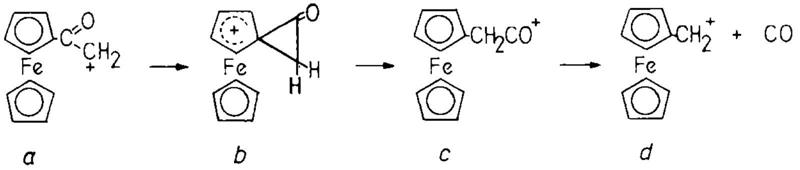
The MIKE spectra of compounds **1**–**4** (Table 2) showed the expected cleavage on both sides of the carbonyl group giving rise to the fragments $FeCO^+$ and $[C_5H_5FeC_5H_4]^+$. The cleavage of the bonds between the iron and two cyclopentadienyl rings then gives corresponding $[M-C_5H_5]^+$ ions and $C_5H_5Fe^+$ ion. According to Mandelbaum and Cais [7] the more interesting mode of the fragmentation of monosubstituted ferrocenes having a carbonyl group α to the cyclopentadienyl group involves the formation of rearranged ions in which a group originating from the ligands becomes associated with the metal atom. It can be assumed that similar rearrangements lead to the formation of $[M-(C_5H_5+CO)]^+$ ions (compounds **1**, **2**, **3**).

*Compounds **5**–**8***

The most important fragmentation of the molecular ions is loss of H_2O and CO_2 and cleavage of the side chain (Table 3). The 328^+ peak for compound **6** corresponds to a McLafferty rearrangement of the ester group (CO_2Et) with loss of an ethylene unit (C_2H_4).

*Compound **9***

This compound fragments mainly by α-cleavage at the carbonyl group ($FeCO^+$ and Fc^+) (Table 3). More interesting is the formation of the ion with m/z 199. The occurrence of rearrangement similar to that revealed in investigations of the primary



SCHEME 1

α-benzoylcarbenium ions [8] can be suggested for α-ferrocenoylcarbenium ion. It is assumed that the loss of CO from ion **a** and the formation of **d** may proceed during the rearrangement via a three-membered cyclic transition state (**b**) and subsequent rearrangement to the ferrocenylacetyl ion **c** (Scheme 1). However, the McLafferty rearrangement arising from γ-hydrogen atom and the carbonyl group adjacent to the ferrocenyl giving the $\mathrm{FcC(\overset{+}{O}H){=}CH_2}$ ion (228) is also a possibility [9].

References

1 J.H. Beynon, R.G. Cooks, J.W. Amy, W.E. Baitinger and T.Y. Ridley, Anal. Chem., 45 (1973) 1023A.
2 M. Laćan and V. Rapić, Croat. Chem. Acta, 44 (1972) 317.
3 M. Laćan and V. Rapić, Croat. Chem. Acta, 51 (1978) 325.
4 M. Laćan and V. Rapić, Croat. Chem. Acta, 51 (1978) 273.
5 M. Cais, M.S. Lupin and I. Sharvit, Israel J. Chem., 7 (1969) 73.
6 G. Innorta, F. Scagnolari, A. Modelli, S. Torroni, A. Foffani and S. Sorriso, J. Organomet. Chem., 241 (1983) 375.
7 A. Mandelbaum and M. Cais, Tetrahedron Lett., 51 (1964) 3847.
8 H.F. Grützmacher and A.M. Dommröse, Org. Mass Spectrom., 18 (1983) 605.
9 V. Rapić and N. Filipović-Marinić, Org. Mass Spectrom., 20 (1985) 104.