

## MASS SPECTROMETRY OF $\pi$ -COMPLEXES OF TRANSITION METALS

### X \*. METHYLFERROCENE

D.V. ZAGOREVSKII \*, Yu.S. NEKRASOV and D.A. LEMENOVSKII

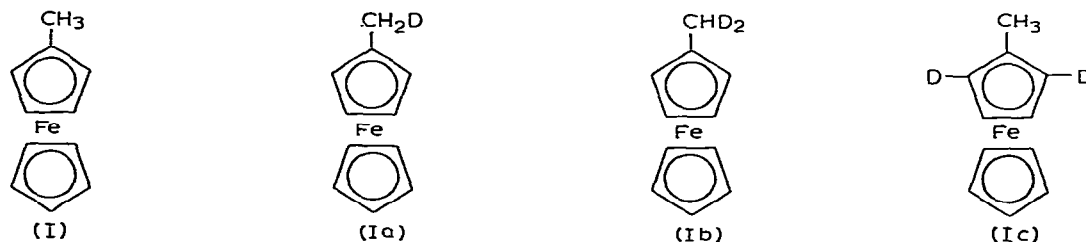
*Institute of Organo-Element Compounds of the Academy of Sciences of the USSR,  
 28 Vavilova Str., 117312 Moscow (U.S.S.R.)*

(Received October 5th, 1977)

#### Summary

The study of deuterium labelled methylferrocenes has shown the ions  $C_{11}H_{11}Fe^+$ ,  $C_6H_6Fe^+$ ,  $C_5H_5Fe^+$  and  $C_5H_6Fe^+$  to originate from the isomerised form of the molecular ion in which all the hydrogen atoms are redistributed among the ligands.

Earlier, while studying the mass spectrum of  $\sigma$ -methyl- $\pi$ -cyclopentadienyl-iron dicarbonyl ( $\eta^5-C_5H_5$ )Fe(CO)<sub>2</sub>CH<sub>3</sub> and its trideuteromethyl analogue we found a partial randomization of hydrogen atoms in the  $C_5H_5FeCH_3^+$  ion during its decomposition with elimination of the H<sub>2</sub> molecule ( $C_6H_6Fe^+$  ion formation) [2]. However the formation process of the analogous ion from the molecular ion of  $\pi$ -cyclohexadienyl- $\pi$ -cyclopentadienyliron as a result of cyclopentadiene molecule elimination occurs with a stereoselective participation of the hydrogen endo-atom of the cyclohexadienylic ring [3]. In the mass spectrum of methylferrocene (an isomer of cyclohexadienylcyclopentadienyliron)  $C_6H_6Fe^+$  ions are also present [1,4]. In order to clear up the mechanism of its formation we studied the mass spectra of methylferrocene (I) and its deuterio analogues Ia–c.



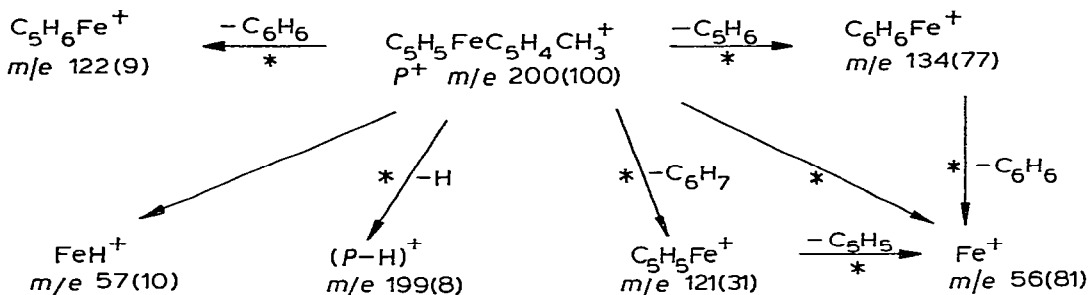
\* For part IX see ref. 1.

TABLE 1  
 INTENSITIES OF  $C_6H_6-nD_nFe^+$  IONS, CALCULATED<sup>a</sup> ACCORDING TO MECHANISMS A-D AND OBTAINED EXPERIMENTALLY FROM THE 15 eV MASS SPECTRA OF COMPOUNDS Ia-c

Mechanism	$C_5H_5FeC_3H_4CH_2D$ <sup>b</sup> (Ia)		$C_5H_5FeC_3H_4CHD_2$ (Ib)		$C_5H_5FeC_5H_2D_2CH_3$ <sup>c</sup> (Ic)	
	$C_6H_6Fe^+$	$C_6H_5DFe^+$	$C_6H_6Fe^+$	$C_6H_5DFe^+$	$C_6H_6Fe^+$	$C_6H_5DFe^+$
A	0.58	0.42	0	0.67	0.06	0.21
B	0.36	0.64	0	0	0.11	0.51
C	0.46	0.54	0	0.14	0.06	0.38
D	0.59	0.31	0.23	0.54	0.30	0.50
Experimental value	0.55	0.35	0.24	0.53	0.23	0.42

<sup>a</sup> Taking into account the isotopic composition of molecular ions (see experimental section), <sup>b</sup> Mixture (64 : 36) with methylferrocene (I), <sup>c</sup> Mixture of tri-, di-, mono- and nondeuterated products (see experimental section); the  $C_6H_5D_3Fe^+$  ions are not included because of their small intensity and bad reproducibility.

The main fragments in the methylferrocene mass spectrum are formed by breaking of the metal–ligand bond (Scheme 1). The breakage of the  $C_5H_5-Fe$



SCHEME 1. The decomposition paths which are confirmed by the presence of the corresponding metastable peaks are marked with asterisks. The relative intensities of the ions (as a percentage of molecular ion intensity — the most intense in the spectrum) for the 50 eV mass spectrum are shown in parentheses after the  $m/e$  values.

bond occurs with migration of the hydrogen atom from the substituted cyclopentadienylic ring; during this process elimination of the cyclopentadiene molecule takes place and the  $C_6H_6Fe^+$  ion is formed (this is substantiated by the presence of a corresponding metastable peak at  $m/e$  89.8). This rearrangement may also be followed by  $C_6H_6$  molecule (benzene or fulvene) elimination with the formation of  $C_5H_6Fe^+$  ions (Scheme 1).

If the molecular ion of methylferrocene is structurally identical to the original molecule then there are two possible mechanisms of cyclopentadiene molecule elimination ( $C_6H_6Fe^+$  ion formation): (1) with the participation of the hydrogen atom from the methyl group (path A); and (2) with the participation of the hydrogen atom of the substituted cyclopentadienyl ring (path B).

As is shown in Table 1, where the calculated and experimentally observed values of  $C_6H_6Fe^+$ ,  $C_6H_5DFe^+$  and  $C_6H_4D_2Fe^+$  ion relative intensities in the mass spectra of the deuterio analogues Ia–c are cited, experimental values disagree with both mechanisms A and B. Furthermore, it is impossible to get a good agreement with the experimental data for any combination of mechanisms A and B. Thus the structure of the methylferrocene molecular ion is rather different from the structure of the parent molecule. It can be suggested that before or during elimination of the cyclopentadiene molecule, the methylcyclopentadienyl ligand isomerises into another structure (for example, to cyclohexadienyl ligand) with the statistical redistribution (randomization) of hydrogen atoms (path C). However there is no agreement of the calculated and observed ion intensities in this case either (Table 1). Moreover none of the combinations of mechanisms A, B and C agree with the experimental data because of the presence of  $C_6H_6Fe^+$  ion in the mass spectrum of the deuteromethyl derivative Ib, the formation of which cannot be explained in terms of mechanisms A–C. This ion can appear only after the full randomization of hydrogen atoms in the whole molecule including both ligands (path D). Actually, the calculated intensities of  $C_6H_6Fe^+$ ,  $C_6H_5DFe^+$  and  $C_6H_4D_2Fe^+$  ions are in good agreement with the experimental data (Table 1).

Thus the fragmentation of methylferrocene molecular ion yielding  $C_6H_6Fe^+$  ion proceeds with the overall randomization of hydrogen atoms as opposed to

the same process in cyclohexadienylcyclopentadienyliron [3] where  $C_6H_6Fe^+$  ion is formed by *endo*-hydrogen atom stereoselective migration.

In connection with the above the formation mechanisms of the other ions, particularly,  $C_5H_6Fe^+$  and  $C_5H_5Fe^+$ , in the mass spectrum of methylferrocene were of interest to us. The  $C_5H_6Fe^+$  ion is probably formed in a way similar to the formation of  $C_6H_6Fe^+$  ion. Formation of  $C_6H_6Fe^+$  and  $C_5H_6Fe^+$  ions can be regarded as the result of decomposition of the isomerized molecular ion of the  $C_6H_6FeC_5H_6^+$  type, in which all the hydrogen atoms are statistically redistributed, with elimination of  $C_5H_6$  and  $C_6H_6$  molecules respectively. From this the series of  $C_5H_6Fe^+$ ,  $C_5H_5DFe^+$  and  $C_5H_4D_2Fe^+$  ions can be expected in dideutero-analogues Ib and Ic mass spectra and they are in fact observed (Table 2). The presence of these ions in the mass spectra of these compounds testifies that the elimination process of  $C_6H_6$  as well as  $C_5H_6$  occurs with the overall randomization of hydrogen atoms in the molecular ion.

Two ways of  $C_5H_5Fe^+$  ion formation in the methylferrocene mass spectrum can be considered: (1) a simple breakage of the metal-ligand bond in the non-isomerized molecular ion (path E); and (2)  $C_5H_5Fe^+$  ion formation after the overall randomization of hydrogen atoms (path F). In the first case only  $C_5H_5Fe^+$  ions should be yielded in the mass spectra of the deuterio analogues Ia-c whereas in the second the series  $C_5H_5Fe^+$ ,  $C_5H_4DFe^+$  and  $C_5H_3D_2Fe^+$  ions should be yielded.

A precise calculation of the relative intensities of  $C_5H_5Fe^+$  (*m/e* 121),  $C_5H_4DFe^+$  (*m/e* 122),  $C_5H_3D_2Fe^+$  (*m/e* 123) and  $C_5H_6Fe^+$  (*m/e* 122),  $C_5H_5DFe^+$  (*m/e* 123),  $C_5H_4D_2Fe^+$  (*m/e* 124) ions is impossible because of their superposition. However it can be established which of the two ways (E or F) of  $C_5H_5Fe^+$  ion formation is the actual one. If  $C_5H_5Fe^+$  ions are formed only by a simple breakage of the bond in the non-isomerized molecular ion (E) then only  $C_5H_5Fe^+$  ions (*m/e* 121) and a series of  $C_5H_{6-n}D_nFe^+$  ions must be present in the mass spectra of the deuterio analogues. In this case it would be expected that the ratio  $C_5H_5Fe^+$  ion intensity to the summarized intensity of  $C_5H_{6-n}D_nFe^+$  ions (*m/e* 122-124) would be equal to the value of  $[C_5H_5Fe^+] : [C_5H_6Fe^+]$  in the mass

TABLE 2

THE INTENSITIES OF IONS (*m/e* 121-124) OBSERVED IN THE MASS SPECTRA (15 eV) OF Ia-c AND CALCULATED ACCORDING TO MECHANISMS E-F.

Compound	Mechanism	<i>m/e</i> value			
		121	122	123	124
Ia	E	0.48	0.36	0.16	
	F	0.36	0.49	0.15	
	observed	0.37	0.42	0.21	
Ib	E	0.48	0.12	0.38	0.12
	F	0.16	0.37	0.35	0.12
	observed	0.22	0.29	0.34	0.15
Ic	E	0.48	0.16	0.26	0.09
	F	0.27	0.31	0.31	0.09
	observed	0.27	0.33	0.30	0.08
I	observed	0.48	0.52		

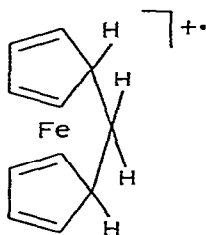
spectrum of the unlabelled methylferrocene I. However, as is seen from Table 2, the latter value exceeds the ratios  $[m/e\ 121] : ([m/e\ 122] + [m/e\ 123] + [m/e\ 124])$  observed in the spectra of the deuterio analogues. This testifies that at least part of the  $C_5H_5Fe^+$  ions are produced from the isomerized form of molecular ion. The relative ion intensities ( $m/e\ 121, 122, 123$  and  $124$ ) calculated in the case of  $C_5H_5Fe^+$  and  $C_5H_6Fe^+$  ion formations after a full randomization of hydrogen atoms in the molecular ion (path F) is in a good agreement with the experimental values (Table 2). This proves once more that  $C_5H_5Fe^+$  ion is of rearrangement character (its formation occurs after a full redistribution of the hydrogen atoms in the molecular ion).

It may be expected that  $(P-H)^+$  ions are formed by hydrogen atom elimination from the methyl group or from a cyclopentadienyl ring (substituted or unsubstituted). The latter is doubtful because of the absence of  $(P-H)^+$  ions in the mass spectra of the ferrocene derivatives  $C_5H_5FeC_5H_4R$  ( $R \neq CH_2R'$ ). If the methyl group is the source of the hydrogen atom then in the dideuteromethylferrocene (Ib) mass spectrum there should be  $(P-H)^+$  and  $(P-D)^+$  ions in the ratio 1 : 2. However, the observed value  $[(P-H)^+ : [(P-D)^+]$  in the mass spectrum of Ib is about 2 : 1\*. This shows that the redistribution of hydrogen atoms according to mechanism C or D also proceeds the formation of  $(P-H)^+$  ions,  $C_{11}H_{11}Fe^+$ , in the mass spectrum of methylferrocene.

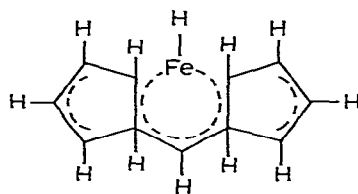
Thus all the main processes of methylferrocene fragmentation under electron impact proceed through the stage of molecular ion formation, in which all the hydrogen atoms are equivalent, i.e. overall randomization takes place.

A series of aromatic systems in which the full randomization of hydrogen atoms is observed under electron impact is already known (for example, in the tropylium cation [5]). However, redistribution of the hydrogen atoms between the  $\pi$ -connected ligands is unexpected. The only example of such processes in molecular ions of  $\pi$ -complexes is a fragmentation of cycloheptatrienylcyclopentadienyl derivatives  $C_7H_7MC_5H_5$  with  $C_6H_6M^+$  ion formation [6]. Probably, the randomization process involves the participation of the metal atom which, in the case of methylferrocene, "catalyzes" the hydrogen atoms migration among the ligands (the presence of  $FeH^+$  and  $FeD^+$  ions in the mass spectra of Ia-c supports this; it is not excluded that the  $C_5H_6Fe^+$  ions partially have the structure of cyclopentadienyliron hydride  $C_5H_5FeH^+$ ).

The results cited tell that a methylferrocene molecular ion structure corre-



(II)



(III)

\* The exact measurement of  $(P-H)^+$  and  $(P-D)^+$  ion intensities is difficult because of their small intensities and of the presence of  $(P-H_2)^+$  ions.

sponds neither to the initial molecule nor to a cyclohexadienylcyclopentadienyliron structure. Evidently, a methylferrocene molecular ion must isomerize into such a structure, in which the process of hydrogen atom redistribution can be easily fulfilled among carbon atoms of both ligands. Bridged (II) or metallocyclic (III) structures can be put forward as possible forms.

## Experimental

Mass spectra were obtained with an MXI303 mass spectrometer by direct introduction of the samples into the ionization chamber [7] at 10–15°C. The ionizing voltage was 50, 15 or 10 V and the ionizing chamber temperature was kept at 150°C. The isotopic composition of the samples was calculated using low voltage (10 V) mass spectra and was for Ia, 36.1%  $d_0$  and 63.9%  $d_1$ ; for Ib, 2.7%  $d_1$  and 97.3%  $d_2$ ; and for Ic, 2.8%  $d_0$ , 23.8%  $d_1$ , 69.7%  $d_2$  and 5.6%  $d_3$ . In calculations of monoisotopic intensities of  $C_6H_{6-n}D_nFe^+$ ,  $C_5H_{6-n}D_nFe^+$  and  $C_5H_{5-n}D_nFe^+$  it was supposed that their isotopical distributions were equal to those in  $C_6H_6Fe^+$ ,  $C_5H_6Fe^+$  and  $C_5H_5Fe^+$  ions respectively. The  $C_6H_{7-n}D_nFe^+$  ions which were 3% of the intensity of the  $C_6H_6Fe^+$  ion in the 15 eV mass spectrum of I were not taken into account.

Methylferrocene and  $\alpha$ -monodeuteromethylferrocene were synthesized according to [8] by the destruction of methylferrocenylmethyl ether by Li and by the hydrolysis of the ferrocenylmethyl lithium formed by  $H_2O$  or  $D_2O$  respectively. Methyl- and deuteromethylferrocenes were purified by chromatography on  $Al_2O_3$  (petroleum ether) and by recrystallisation from MeOH.

## Acknowledgements

The authors thank A.A. Koridze for the loan of dideuterated methylferrocene Ib and Ic samples.

## References

- 1 N.V. Zakurin, Yu.S. Nekrasov and D.V. Zagorevskii, *J. Organometal. Chem.*, **144** (1978) 195.
- 2 Yu.S. Nekrasov, V.F. Sizoy, T.Yu. Orlova and D.N. Kursanov, *Dokl. Acad. Nauk SSSR*, **222** (1975) 111.
- 3 A.N. Nesmeyanov, Yu.S. Nekrasov, N.I. Vasyukova, L.S. Kotova and N.A. Vol'kenau, *J. Organometal. Chem.*, **96** (1975) 265.
- 4 I.J. Spilners and J.G. Larson, *Org. Mass Spectrom.*, **3** (1970) 915.
- 5 S. Meyerson, H. Hart and L.C. Leitch, *J. Amer. Chem. Soc.*, **90** (1968) 3419.
- 6 M.F. Rettig, C.D. Stout, A. Klug and P. Farnham, *J. Amer. Chem. Soc.*, **92** (1970) 5100.
- 7 S.E. Trochov, V.P. Scherbinin, Yu.G. Seroklin and Yu.S. Nekrasov, *Prib. i. Tekh. Exsp.* (Russian), (1975) 255.
- 8 A.N. Nesmeyanov, E.G. Perevalova and Yu.A. Ustynuk, *Dokl. Acad. Nauk SSSR*, **133** (1960) 1105.