Journal of Organometallic Chemistry, 194 (1980) 77—81

MASS SPECTROMETRY OF π-COMPLEXES OF TRANSITION METALS

XVI. ION—MOLECULE REACTION PRODUCTS IN MASS SPECTRA OF FERROCENE DERIVATIVES

D.V. ZAGOREVSKII*, Yu.S. NEKRASOV, G.A. NURGALIEVA

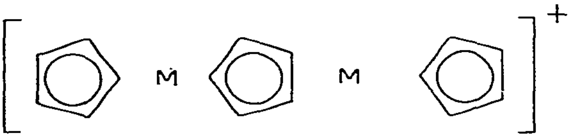
Institute of Organoelement Compounds of the U.S.S.R. Academy of Sciences, Vavilova St. 28, Moscow (U.S.S.R.)

(Received January 30th, 1980)

Summary

The ionization of vapours of ferrocene and its derivatives in the usual mass spectral investigations involves ion—molecule reactions leading to bimetallic ions. The combined vapourisation in the mass spectrometer of ferrocene derivatives and various organic and inorganic compounds gives rise to ions containing a new metal—ligand bond. The possibility of some of these particles being synthesized in the condensed phase is suggested.

The occurrence of ion—molecule reactions in the gas phase under the usual conditions of mass spectrometric experiments is characteristic of some π-complexes of transition metals. In particular, the mass spectra of ferrocene and nickelocene were found to contain the binuclear ions $[(C_5H_5)_3M_2{}^+]$ and $[(C_5H_5)_2M_2]^+$ [1—4] formed on interaction of the neutral metallocene molecule with $[C_5H_5M]^+$ and M^+ ions, respectively [3,4]. The ions $[(C_5H_5)_3M_2]^+$ were assigned the structure of a "triple-decker sandwich" (I). Such a complex, containing two nickel atoms, was subsequently synthesized under normal experimental conditions [5].



(I)

The investigation of the behaviour of mono-substituted and di-substituted ferrocenes under electron impact revealed a large number of fragments (Table 1) whose formation cannot be explained by an intramolecular dissociation of

TABLE 1

ION–MOLECULE REACTION PRODUCT INTENSITIES IN MASS SPECTRA OF $R'C_5H_4FeC_5H_4R$ [c]

Ion	R = H R′ = H	H CN	H [a] $COCH_3$	H COOH	H $COOCH_3$	CN CN	CN $COCH_3$	CN Cl
$[R'C_5H_4(RC_5H_4)_2Fe_2]^+$	100		3			28		1
$[RC_5H_4(R'C_5H_4)_2Fe_2]^+$	(100)	12	16			(28)		2
$[C_5H_4R(R'C_5H_4)C_5H_4Fe_2]^+$				100	20			
$[RC_5H_4(R'C_5H_4)Fe_2]^+$	20	100	33		100	100		100
$[(RC_5H_4)_2Fe_2]^+$	(20)	38	1			(100)		12 [b]
$[(RC_5H_4)_2Fe]^+$							28	10
$[(R'C_5H_4)_2Fe]^+$		15					100	5

[a] Other ions: $[(C_5H_4COCH_3)C_5H_4Fe_2]^+$ (100%) and $[(C_5H_5)_2C_5H_4Fe_2]^+$ (1%). [b] For ion $[(C_5H_4Cl)_2Fe_2]^+$. [c] In spectra of mono-substituted ferrocenes (R = H; R′ = $COCH_2Cl$, CH_2NH_2, $C(CH_3)=CH_2$) and disubstituted (R = R′ = COOH; R′ = R = CH_2OH; R = R′ = Cl) ferrocenes only ions of $[RC_5H_4(R'C_5H_4)Fe_2]^+$ type were found.

molecular ions. As the pressure in the mass spectrometer ionisation chamber varies, the intensities of these fragments change proportionally to the square of the molecular ion intensity. This is indicative [2] of these fragments resulting from ion—molecule reactions.

The overall intensity of the ion—molecule reaction products attains 5% of the intensity of the molecular ion. The mass spectra of some of the compounds listed in Table 1 contain ions of type I "triple-decker sandwiches". Their formation can be visualized as being the result of reaction between the fragment ions $[RC_5H_4Fe]^+$ or $[R'C_5H_4Fe]^+$ (Scheme 1) and the neutral molecule RC_5H_4Fe-C_5H_4R' (reactions 1 and 2). The ratio of the intensities of the ions $[(C_5H_5)_2$-$C_5H_4R'Fe_2]^+$ and $[(C_5H_4R')_2C_5H_5Fe_2]^+$ in the mass spectra of mono-substituted ferrocenes (R' = CN or $COCH_3$) is approximately 5 times greater than the ratio $[C_5H_5Fe]^+/[C_5H_4R'Fe]^+$, which is probably related to a higher reactivity of the non-substituted ions $[C_5H_5Fe]^+$ and/or a greater stability of the ions $[(C_5H_5)_2$-$C_5H_4R'Fe_2]^+$ as compared to their substituted analogues.

SCHEME 1

$$\begin{tikzcd}
{[RC_5H_4FeC_5H_4R']^+} \arrow[r] \arrow[d] \arrow[dr] & {[RC_5H_4Fe]^+} \arrow[d] \\
{[R'C_5H_4Fe]^+} \arrow[r] & Fe^+
\end{tikzcd}$$

$$[RC_5H_4Fe]^+ + RC_5H_4FeC_5H_4R' \rightarrow [(RC_5H_4)_2R'C_5H_4Fe_2]^+ \qquad (1)$$

$$[R'C_5H_4Fe]^+ + RC_5H_4FeC_5H_4R' \rightarrow [(R'C_5H_4)_2RC_5H_4Fe_2]^+ \qquad (2)$$

The asymmetric mono- and di-substituted "triple-decker sandwich" ions are also present in spectra obtained by combined vapourization in the mass spectrometer of ferrocene and its symmetric 1,1'-di-substituted derivatives. The paths of formation of these ions are presented by the reactions 3 and 4:

$$[C_5H_5Fe]^+ + (C_5H_4CN)_2Fe \rightarrow [(C_5H_5CN)_2C_5H_5Fe_2]^+ \qquad (3)$$

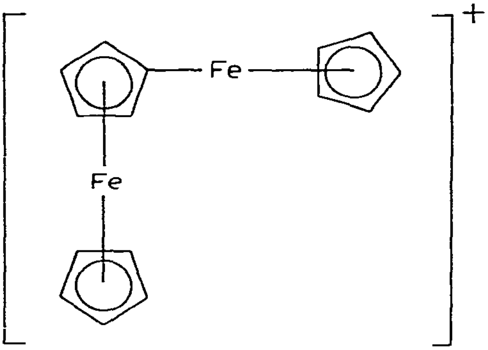
$$[C_5H_4CNFe]^+ + (C_5H_5)_2Fe \rightarrow [(C_5H_5)_2C_5H_4CNFe_2]^+ \qquad (4)$$

The mass spectra of ferrocene carbonyl derivatives include the ions $[(C_5H_5)_2$-$C_5H_4Fe_2]^+$ and $[C_5H_5(R'C_5H_4)C_5H_4Fe_2]^+$ containing the C_5H_4 ligand. One may suppose that the formation of these ions results from the substitution reaction of R' in the neutral molecule of the π-complex by the $[C_5H_5Fe]^+$ or $[R'C_5H_4Fe]^+$ cation. The structure of these ions is probably similar to that of the decarbonylated molecular ions (II) of the mixed π-, σ-cyclopentadienyl iron complex $C_5H_5FeC_5H_4Fe(CO)_2C_5H_5$ [6].

The greatest intensity among ion—molecule reaction products in the mass spectra of the majority of the studied ferrocenes is that of the binuclear ions $[(RC_5H_4)(R'C_5H_4)Fe_2]^+$. Their formation is related to the addition of the Fe^+ ion (intramolecular fragmentation product) to the neutral molecule of the complex (reaction 5):

$$Fe^+ + R'C_5H_4FeC_5H_4R \rightarrow [R'C_5H_4(C_5H_4R)Fe_2]^+ \qquad (5)$$

A substantiation of this pattern is a rise in intensity of $[C_5H_5(C_5H_4CN)Fe_2]^+$



(II)

in the cyanoferrocene mass spectrum with increasing Fe^+ ion concentration, this being achieved by introduction in the ionization chamber of iron pentacarbonyl which dissociates under electron impact to free iron ions.

The symmetric mononuclear ions $[(R'C_5H_4)_2Fe]^+$ and $[(RC_5H_4)_2Fe]^+$, probably formed by interaction of the fragment ions $[R'C_5H_4Fe]^+$ and $[RC_5H_4Fe]^+$ with the neutral molecule of the complex (reaction 6), are present in the mass spectra of some asymmetric complexes (Table 1) besides the bimetallic ions. It is possible that at least some of these ions appear on decomposition of the heavier ion—molecule reaction products (for example, according to reaction 7):

$$[RC_5H_4Fe]^+ + R'C_5H_4FeC_5H_4R \rightarrow (RC_5H_4)_2Fe^+ + R'C_5H_4Fe \qquad (6)$$

$$[(RC_5H_4)_2R'C_5H_4Fe]^+ \rightarrow [(RC_5H_4)_2Fe]^+ + R'C_5H_4Fe \qquad (7)$$

The mass spectra of ferrocene and cyanoferrocene obtained by combined vapourisation with various organic and inorganic compounds comprise ions containing a new metal—ligand bond (Table 2). A decrease in the energy of the ionizing electrons to a level where no molecular ion fragmentation occurs (the spectrum comprises a molecular ion only) leads to the disappearance of the secondary ions. Proceeding from this, their formation may be represented as resulting from the interaction of the fragment ions $[C_5H_5Fe]^+$ and Fe^+ with the neutral molecule of the organic compound (reactions 8 and 9), but not from the substitution of the cyclopentadienyl ring by a new ligand in the molecular ion (reaction 10). This substantiates the previous conclusion [3,7] on the low reactivity of the ferricenium cation in the gas phase. In contrast to the ferro-

TABLE 2

ION—MOLECULE INTERACTION PRODUCTS IN MASS SPECTRA OF FERROCENE AND CYANOFERROCENE OBTAINED IN COMBINED VAPORIZATION WITH L COMPOUNDS

L	C_2H_5OH	C_6H_6	acacH	$Fe(CO)_5$
Ion	$[C_2H_5OHFe]^+$	$C_6H_6FeC_5H_5$ $[C_6H_6Fe]^+$	$[(acac)_2Fe]^+$ $[acacFe]^+$	$[C_5H_5Fe_2(CO)_2]^+$

cenium cation, the ions $[C_5H_5Fe]^+$ and Fe^+ undergo addition reactions with

$$C_6H_6 + C_5H_5Fe^+ \rightarrow [C_5H_5FeC_6H_6]^+ \tag{8}$$

$$C_6H_6 + Fe^+ \rightarrow [C_6H_6Fe]^+ \tag{9}$$

$$C_6H_6 + R'C_5H_4FeC_5H_5^+ \rightarrow [C_6H_6FeC_5H_5]^+ \tag{10}$$

molecules capable of forming π- or σ-bonds with the iron atom.

Of particular interest among the ion—molecule reaction products are ions containing such ligands as benzene. The formation of these ions (see also ref. 7) evidences their relatively high stability and suggests that type $[C_6H_6Fe]^+X^-$ complexes can be synthesized under usual preparative conditions. It should be noted that the charged and electroneutral complexes of benzenecyclopentadienyliron have been described previously [8,9].

Experimental

The mass spectra were obtained on a MS-30 apparatus with the DS-50 data processing system at ionizing voltages of 70, 20 and 12 V, ionization chamber temperature of 250°C and also on a type MX 1303 mass spectrometer at ionizing voltage of 50 V and ionization chamber temperature of 150°C. The vapour pressure of the investigated compounds in the mass spectrometer ionization chamber was 10^{-6}—10^{-5} Torr.

References

1 E. Schumacher and R. Taubenest, Helv. Chim. Acta, 47 (1964) 1525.
2 S.M. Schildcrout, J. Amer. Chem. Soc., 88 (1975) 3846.
3 M.S. Foster and J.L. Beauchamp, J. Amer. Chem. Soc., 97 (1975) 4814.
4 M.S. Foster and J.L. Beauchamp, Inorg. Chem., 15 (1976) 665.
5 H. Werner and A. Salzer, Synth. Inorg. Metal-Org. Chem., 2 (1972) 239.
6 K.H. Pannel, J.B. Cassias, G.M. Crawford and A. Flores, Inorg. Chem., 15 (1976) 2671.
7 P.H. Hemberger and R.C. Dunbar, Inorg. Chem., 16 (1977) 1246.
8 A.N. Nesmeyanov, N.A. Vol'kenau, L.S. Shilovtseva and V.A. Petrakova, J. Organometal. Chem., 61 (1973) 329.
9 A.N. Nesmeyanov, N.A. Vol'kenau and I.N. Bolesova, Dokl. Akad. Nauk SSSR, 149 (1963) 615.