Journal of Organometallic Chemistry, 144 (1978) 195—203
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MASS SPECTROMETRY OF π-COMPLEXES OF TRANSITION METALS

IX *. ANALYSIS OF ALKYLFERROCENE MIXTURES

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(Received June 30th, 1977)

Summary

Qualitative analysis of product mixtures from electrochemical alkylation of ferrocene has been performed by the method of electron impact mass spectrometry, on the basis of the fragmentation patterns observed for individual alkylferrocenes. The possibility of a semi-quantitative mass spectrometric determination of alkylferrocene mixtures is discussed.

The Friedel—Crafts alkylation of ferrocene leads to mixtures of alkylated ferrocene homologues [2]. Product mixtures also occur in the recently reported electrochemical alkylation of ferrocene [3]. In both cases, the problem of characterization of the products arises. The usual methods, based on isolation and then identification of the components, are hardly applicable with alkylferrocenes, particularly with isomer mixtures. In fact, separation of such mixtures by the known physical methods has generally resulted in failure [4]. For this reason ferrocene alkylation products are better analyzed without prior separation.

The present paper describes a mass spectrometric analysis of the products of the electrochemical alkylation of ferrocene.

The mass spectra of individual alkylferrocenes are discussed in a number of works [5—10]. In particular, the mass spectra of monosubstituted alkylferrocenes (FcR) **, have been studied (R = CH_3 [5,6], C_2H_5 [5,7], n-C_4H_9, t-C_4H_9, and n-C_5H_{11} [5]). Data also exists on 1,1′-dialkylferrocenes, $(C_5H_4R)_2Fe$ (R = CH_3, C_2H_5 [5,7,8], n-C_3H_7, i-C_3H_7 [7], n-C_4H_9 [7,9], and t-C_4H_9 [7]), and polyalkylferrocenes $[(t\text{-}C_4H_9)_2C_5H_3]_2Fe$ [7] and $(C_5H_{5-n}Me_n)_2Fe$ (n = 1—4 [8], n = 5

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* For part VIII, see ref. 1.

** Throughout the paper, Fc = $C_5H_5FeC_5H_4$.

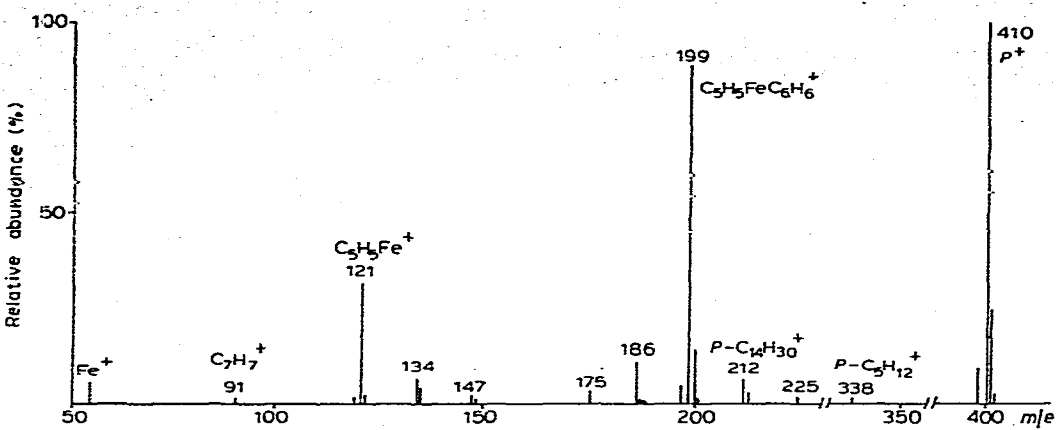

Fig. 1. Mass spectrum of cetylferrocene, n-$C_{16}H_{33}Fc$.

[8—10]). Certain specific features of fragmentation of these compounds under electron impact are discussed in refs. 5 and 6.

In order to explore the applicability of electron impact mass spectrometry to analysis of alkylferrocenes and their mixtures we have studied the mass spectra of FcR with R = n-$C_{16}H_{33}$ (Fig. 1), i-C_3H_7 (Fig. 2), CH_3, and reinvestigated the mass spectra of a number of alkylferrocenes studied earlier (Table 1). The literature data and that obtained in this work indicates the presence of three types of ions in the spectra of alkylferrocenes.

(1) Ions containing two metal—ligand bonds. Molecular ions (P^+) and ions formed from molecular ions by cleavage of the C—C and C—H bonds.

(2) Iron-containing ions formed by cleavage of metal—ligand bonds.

(3) Hydrocarbon ions that do not contain metal (these are unimportant for analysis of alkylferrocene mixtures).

Molecular ions give base peaks in the mass spectra of all alkylferrocenes and can thus be used for the determination of the elemental composition of the

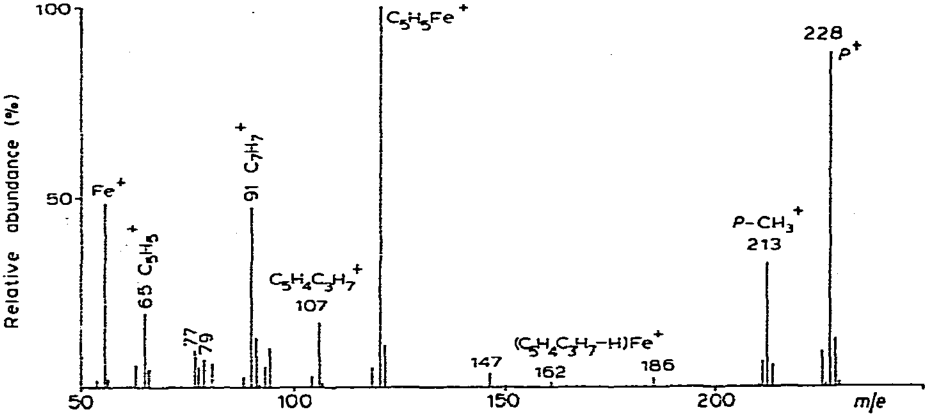

Fig. 2. Mass spectrum of i-propylferrocene, i-C_3H_7Fc.

TABLE 1

THE MASS SPECTRA (50 eV) OF MONOALKYLFERROCENES (FcR) NAD SYMMETRIC METHYLFERROCENES, $(C_5H_{5-n}Me_n)_2Fe$

	R = Me	Et	i-Pr	t-Bu	n-$C_{16}H_{33}$	*n*		
						1	3	4
P^+	28.5	29.0	20.8	31.5	39.4	31.3	40.8	43.2
L_2Fe^+ [a] (without P^+)	3.7	29.3	11.1	42.4	39.2	5.5	9.7	17.8
LFe^+	24.3	26.9	28.5	16.0	14.6	24.2	14.8	13.8
Fe^+ (with FeH^+)	35.2	10.3	10.1	5.3	1.5	21.9	6.6	1.9
L^+	10.5	4.6	21.6	2.0	0.8	10.2	24.3	18.9
P^{2+}	1.5	—	—	—	—	2.0	3.0	4.1
L_2Fe^+ (with P^+)	32.2	58.3	31.9	73.9	48.6	36.8	50.5	61.0

[a] L = hydrocarbon ligand.

sample. Unlike alkylbenzenes [11], stabilities of alkylferrocene molecular ions are almost independent of the side chain length (Table 1) and, in the methylferrocene series, increase with the number of methyl substituents (Table 2) *.

Cleavage of the alkyl chain C—C bond positioned β with respect to the cyclopentadienyl nucleus is typical of alkylferrocene fragmentation. The resulting fragment ions may be used in the identification of isomeric alkylferrocenes. Thus, the mass spectra of n- and t-butylferrocenes differ significantly in the intensities of the ions *m/e* 227 and 199 (0 and 62% for the former [5] and 76 and 5% for the latter (this work), respectively).

With monoalkylferrocenes, α-cleavage (the loss of the substituent) has not been observed, while heteroannular dialkylferrocenes $(C_5H_4R)_2Fe$ (R = Me, Et [5,7]) give rather intense ions $[P - R]^+$. A specific feature of fragmentation of methylferrocenes $(C_5H_{5-n}Me_n)_2Fe$ is that intensities of ions $P - R^+$ are practically independent on the extent of methylation. The ratio $[P - Me]^+/P^+$ remains near 10%, with $n = 1$, 3, and 4.

The α-cleavage with hydrogen transfer from the substituent R to the ferrocene nucleus and the loss of the olefin molecule, (R—H), leading to FcH^+ ions also occurs. Intensities of $[P - (R{-}H)]^+$ are mostly below 8%, only for t-BuFc does it amount to 22% [5] (our data 26%) (ion FcH^+, *m/e* 186).

The elimination of the methylene group is not characteristic for methylferrocenes; ion $[P - CH_2]^+$ is only observed for 1,1'-dimethylferrocene. For this reason, fragmentation of the higher homologues cannot lead to appreciable amounts of ions corresponding to molecular ions from the lower homologues. This circumstance can be used to advantage in qualitative determinations of multicomponent mixtures of alkylferrocenes. The cleavage of the C—H bonds of alkylferrocenes yields low intensity ions $[P - H]^+$ (~8%) and $[P - H_2]^+$ (3%).

Dicyclopentadienyl compounds are known to fragment under electron impact with the cleavage of the metal—ligand bonds [13]. One may therefore expect monoalkylferrocenes, $C_5H_5FeC_5H_4R$, to give both $C_5H_5Fe^+$ and $RC_5H_4Fe^+$ ions.

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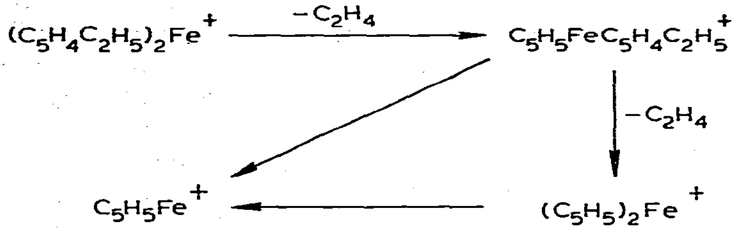
[*] Similar trends are observed in the $(C_6H_{6-m}Me_m)Cr$ series [12].

TABLE 2

POSSIBLE COMPONENTS, LFeL′, OF METHYLFERROCENE MIXTURES A (I—XII) AND B (I—X)

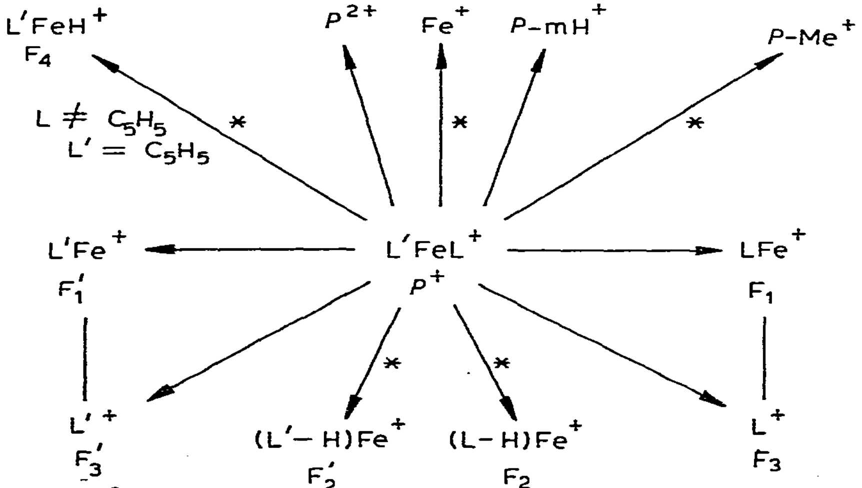
L L′	C_5H_5 C_5H_5	C_5H_4Me C_5H_5	$C_5H_3Me_2$ C_5H_5	C_5H_4Me C_5H_4Me	$C_5H_2Me_3$ C_5H_5	$C_5H_3Me_2$ C_5H_4Me	C_5HMe_4 C_5H_5	$C_5H_2Me_3$ C_5H_4Me	$C_5H_3Me_2$ $C_5H_3Me_2$	C_5HMe_4 C_5H_4Me	$C_5H_2Me_3$ $C_5H_3Me_2$	C_5HMe_4 $C_5H_3Me_2$	$C_5H_2Me_3$ $C_5H_2Me_3$
	—	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
P	186	200	214	214	226	228	242	242	242	256	256	270	270
F_1	121	135	149	135	—	149	—	—	149	—	—	—	—
F_2	—	134	148	134	162	148	176	162	148	176	162	176	162
F_3	65	79	93	79	106	93	—	107	93	107	—	—	107
F'_1	121	121	121	135	121	135	121	135	149	135	149	149	—
F'_2	—	—	—	134	—	134	—	134	148	134	148	148	162
F'_3	65	64	65	79	65	79	65	79	93	79	93	93	107
F_4	—	122	122	—	122	—	122	—	—	—	—	—	—



SCHEME 1

However, the presence of the $C_5H_5Fe^+$ ion does not always suggest a homoannular structure, because these ions may be other than molecular ions precursors and often occur in the spectra of heteroannular compounds. Thus, the $C_5H_5Fe^+$ ion in the spectrum of 1,1'-diethylferrocene may originate from fragment ions $C_7H_7Fe^+$ [5,7], $C_7H_9Fe^+$ [7], $C_5H_5FeC_5H_4C_2H_5^+$ and $(C_5H_5)_2Fe^+$ (the latter two ions are formed via hydrogen transfer from the alkyl chain to the cyclopentadienyl ring followed by the elimination of the olefin molecule, Scheme 1). It follows that the presence of the $C_5H_5Fe^+$ ion provides no proof of heteroannular substitution.

Cleavage of metal—ligand bonds in alkylferrocenes is usually accompanied by hydrogen transfer from one ligand to another, followed by the loss of the cyclopentadienyl molecule with the formation of $(C_5H_4R{-}H)Fe^+$ ions. The corresponding metastables are often observed (Scheme 2). Mere cleavage of metal—ligand bonds leads to low intensity $RC_5H_4Fe^+$ ions (~6%). With 1,1'-dialkylferrocenes, relative intensities of these ions decrease with elongation of side chains [7] from ~6% (R = Me) to ~1% (R = Bu). Fragmentation of $RC_5H_4Fe^+$ ions via cleavage of metal—ligand bonds leads to the Fe^+ ion whose intensity decreases rapidly as the number of methyl substituents in the parent molecule increases (Table 1). This observation, as well as a decrease of relative abundances of ions with 1 : 1 metal to ligand ratio with increase in the length of the side chains (Table 1), points to strengthening of the metal—ligand bonds with increase in the number or length of alkyl substituents.



SCHEME 2

Thus, the following fragment ions are characteristic for the spectra of various ferrocenes: molecular ions (base peaks), rearrangement ions of the type (L—H)Fe^+ (L = hydrocarbon ligand) (ions F_2 and F'_2, Scheme 2) and ions formed by mere cleavage of the metal—ligand bonds, F_1 and F'_1, and the β-cleavage products. These observations allow qualitative determination of alkylferrocene mixtures and, in certain cases, determination of structures of isomeric alkylferrocenes. As was mentioned, the loss of $(CH_2)_m$ from alkylferrocenes $C_{10}H_{10}(CH_2)_nFe$ with the formation of ions indistinguishable from the molecular ions of the lower homologues, occurs to only a negligible extent. The mass spectra can thus be used in the qualitative analysis (determination of the extent of alkylation) of alkylferrocenes. Moreover, consideration of the fragment ions observed or of the corresponding metastables, provides information about the structures of the components present.

The fragmentation patterns described above proved useful in the identification of product mixtures from electrochemical alkylation of ferrocene; mixtures of methylation products A and B, and a mixture of ethylferrocenes C.

The mass spectrum of mixture A (Fig. 3) contains the ions with *m/e* 186(1%), 200(8%), 214(34%), 228(86%), 242(100%), 256(30.5%) and 270(1.5%), corresponding to molecular ions $C_{10}H_{10-n}Me_nFe^+$, with n = 0, 1, 2, 3, 4, 5 and 6, respectively. The ions *m/e* 121, 134(135), 148, 162, and 176, corresponding to the $[(C_5H_{5-m}Me_mFe)—H]^+$ ions, with m = 0, 1, 2, 3 and 4, respectively, should be assigned to species containing 1 to 4 methyl groups per cycle as well as to species with unsubstituted rings.

The spectrum of mixture A thus reveals the presence of unsubstituted ferrocene and methylated ferrocenes with up to six methyl substituents in a molecule and up to four substituents in a ring. Mixture A can therefore contain not more than twelve methylferrocenes (I—XII, Table 2). No conclusions as to the nature of isomers present (e.g. II or III, IV or V, etc.) can be drawn.

Additional information about structures of methylferrocenes can be derived from the observation of metastables that occur in fragmentations of molecular ions. Thus, mixture B (Fig. 4) gives molecular ions $C_{10}H_{10-n}Me_nFe^+$, with *m/e* 186 (n = 0), 200 (n = 1), 214 (n = 2), 228 (n = 3), 242 (n = 4), and 256 (n = 5)

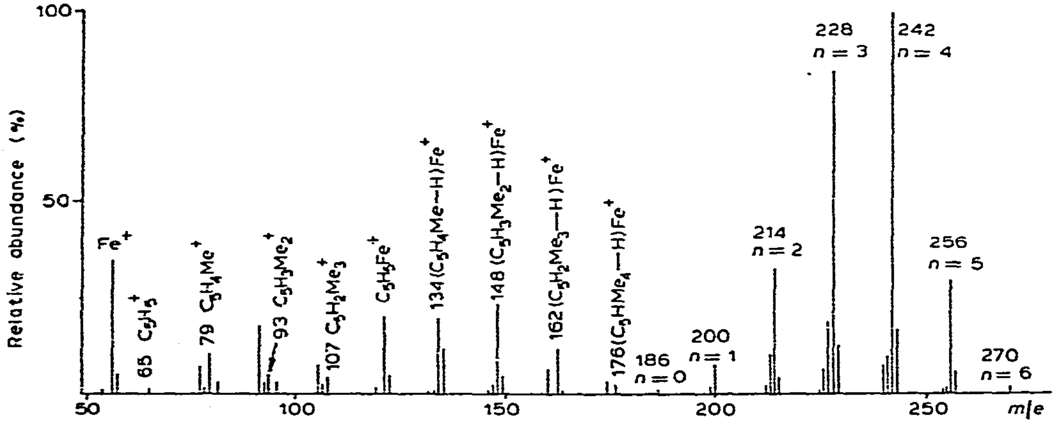


Fig. 3. Mass spectrum of mixture A of methylferrocenes, $C_{10}H_{10-n}Me_nFe$.

TABLE 3

THE COMPOSITION OF MIXTURE A OF METHYLFERROCENES, $C_{10}H_{10-n}Me_nFe$, DETERMINED BY THE GLC (PEAK AREA MEASUREMENTS) AND MASS SPECTROMETRIC (MOLECULAR ION INTENSITIES) TECHNIQUES

	n						
	0	1	2	3	4	5	6
GLC[a]	0.6	4.7	15.7	35.6	35.9	7.5	—
MS	0.4	3.0	13.0	32.7	38.5	11.9	0.5

[a] Reproducibility 3.5 rel. %.

and fragment ions $[(C_5H_{5-m}Me_mFe)-H]^+$, with m/e 121 ($m = 0$), 134 and 135 ($m = 1$), 148 ($m = 2$), 162 ($m = 3$), and 176 ($m = 4$) and should therefore contain ferrocene and methylferrocenes I—X (Table 2). The presence of the metastable ions m/e 78.9, 84.0, 89.9, and 102.5 is indicative of the processes 1—4.

$$C_5H_5FeC_5H_5^+ \xrightarrow{m^*\ 78.9} C_5H_5Fe^+ + C_5H_5 \qquad (1)$$

m/e 186 m/e 121

$$C_5H_5FeC_5H_4CH_3^+ \xrightarrow{m^*\ 89.9} C_6H_6Fe^+ + C_6H_6 \qquad (2)$$

m/e 200 m/e 134

$$C_5H_5FeC_5H_3(CH_3)_2^+ \xrightarrow{m^*\ 102.5} C_7H_8Fe^+ + C_5H_6 \qquad (3)$$

m/e 214 m/e 148

$$(CH_3C_5H_4)_2Fe^+ \xrightarrow{m^*\ 84.0} C_6H_6Fe^+ + C_5H_5CH_3 \qquad (4)$$

m/e 214 m/e 134

The occurrence of processes 3 and 4 points unambiguously to the presence of

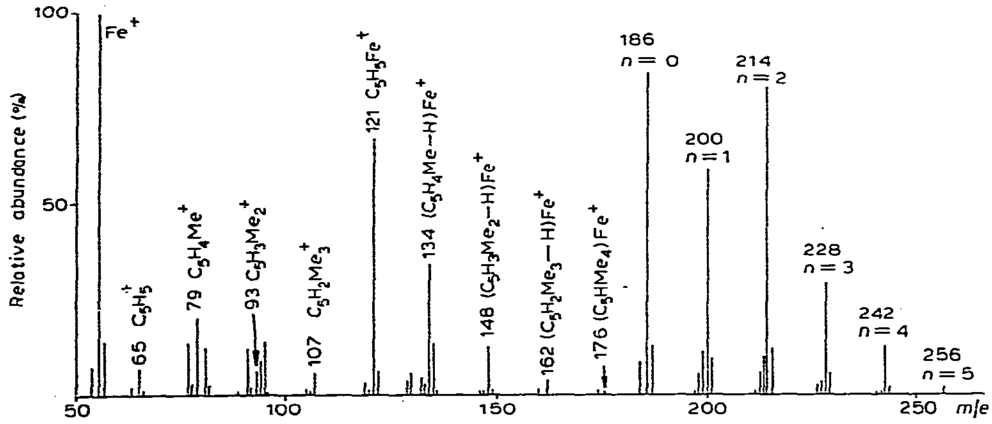


Fig. 4. Mass spectrum of mixture B of methylferrocenes, $C_{10}H_{10-n}Me_nFe$.

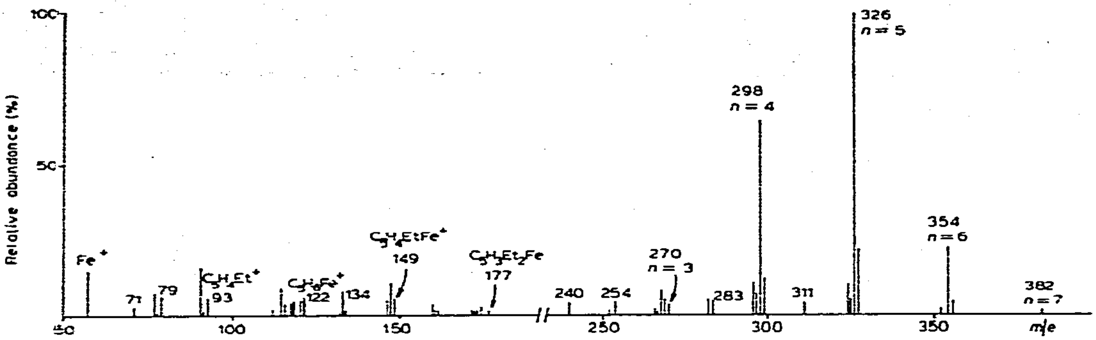


Fig. 5. Mass spectrum of mixture C of ethylferrocenes, $C_{10}H_{10-n}Et_nFe$.

two isomeric dimethylferrocenes; homoannular (II) and heteroannular (III).

Analysis of ethylferrocene mixtures is a more complicated task, since these fragment readily with the loss of ethylene to yield ions indistinguishable from molecular ions of ethylferrocenes containing one substituent less than the parent compound. Thus, diethylferrocene successively looses two ethylene molecules to give ethylferrocene and ferrocene ions (Scheme 1). The intensities of these ions do not, however, exceed 3% of the parent peak.

The mass spectrum of ethylferrocene mixture C (Fig. 5) contains ions $C_{10}H_{10-n}(C_2H_5)_nFe^+$, with *m/e* of 382 ($n = 7$), 354 ($n = 6$), 326 ($n = 5$) and 298 ($n = 4$), that reveal the presence of tetra- to hepta-ethylferrocenes. The ion *m/e* 270 ($n = 3$) has a very low intensity and may originate from the ion *m/e* 298 ($-C_2H_4$). The amount of triethylferrocene in the mixture, if there is any, should therefore be fairly small. The maximum number of ethyl substituents per ligand molecule can not be inferred from the spectrum because only ions $C_5H_{5-m}Et_mFe^+$, with $m = 1$ or 2, are observed (*m/e* 149, 177) while it is evident that the species with more than two substituents in a ring should be present.

A similar approach has been applied to a mixture of propylferrocenes $C_{10}H_{10-n}$-(n-Pr)$_n$Fe containing species with $n = 1$—4 (*m/e* 228, 270, 312, and 354) and to a mixture of cetylferrocenes $C_{10}H_{10-n}(n\text{-}C_{16}H_{33})_n$ Fe which has been found to give the ions *m/e* 410 and 634, indicating the presence of mono- and di-alkylated products. Structure analysis of these systems as well as of the ethylferrocene system could not be made.

Above, we have discussed applications of mass spectra to qualitative analysis of alkylferrocene mixtures. Quantitative determination of such mixtures is only possible after calibrating the mass spectrometer against reference samples.

The molecular ion intensity cannot be related directly to the vapour concentration in an ion source. The relationship 5 where P_1^+ and P_2^+ are the molecular

$$P_1^+/P_2^+ = C_1/C_2 \qquad (5)$$

ion intensities and C_1 and C_2 are the concentrations of the respective components, does not hold. The reason for this lies in different ionization cross sections and the different extents of fragmentation of various compounds under electron impact. Also, the concentration itself depends on the relative volatility of a given component (with a direct inlet system). It should be noted that substitution in the cyclopentadiene ring only slightly affects ionization potentials in the ferrocene series [14] (and probably, ionization cross sections as well) and has little effect on the extent of fragmentation of molecular ions (see Table 1). Further alkyl substituents seem to have no marked influence on the heats of sublimation. One may expect from these considerations that relationship 5 would hold, at least approximately, for alkylferrocenes.

In order to check this suggestion, we have measured the mass spectra of a mixture containing ferrocene and tetra- and hexa-methylferrocenes in the ratio 20.9 : 66.7 : 15.5 and obtained a (25.2 ± 0.6) : (66.7 ± 0.5) : (8.1 ± 0.3) ratio of molecular ion intensities. This result demonstrates the possibility of a semi-quantitative determination of alkylferrocenes from the mass spectra of their mixtures.

Comparison of the analytical data on a product mixture from electrochemical alkylation of ferrocene obtained by the methods of GLC (peak area measurements) and mass spectrometry (molecular ion intensities) lends further support to this conclusion. Both techniques give closely similar results.

Experimental

The mass spectra of individual alkylferrocenes were obtained on an AEI MS-30 instrument. The mass spectra of alkylferrocene mixtures were obtained on AEI MS-30, LKB-2091 and MX-1303 spectrometers equipped with direct inlet systems. The operating conditions were: ionizing energy 50 eV, sample compartment temperature 150°C.

Acknowledgements

The authors wish to express their thanks to Drs. S.P. Gubin and L.I. Denisovich who proposed this investigation and supervised the electrochemical alkylation of ferrocene. We are also indebted to Dr. R.B. Materikova for the pure samples of tetra-, hexa-, and octa-methylferrocenes and to Dr. V.G. Zaikin for the mass spectra of a number of alkylferrocene mixtures.

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