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FRAGMENTATION OF SOME SUBSTITUTED FERROCENES UNDER ELECTRON IMPACT (1)

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A recent report (2) on the mass spectra of some ferrocenes claims that there is little evidence for the loss of fifty-six mass units corresponding to the iron atom. Since this result is somewhat in contradiction to our findings and, further more, since the above mentioned report (2) gives no details of fragmentation patterns of the ferrocenes studied, we wish to communicate some preliminary interesting results of a systematic investigation of mass spectral measurements (1c) of π-bonded organometallic compounds currently in progress in our laboratories.

All the compounds reported in this communication are monosubstituted ferrocenes, containing a carbonyl group in the α-position to the cyclopentadienyl ring.

The major fragments are shown in Chart I and their <u>m/e</u> values are tabulated in Table I together with their % relative abundance with respect to the most abundant ion. In all cases, but one, the molecular ion peak is also the base peak.

The expected (3) fragments a and b arising from bond cleavage on both sides of the carbonyl group were observed in all cases except for carboxyferrocene, IV. Similarly, as expected (4), we observed the two fragments c and d resulting from cleavage of the bonds between the metal atom and each of the two cyclopentadienyl rings.

The m/e values under column e are interpreted as representing the fragments arising from transfer of the group R to the metal atom with the concomitant cleavage of the bond between the substituted cyclopentadienyl ring and the iron atom. This ion, e, can give rise to fragment f by cleavage of the remaining cyclopentadienyl ring. The correctness of assigning these structures to fragments e and f is supported by the expected shifts obtained in the mass spectrum of the deuterated acid V.

A most interesting feature of all the measured spectra is the appearance of peaks corresponding to m/e values of 129 and 128, g and h respectively.

We believe that fragment g arises from removal of the iron atom from fragment b. The corresponding metastable peak at m/e ~90 expected from such a fragmentation pattern was detected in the measured spectra. Loss of one hydrogen atom from g would give rise to fragment h, which could be the fulvalene cation or some rearranged product thereof.

It should be noted that the peaks m/e = 129 and m/e = 128 were also observed in the mass spectrum of unsubstituted ferrocene. In the latter case the corresponding value of the metastable peak was shifted, as required to m/e ~ 89.

CHART I

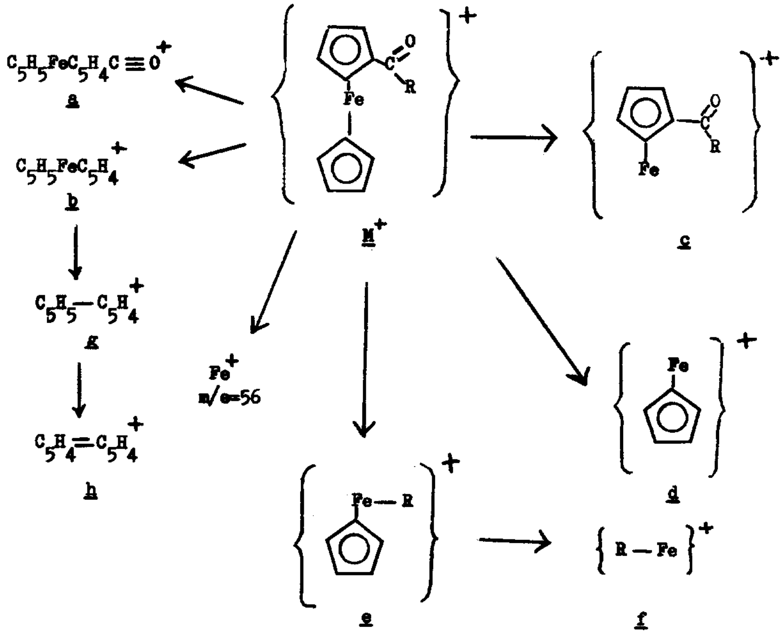
C5H5FeC5H4C≡O+
a
C5H5FeC5H4+
b
C5H5—C5H4+
g
C5H4=C5H4+
h
Fe+
m/e=56
O
C
R
Fe
M+
c
Fe
d
Fe—R
e
R—Fe
f

TABLE I

m/e Values (and Relative Abundance) of Major Fragments

in the Mass Spectra of Ferrocenes

$C_5H_5FeC_5H_4$–CO–R

	R	M^+	a	b	c	d	e	f	g	h	Fe^+
I	CH_3	228 (100)	213 (13)	185 (63)	163 (5)	121 (20)	–	71 (11)	129 (27.5)	128 (5.5)	(50.5)
II	C_6H_5	290 (100)	213 (1.5)	185 (3.8)	225 (3)	121 (5.8)	198 (2.8)	133 (8.5)	129 (3.5)	128 (1.5)	(19)
III	p–$CH_3OC_6H_4$	320 (100)	213 (1)	185 (1.7)	255 (3)	121 (8.2)	228 (1.0)	163 (3.3)	129 (3)	128 (2.8)	(13)
IV	OH	230 (87)			165 (15)		138 (100)	73 (23)	129 (2.5)	128 (2.3)	(89)
V	OD	231			166		139	74	129	128	
VI	OCH_3	244 (100)	213 (3.6)	185 (3.6)	179 (1.0)	121 (26)	152 (44)	87 (1.4)	129 (6)	128 (3.4)	(36)
VII	$NHCH_3$	243 (100)	213 (8)	185 (8)	178 (40)	121 (25)	151 (13)	86 (2)	129 (9)	128 (3.5)	(29)

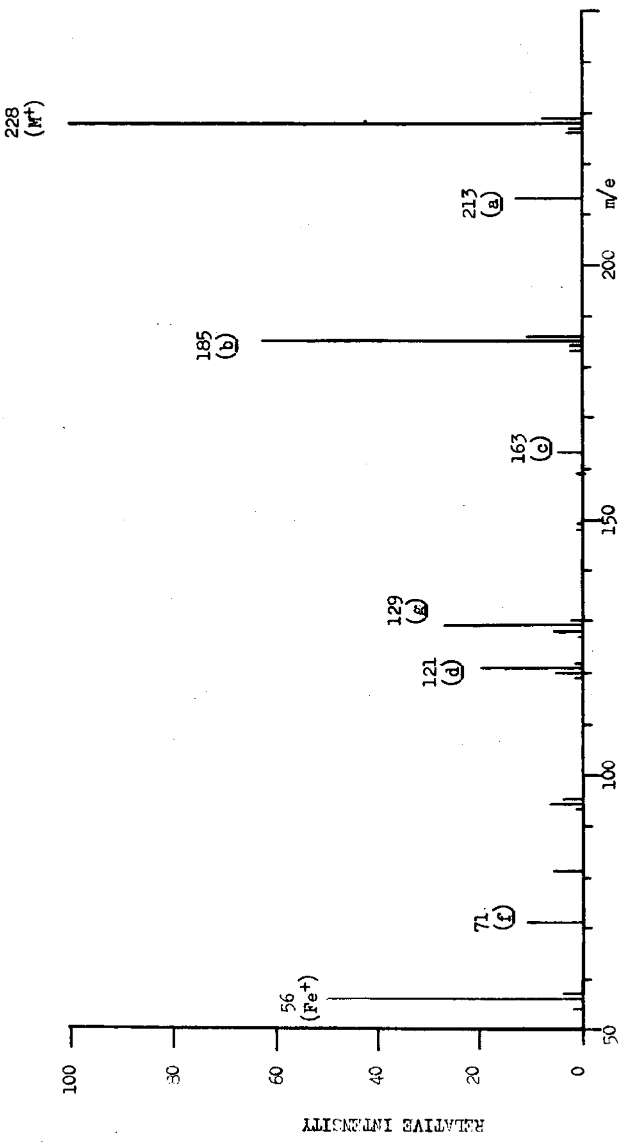

FIG. 1. Mass spectrum of acetylferrocene (I).

The relatively highly abundant Fe^+ ion could arise from any of the fragments a - f, or from the molecular ion.

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