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MASS SPECTROMETRY OF π-COMPLEXES OF TRANSITION METALS

XXII *. FRAGMENTATIONS OF FERROCENYL-SUBSTITUTED PYRAZOLINES-2 UNDER ELECTRON IMPACT **

A.N. NESMEYANOV, D.V. ZAGOREVSKII *, Yu.S. NEKRASOV, V.N. POSTNOV and A.M. BARAN
Institute of Organo-Element Compounds of the U.S.S.R., Academy of Sciences, Moscow 117813, 28 Vavilova st. (U.S.S.R.)

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Summary

The mass spectra of 1-*N*-acetyl- and 1-*N*-phenyl-3-ferrocenyl-5-arylpyrazolines-2, their 5-ferrocenyl-3-aryl isomers and their 3,5-diferrocenyl analogues have been studied. The "pyrazoline" type of the molecular ion fragmentation involves various processes of heterocyclic nucleus destruction and elimination of the substituents or their fragments. The directions and intensities of the processes observed are interpreted in terms of preferred positive charge localization on the transition metal atom. Interactions between the acetyl and ferrocenyl groups manifest themselves by the appearance of intense $[P - C_5H_5]^+$ ions (ferrocenyl type fragmentation products) in the mass spectra of 1-*N*-acetyl-3-aryl-5-ferrocenylpyrazolines-2 only. The fragmentation mechanism leading from $[P - C_5H_5]^+$ to $C_7H_7OFe^+$ is discussed.

As stated in the previous communications [2,3], the direction and degree of fragmentation of some ferrocene derivatives under electron impact depend on specific interactions between the substituent and the transition metal atom which is the most probable centre of positive charge localization. We now report the mass spectra of pyrazolines-2 containing the ferrocenyl group in positions 3- and/or 5- of the heterocycle (compounds I—XIX, Tables 1 and 2). These compounds contain the pyrazoline ring together with the ferrocenyl and aryl groups, and the positive charge may be localized on either of these moieties.

The behaviour of aryl- and diarylpyrazolones-2 under electron impact has

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* For Part XXI see ref. 1.
** Dedicated to Prof. G.A. Razuvaev on the occasion of his 85th birthday on August 23rd, 1980.

TABLE 1

MASS SPECTRA OF FERROCENYL SUBSTITUTED 1-*N*-ACETYL-PYRAZOLINES-2 I—X AND 1-*N*-PROPIONYL-3-PHENYL-5-FERROCENYLPYRAZOLINE-2 IV-EtCO

(Relative intensities of ions are given in % of total ion current)

Ion	Compound										
	I	II	III	IV	V	VI	VII	IV-EtCO	VIII	IX	X
P^+	17.8	34.3	22.0	10.9	20.0	14.2	15.7	19.5	26.1	16.7	29.6
$[P-H]^+$	1.6	2.8	1.9	—	—	—	—	—	—	—	—
$[P-CH_2CO]^+$	6.2	10.2	6.7	—	—	—	—	0.5 [a]	—	0.4	0.2
$[P-CH_2CO-H]^+$	0.2	1.2	0.6	0.5	1.0	1.0	0.6	0.9 [a]	—	0.4	0.2
$[P-C_5H_5]^+$	—	—	0.6	6.4	12.2	8.4	6.3	10.8	7.8	7.8	5.1
$[P-C_5H_5-N_2H]^+$	—	—	—	0.4	0.7	0.4	0.4	0.5	—	1.0	0.2
$[P-C_5H_5-R_1N]^+$	—	—	0.6	0.3	0.3	0.6	0.2	1.5	0.3	0.2	0.8
$[P-CH_2CO-R_5]$	0.4	0.4	0.6	—	0.1	0.1	0.2	—	—	0.5	—
$[P-R_5CN]$	—	—	—	3.1	6.8	4.5	3.3	2.7	0.1	6.3	2.5
$[P-C_5H_5-R_5CN]$	—	—	0.1	3.6	3.9	4.5	2.6	2.2	1.0	3.4	2.3
$[P-FcC_2H_3]$	—	—	—	1.3	0.5	1.8	—	—	—	—	—
$FcC_2H_3^+$	—	—	—	0.5	0.4	0.7	3.0	0.8	2.0 [a]	2.7 [a]	1.5 [b]
$FcCN^+$	1.4	1.9	2.2	0.1	—	0.2	6.8	—	5.4	7.5	10.0
$[P-CH_2CO-R_5C_2H_2]$	1.0	1.4	1.9	—	0.1	—	1.5	—	—	—	—
$[P-CH_3CO-R_5C_2H_3]$	1.4	1.9	1.9	—	—	—	0.1	—	—	—	—
$FCCH_2^+$, FcN^+	1.6	2.1	1.3	—	—	0.1	0.5	—	—	0.3	—

FcH^+	1.9	0.4	1.6	1.0	0.7	0.2	1.9	0.9	2.4	3.5	1.9
Fc^+	3.9	4.0	2.2	—	—	0.2	0.4	—	0.5	1.0	0.5
$C_{14}H_{10}^+$	3.1	0.8q	0.3	1.7	0.4	0.3	—	1.7	0.5	—	—
$C_{14}H_9^+$	3.0	4.2	2.1	1.9	2.4	0.5	—	1.5	—	—	—
$C_{13}H_{11}^+$	—	—	0.5	—	0.1	0.2	0.4	—	0.2	—	0.6
$C_{13}H_9^+$	0.6	0.5	2.1	0.3	0.2	1.5	1.7	0.1	0.4	—	1.6
$C_7H_7OFe^+$	—	0.1	—	15.1	14.6	12.5	3.6	6.7	2.5[a]	6.3[a]	2.3[b]
$C_7H_7Fe^+$	0.2	—	0.3	2.8	1.3	2.4	0.8	3.2	0.6	1.3	7.5[b]
$C_7H_6Fe^+$	0.7	0.3	0.8	0.9	0.3	0.4	0.5	0.4	0.3	0.1	—
$C_7H_5Fe^+$	0.2	0.2	0.2	1.1	0.5	0.8	0.6	0.7	0.4	0.1	—
$C_6H_7Fe^+$	—	—	—	5.0	3.3	3.4	0.8	2.0	0.6[a]	1.3[a]	10.0[b]
$C_6H_6Fe^+$	1.3	0.4	1.6	1.4	1.1	1.5	0.5	0.5	0.9	0.8	—
$C_6H_5Fe^+$	1.1	0.3	1.3	0.7	0.4	1.4	0.3	0.2	0.5	—	0.9
$C_5H_5Fe^+$	11.9	6.2	7.5	9.0	5.7	6.0	11.3	8.0	6.8	5.3	2.0
$FeCH_2CO^+$	0.1	—	—	0.5	—	0.2	0.3	0.3	0.1	—	—
FeH^+	—	—	—	1.0	0.7	0.6	0.6	1.0	0.5[a]	—	0.9[b]
Fe^+	7.9	3.0	3.5	6.4	3.0	3.4	5.9	6.1	4.7	1.1	0.6
$R_5C_2H_3^+$	0.9	0.1	1.4	0.4	—	—	(3.0)	—	—	—	—
$R_5C_2H_2^+$	1.2	0.4	0.6	0.8	—	—	(6.8)	1.5	—	—	—
P^{2+}	—	—	—	—	—	—	1.1	—	2.0	1.3	3.2
$[P-C_5H_5-R_1NH_2]^+$	—	—	—	—	—	—	1.9	—	5.1	1.2	0.1
$[P-H_2O]$	—	—	0.2	0.4	—	0.6	0.3	0.5	—	0.2	—
ΣM	76	84	83	83	87	87	90	82	90	98	96

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[a] Composition of ion differs from the given one by 14 amu (CH_2). [b] Composition of ion differs from the given one by 76 amu (C_6H_4).

TABLE 2

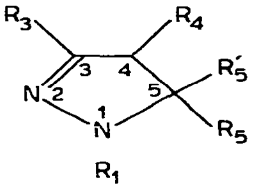
MASS SPECTRA OF FERROCENYL SUBSTITUTED 1-*N*-PHENYL-PYRAZOLINES-2 XI—XVII AND 3-PHENYL-5-FERROCENYLPYRAZOLINE-2 XVII (Relative intensities are given in % of total ion current)

Ion	Compound							
	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII
P^+	28.1	36.2	24.3	25.7	15.5	21.8	33.0	22.3
$[P-H]^+$	2.2	—	1.7	1.1	0.5	1.3	0.9	1.6
$[P-H_2]^+$	1.2	—	3.2	1.1	0.9	2.4	3.0	2.8
$[P-2\,H_2]^+$	—	—	—	0.9	0.3	0.8	—	1.1
$[P-C_5H_6]^+$	—	—	—	0.8	0.6	0.6	0.3	1.4
$[P-R_5]^+$	0.4	0.1	0.7	0.1	0.5	0.2	0.6	0.5
$[P-R_5]^+$	3.3	2.1	3.2	—	—	—	2.2	—
$[P-R_5H]^+$	—	—	—	—	—	—	4.5	—
$[P-R_1NH]^+$	0.6	0.2	1.0	4.6	2.9	5.0	0.3	1.1
$[P-R_3CN]^+$	—	—	—	0.7	0.5	0.6	0.7	3.3
$[P-C_5H_6-R_5]^+$	1.3	0.9	0.8	—	—	—	—	—
$[P-C_5H_5-R_1NH]^+$	—	—	1.3	3.9	0.1	3.9	4.0	1.4
$[P-R_5-R_1N]^+$	0.6	—	—	00.7	0.5	0.6	0.4	—
$[P-R_5-R_1NH]^+$	—	—	—	1.1	1.1	1.1	1.7	—
$[P-R_5-R_1NH_2]^+$	0.8	—	—	—	—	0.7	4.0	—
$FcC_2H_3^+$	0.5 [a]	0.5 [a]	0.5 [a]	12.0	11.0	11.4	6.2	6.9
$FcCN^+$	7.6	7.1	7.6	0.2 [b]	0.6 [b]	0.3 [b]	3.1	0.3 [b]
FcH^+	2.3	1.0	2.2	9.5	12.7	9.9	5.0	7.4
Fc^+	2.7	3.5	4.0	—	—	—	—	0.3
$C_{13}H_9^+$	0.3	0.6	1.0	0.4	0.4	0.5	0.7	—
$C_{12}H_8^+$	0.8	0.9	0.8	0.6	0.6	0.5	0.5	0.6
$C_{10}H_9^+$	3.3	3.0	4.3	0.3	0.6	0.6	0.8	0.4
$R_5C_2H_3^+$	—	—	—	0.5	—	—	(6.2)	—
R_5CN^+	0.8	—	—	0.6	—	—	(3.1)	0.6
$C_7H_7Fe^+$	0.2	—	0.3	0.9	0.9	0.8	0.7	0.8
$C_6H_7Fe^+$	0.2	—	—	0.3	0.6	0.2	0.3	1.0
$C_6H_6Fe^+$	0.8	0.3	0.8	0.5	0.6	0.8	0.4	0.6
$C_5H_5Fe^+$	11.9	8.3	10.2	8.6	8.5	7.8	8.6	7.7
R_1N^+	2.0	1.1	1.7	3.0	4.4	3.3	0.3	1.3
R_1^+	5.5	4.5	4.0	2.3	2.2	1.8	0.6	1.6
Fe^+	5.5	5.4	3.9	3.6	3.5	2.7	3.3	6.9
P^{2+}	0.6	1.4	—	0.4	1.2	—	1.6	0.9
$(P-R_5)^{2+}$	0.3	0.7	—	—	—	—	—	—
$(P-Br)^{2+}$	—	—	—	—	1.8	—	—	—
ΣM	76	82	74	86	81	85	93	84

[a] For the $FcCHN^+$ ion. [b] For the $FcC_2H_2^+$ ion.

been previously studied [4—7]. Mass spectra of some ferrocenyl(α-furyl)pyrazolines are reported in ref. 8.

The mass spectra of mono- and diferrocenylpyrazolines-2 I—XIX studied in this work all contain intense molecular ions (P^+). Their fragmentation paths may conventionally be divided into two types, the "ferrocenyl" and "pyrazoline" fragmentation types. The latter one involves rupture of metal—ligand bonds leading to $C_5H_5Fe^+$ and $[P-C_5H_5]^+$. The specific feature of the "pyrazoline" fragmentation type is heterocyclic nucleus destruction with the loss of the substituents or of their parts from the pyrazoline ring. To this type belong the elimination of the pyrazoline 5-H atom and the loss of ketene from the molecular ions I—III.



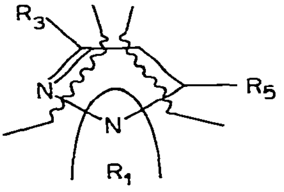
Compound	R_1	R_3	R_5	R_4	R_5'	Table
I	COMe	Fc	Ph	H	H	1
II	COMe	Fc	C_6H_4Br	H	H	1
III	COMe	Fc	C_6H_4OMe	H	H	1
IV	COMe	Ph	Fc	H	H	1
IV-$COCD_3$	$COCD_3$	Ph	Fc	H	H	1
IV-COEt	COEt	Ph	Fc	H	H	1
V	COMe	C_6H_4Br	Fc	H	H	1
VI	COMe	C_6H_4OMe	Fc	H	H	1
VII	COMe	Fc	Fc	H	H	1
VIII	COMe	Fc	Fc	H	Me	—
IX	COMe	Fc	Fc	Me	H	—
X	COMe	Fc	Fc	Ph	H	—
XI	Ph	Fc	Ph	H	H	2
XII	Ph	Fc	C_6H_4Br	H	H	2
XIII	Ph	Fc	C_6H_4OMe	H	H	2
XIV	Ph	Ph	Fc	H	H	2
XV	Ph	C_6H_4Br	Fc	H	H	2
XVI	Ph	C_6H_4OMe	Fc	H	H	2
XVII	Ph	Fc	Fc	H	H	2
XVIII	H	Ph	Fc	H	H	2
XIX	H	Fc	Fc	H	Me	—

Fc = $C_5H_5FeC_5H_4$, ferrocenyl

The *N*-acetyl (I) and *N*-phenyl (XI) derivatives lose the aryl radical under electron impact. As the mass of the corresponding ion does not change on going from XI to XII or XIII, the process may only involve the elimination of the pyrazoline 5-phenyl substituent.

Cleavage of the C—C bond between the pyrazoline ring and ferrocenyl moiety in the 3-ferrocenyl isomers gives the Fc^+ ion. With compounds containing the ferrocenyl substituent in the position 5 of the ring, the process is accompanied by H shift to the ferrocenyl group and formation of FcH^+.

As with arylpyrazolines, the mass spectra of their ferrocenyl analogues contain many fragment ions formed by dissociation of the pyrazoline cycle, such as $FcCH_2^+$, FcN^+, $ArCH_2^+$, and ArN^+. The $(P - R_1NH_n)^+$, $(P - C_5H_5 - R_1NH_n)^+$ and $(P - R_1NH_n - Ar)^+$ ions ($R_1 = H$, $n = 2, 3$; $R_1 = Ph$, $n = 1, 2$; $R_1 = Ac$, n $n = 0$—2) which are the products of simultaneous cleavage of the N—N and N— N—C(5) bonds are also observed. Simultaneous dissociation of the N—N and C(3)—C(4) or C(5)—N and C(3)—C(4) bonds leads to the R_3CN^+ and $R_5C_2H_3^+$ fragments. Irrespective of the ferrocenyl groups position, metal-containing ions such as $FcCN^+$, $FcC_2H_3^+$ or $[P—ArCN]^+$ are observed.



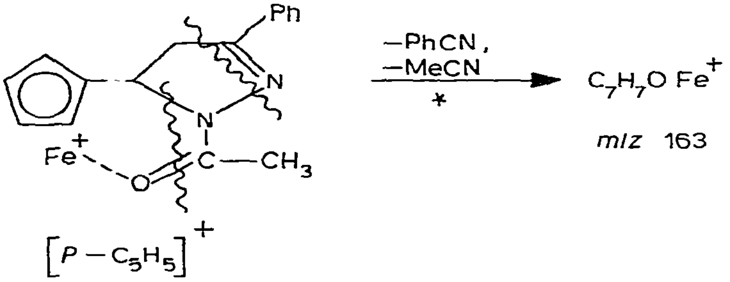
The behaviour of compounds I—XIX under electron impact is characterized by predominant formation of iron-containing ions. The total intensity of metal-containing ions amounts to not less than 80% of the total ion current which is indicative of preferred positive charge localization on the transition metal atom in the molecular ions. Charge localization on the ferrocenyl moiety leads to new fragmentation paths mostly involving rearrangement processes. In isomeric ferrocenylarylpyrazolines-2, these paths are characterized, together with general features, by a number of points specific for a given compounds. Thus, the formation of the $FcCN^+$ ion from the 3-ferrocenyl derivatives and $[P - ArCN]^+$ from their 5-ferrocenyl substituted analogues may be regarded as reactions of the same type.

One of the major differences is the occurrence in the mass spectra of 3-aryl-5-ferrocenylpyrazolines of ions absent from the mass spectra of the corresponding 3-ferrocenyl derivatives of their aromatic analogues containing no metal atom. Thus, the mass spectra of 1-phenyl-3-aryl-5-ferrocenylpyrazolines-2 XIV—XVI contain intense $[P - PhNH]^+$ ions and the products of their further fragmentations, $[P - PhNH - C_5H_n]^+$ ($n = 5, 6$) and $[P - PhNH - Ar]^+$. The molecular ions of these compounds undergo an unexpectedly deep dehydrogenation and give a series of ions $[P - nH_2]^+$ were n ranges from 1 to 3.

The differences are most clearly seen in the 1-acetyl derivatives. A number of new processes involving dissociation of the pyrazoline ring and the elimination of N_2H, H_2O, C_2H_3N, CH_3CON and CH_3CONH_2 as neutral particles from P^+ or $[P - C_5H_5]^+$ occur in the mass spectra of 5-ferrocenylpyrazolines IV—VI.

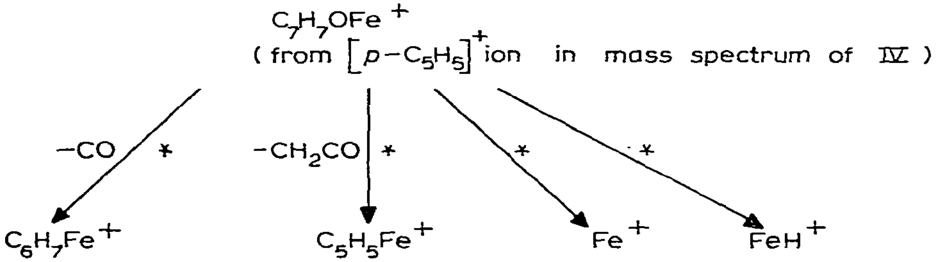
One more distinguishing feature of 1-acetyl-5-ferrocenylpyrazoline fragmentations is the presence of intense $[P - C_5H_5]^+$ ions formed by the elimination of an unsubstituted cyclopentadienyl ligand from the molecular ion (the other product of the "ferrocenyl"-type fragmentation, $C_5H_5Fe^+$, is present in all the spectra studied). The study of chalcone organometallic analogues [2] has shown that the formation of intense $[P - C_5H_5]^+$ in the mass spectra of monosubstituted ferrocenes is due to their high stabilities arising from specific electrostatic or coordination type interactions of the substituent with the positively charged and/or coordinatively unsaturated metal atom. Direct interactions between close-lying ferrocenyl and acetyl groups also provide an explanation of the "anomalous" behaviour of compounds IV—VI.

The dissociation of $[P - C_5H_5]^+$ in the mass spectra of IV, V and VI leads to $C_7H_7OFe^+$ as one of the products (m/z: found, 162.9844; calcd., 162.9846). One might suggest that its formation involves acetyl group shift to metal and cleavage of the C(5)—Fc bond. In trideuteroacetyl and *N*-propionyl derivatives IV-CD_3CO and IV-EtCO these ions, however, do not shift to the larger m/z values. Hence the acetyl group hydrogen atoms do not participate in the formation of $C_7H_7OFe^+$ ions. The introduction of methyl substituents in the 4- or 5-positions of the pyrazoline ring (compounds VIII and IX) increases the ion mass by 14 amu. A 76 amu shift occurs on the introduction of the phenyl group in the ring (compound X). It thus follows that the $C_7H_7OFe^+$ ions contain the heterocycle C(4) and C(5) atoms. Consequently, the cyclopentadienyl and pyrazoline ring carbon and hydrogen atoms only participate in the formation of the $C_7H_7OFe^+$ ion together with the acetyl group oxygen atom. The formation of $C_7H_7OFe^+$ may therefore be treated as simultaneous elimination of the acetonitrile and benzonitrile molecules from $[P-C_5H_5]^+$. The reaction involves rupture of four bonds, one of which (the C=O bond) dissociates only very infrequently. The latter process, seemingly, involves direct participation of the iron atom.

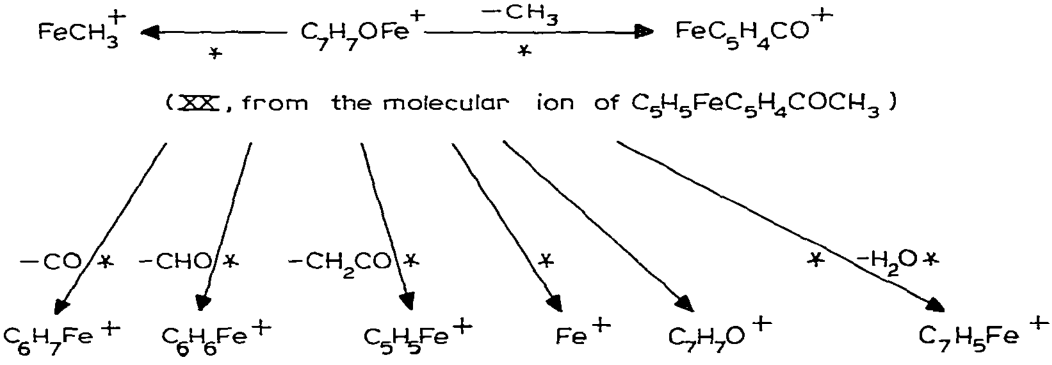


The high probability of this complex rearrangement process implies a high stability of the $C_7H_7OFe^+$ ion formed. The latter may have the structure of the (acetylcyclopentadienyl)iron cation XX. Comparison of the behaviour of XX and $C_7H_7OFe^+$ in the mass spectra points to some similarity (the formation of the $C_6H_7Fe^+$, $C_5H_5Fe^+$ and Fe^+ ions, see Schemes 1 and 2) between these species,

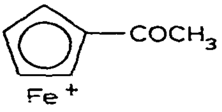
SCHEME 1



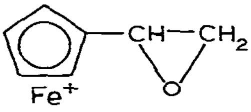
SCHEME 2



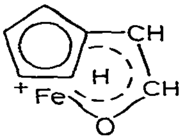
but also reveals certain differences, e.g. the loss of Me$^\cdot$, H_2O and HCO$^\cdot$, characteristic for XX, is not observed with the $C_7H_7OFe^+$ ion. The latter may also have the epoxide (XXI) and metalchelate (XXII) structures. The study of the mass spectra of other model ions of the same composition may shed light on the structure of the ion under discussion. The occurrence of the $C_7H_7OFe^+ \rightarrow FeH^+$ process, however, is indicative of the presence of a labile hydrogen atom(s) in the system.



(XX)



(XXI)



(XXII)

Experimental

Compounds I—XIX were prepared as described in ref. 9. The mass spectra were obtained with an AEI MS-30 mass spectrometer equipped with a DS-50 data processing system. The conditions were: the ionizing voltage 70 eV, direct inlet system temperature 180—220°C, ionization chamber temperature 250°C. Precision mass measurements were done by the peak coincidence technique at a resolution of 3 000. The metastables were measured with Varian MAT-111 (the DADI technique) and MS-30 (the defocussing, combined scan and high tension scan techniques) instruments.

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