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IRON CARBONYL COMPLEXES CONTAINING AN AZOMETHYLENE MOIETY

III *. MASS-SPECTROMETRIC STUDY OF DIIRON HEXACARBONYL COMPLEXES FROM AZOMETHYNES AND AZINES

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Summary

The electron impact mass spectra of diironhexacarbonyl complexes prepared from benzylidene- and α-naphthylidene-anilines, benzalazine and ketazines of acetophenone, *p*-bromoacetophenone and benzophenone are studied. The main fragmentation of the ligands occurs only after complete decarbonylation of the molecular ions and involves rupture of metal–ligand bonds, elimination of a part of the central ligand in the form of HCN and RCN, elimination of a neutral aromatic fragment or elimination of a part of the ligand.

Introduction

Recently, a large number of articles have been published on the synthesis of binuclear iron carbonyl complexes with nitrogen-containing bridges [2]. Such compounds have received attention generally in the context of the study of stabilization of the unstable particles, their variable biological activity and practical applications. The present study is concerned with analysis of the mass spectra of several binuclear iron carbonyl complexes prepared from azomethynes (I, II) and azines (III–VII) to elucidate the influence of the nature of substituents on the nitrogen atom and their molecular structures on the electron impact-induced fragmentation.

Results and discussion

Partial data from the 70 eV mass spectra of compounds I–VII are shown in Tables 1–3. The molecular ions of all these complexes are of low abundance in the

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* For part II, see ref. 1.

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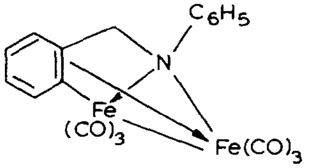
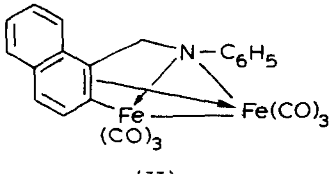
70 eV mass spectra and are observed with moderate intensity in the lowvoltage (12 eV) spectra.



(I)



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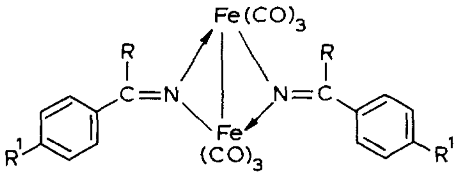
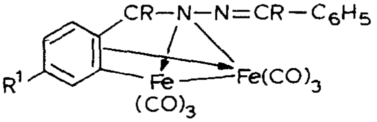


(III : R = R^1 = H ;
IV : R = CH$_3$, R^1 = H ;
V : R = CH$_3$, R^1 = Br ;
VI : R = C$_6$H$_5$, R^1 = H)



VII : R = R^1 = H

The initial fragmentation of the compounds I–VII occurs with stepwise loss of six carbonyl groups; the carbonyl-free $[M-6\ \mathrm{CO}]^{+\cdot}$ ions being always the base peaks at 70 eV (Table 1). However, at low voltage (12 eV) the $[M-2\ \mathrm{CO}]^{+\cdot}$ ions become the base peaks for all the investigated complexes (I–VII). It should be noted that the spectra of I–VII exhibit pronounced peaks of m/z 28 ($[\mathrm{CO}]^{+\cdot}$ ions) whose intensities depend sharply on the mass spectrometric conditions. Formation of the $[\mathrm{CO}]^{+\cdot}$ ion-radicals may be explained by both electron-impact fragmentation and by ionisation after pyrolysis. Thermogravimetric analysis of compounds (III–VII) shows [3] that the initial thermal degradation of these complexes involves elimination of six CO groups. Further thermal decomposition of the molecules is more complicated and could not be identified with the aid of thermogravimetric analysis. All the mass spectra investigated exhibit intense Fe^+ and Fe_2 ions, which could originate at different fragmentation stages.

The diagnostically most interesting fragmentation processes for complexes I–VII are realized both in completely decarbonylated $[M-6\ \mathrm{CO}]^{+\cdot}$ ions and other fragment ions and may involve a variety of processes such as: (A) cleavage of the metal–ligand bond; (B) elimination of a part of the central ligand in form of HCN or RCN; (C) elimination of a neutral aromatic fragment; (D) elimination of a ligand fragment corresponding formally to its cleavage "in half" (for azine complexes). The latter pathway could be due both to simple cleavage and a rearrangement process.

The carbonyl-free $[M-6\ \mathrm{CO}]^{+\cdot}$ ions for the binuclear complexes I and II undergo stepwise elimination of two iron atoms giving rise to $[M-6\ \mathrm{CO}-\mathrm{Fe}]^+$ and $[M-6\ \mathrm{CO}-2\mathrm{Fe}]^+$ ions. The spectra of both compounds I and II show a doublet of peaks for the ions $[M-6\ \mathrm{CO}-2\mathrm{Fe}]^+$ and $[M-6\ \mathrm{CO}-2\mathrm{Fe\text{-}H}]^+$, which are possibly identical to the ions $M^{+\cdot}$ and $[M-\mathrm{H}]^{+\cdot}$ arising from the corresponding azomethynes. This is corroborated by the fact that the mass spectra of complexes I

TABLE 1

COMMON IONS IN THE 70 eV MASS SPECTRA OF COMPLEXES I–VII (*m/z*, AND RELATIVE ABUNDANCE)

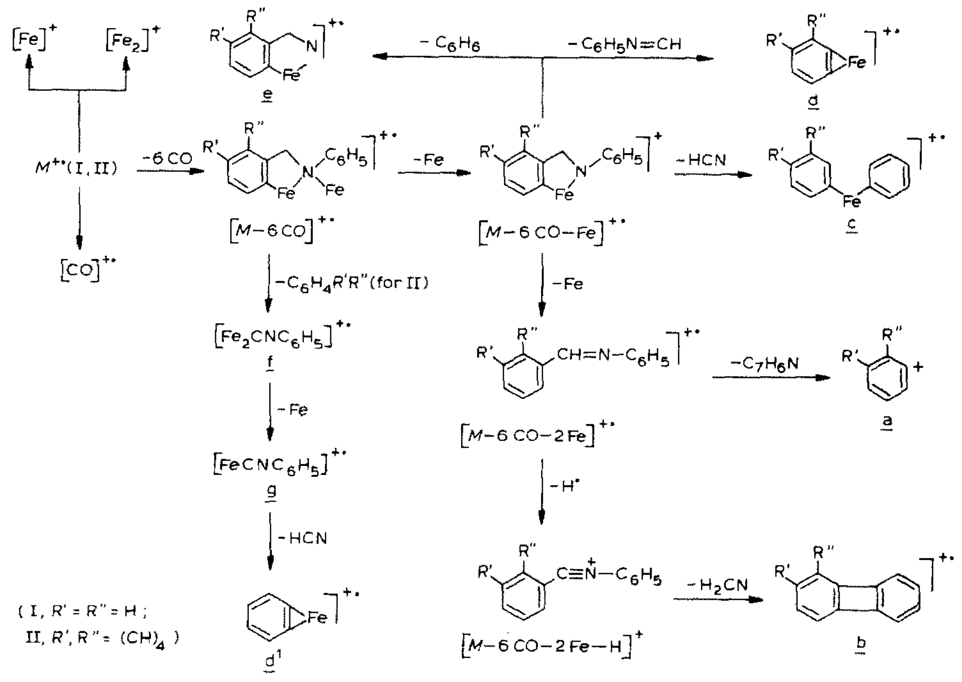
Ions	I	II	III	IV	V	VI	VII
$M^{+\cdot}$	461(7)	511(9)	488(4)	516(2)	672/674/676 (2/4/3)	640(0.2)	488(8)
$[M-CO]^{+\cdot}$	433(2)	483(8)	460(12)	488(12)	644/646/648 (6/10/6)	612(2)	460(10)
$[M-2CO]^{+\cdot}$	405(27)	455(40)	432(24)	460(20)	616/618/620 (12/27/14)	584(7)	432(21)
$[M-3CO]^{+\cdot}$	377(20)	427(11)	404(19)	432(16)	588/590/592 (11/19/10)	556(4)	404(49)
$[M-4CO]^{+\cdot}$	349(25)	399(32)	376(6)	404(10)	560/562/564 (16/26/14)	528(7)	376(23)
$[M-5CO]^{+\cdot}$	311(50)	371(67)	348(26)	376(25)	532/534/536 (22/31/21)	500(14)	348(66)
$[M-6CO]^{+\cdot}$	293(100)	343(100)	320(100)	348(100)	504/506/508 (60/100/40)	472(100)	320(100)
Fe_2^+	112(14)	112(7)	112(5)	112(9)	112(14)	112(7)	112(22)
Fe^+	56(16)	56(25)	56(22)	56(26)	56(95)	56(10)	56(20)

and II contain also considerable peaks of ions a and b characteristic of azomethynes [4,5].

Further fragmentation of the $[M-6CO-Fe]^+$ ions may also involve an elimination of HCN (path B), $C_6H_5N{=}CH$ and C_6H_6 (path C) giving rise to the ions c, d and e, respectively. It has been shown earlier with deuteriated analogue of I [6,7] that the elimination of a benzene molecule could from both aromatic rings. No such process is observed for the naphthyl derivative II. However, the naphthalene molecule may be eliminated from the carbonyl-free $[M-6CO]^{+\cdot}$ ions of this compound giving rise to the ion f. Elimination of Fe and HCN from the latter ion result in the formation of ions g and d′. The fragmentation pathway of complexes I and II are shown in Scheme 1 and principal ions observed in the mass spectra of these complexes are listed in Table 2.

The most important fragmentation of complexes III–VII also begins after six carbon monoxides are eliminated from their molecular ions. Unlike complexes I and II, no $M^{+\cdot}$ ions of the corresponding azines were produced in the course of fragmentation of complexes III–VII [8,10]. The fragmentation patterns of the two isomeric derivatives III and VII are essentially identical and do not permit mass spectrometric differentiation to be made.

The spectrum reported here for VII is in excellent agreement with the spectrum reported earlier [11]. The fragmentation patterns for complexes III–VII are given in Scheme 2. Table 3 compares the principal fragment ions in the mass spectra of these compounds. The common fragmentation of completely decarbonylated $[M-6CO]^{+\cdot}$ ions involves the successive elimination of two molecules of RCN/HCN for III and VII, CH_3CN for IV and V and C_6H_5CN for VI, generating the ions h and i. To a lesser extent, the same sequence of reactions is realized in ion k generated from $[M-6CO]^{+\cdot}$ ions by elimination of Fe. The sequence leads to the ions l and m, the latter being also formed after elimination of Fe from ion i.



SCHEME 1

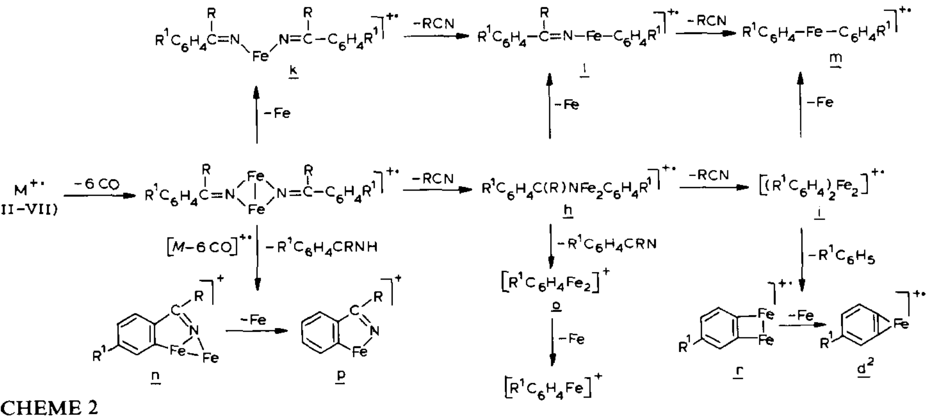
Eliminations of $R'C_6H_4CRNH$ molecules from the ions $[M-6CO]^{+\cdot}$ and $R'C_6H_4CRN$ radicals from the ions h, leading to the ions n and o, respectively, are also characteristic of the complexes under study. Both resulting ions appear to be capable of losing a Fe atom, forming the ions p and $d^2 + H$, respectively. The origin of the ions p may be formally attributable to a cleavage "in half" of the carbonyl-free $[M-6CO]^{+\cdot}$ ions (path D).

One of the decomposition pathways of complexes prepared from azines is due to elimination of benzene (for IV and VI) or bromobenzene (for V). Unlike complexes I and II, however, this process (path C) is realised in the ions i generated as a result of

TABLE 2

CHARACTERISTIC IONS IN THE 70 eV MASS SPECTRA OF COMPLEXES I AND II (m/z AND RELATIVE ABUDANCE)

Ions	I	II	Ions	I	II
$[M-6CO-Fe]^+$	237(45)	287(35)	g	–	159(4)
$[M-6CO-2Fe]^+$	181(25)	231(20)	$[C_6H_4CH_2Fe]^+$	146(25)	–
$[M-6CO-2Fe\text{-}H]^+$	180(30)	230(32)	$[C_{10}H_7CH_2]^+$	–	141(8)
a	77(24)	127(5)	$[C_6H_5CH_2]^+$	91(12)	–
b	152(9)	202(10)	$[C_6H_5CNH]^+$	104(5)	–
c	210(8)	260(6)	$[C_6H_6]^{+\cdot}$	78(6)	–
d	132(14)	132(11)	$[C_6H_5]^+$	77(24)	77(7)
d^1	132(14)	132(3)	$[C_6H_4]^{+\cdot}$	76(2)	–
e	159(11)	–			
f	–	215(9)			



SCHEME 2

successive elimination of two molecules of RCN from decarbonylated ions $[M-6CO]^{+\cdot}$. The resulting ions r then undergo elimination of Fe to yield the ions d^2.

A characteristic fragmentation pathway is observed for complex V obtained from *p*-bromoacetophenone azine. The ion i derived from this compound loses readily a Br radical followed by FeBr to yield $[C_6H_4FeC_6H_4]^+$ (*m/z* 208). The latter in turn decomposes readily giving very intense $[C_6H_4C_6H_4]^{+\cdot}$ and $[C_6H_4Fe]^{+\cdot}$ ions. It could

TABLE 3

CHARACTERISTIC IONS IN THE 70 eV MASS SPECTRA OF COMPLEXES III–VII (*m/z*, relative abundance)

Ions	III	IV	V	VI	VII
d^2	132(12)	132(20)	210/212(33/33)	132(32)	132(21)
d^2+H	133(6)	133(30)	–	133(35)	133(19)
h	293(10)	307(40)	463/465/467 (50/92/55)	369(28)	293(4)
i	–	266(74)	422/424/426 (28/56/27)	266(52)	–
k	264(24)	–	–	–	264(17)
l	237(6)	–	–	313(3)	237(21)
m	–	210(20)	–	210(17)	–
n	215(36)	–	–	–	215(40)
o	–	189(9)	267/269(17/15)	189(8)	–
p	159(27)	–	–	–	159(24)
r	–	188(18)	266/268(5/5)	188(14)	–
h – Br	–	–	384/386(22/22)	–	–
i – Br	–	–	343/345(12/11)	–	–
$[C_6H_4FeC_6H_4]^{+\cdot}$	–	–	208(79)	–	–
$[R^1C_6H_4CRN]^+$	–	–	–	180(25)	–
$[C_6H_5CNH]^+$	104(67)	104(26)	104(17)	104(46)	104(10)
$[C_6H_5CN]^{+\cdot}$	103(32)	103(5)	103(17)	103(4)	103(50)
$[C_6H_4C_6H_4]^{+\cdot}$	152(3)	–	152(78)	152(13)	152(4)
$[C_6H_6]^{+\cdot}$	78(11)	78(3)	–	78(10)	78(5)
$[C_6H_5]^+$	77(18)	77(19)	77(10)	77(41)	77(12)
$[C_6H_4]^{+\cdot}$	76(21)	76(4)	76(32)	76(7)	76(20)

be pointed out that in case of the binuclear complex prepared from the azomethyne of the *o*-chlorobenzaldehyde derivative, an elimination of FeCl from the $[M-6CO]^{+\cdot}$ ions was observed [7]. The mass spectra of complexes III-VII show the peaks of aromatic fragments listed in Table 3.

Experimental

Compounds I and II were synthesized according to the methods reported in the literature [12]. Complexes III–VII have been described previously [13,14].

μ-(o-I-$C_{10}H_6CH_2NC_6H_5$)$Fe_2(CO)_6$ (II). Yield 60%, red-orange needles, m.p. 123.5–4.5°C (benzene-heptane). IR (hexane): ν(CO) 2072, 2036, 2000, 1994, 1983, 1965, 1953, 1947 cm^{-1}. ^1H NMR (δ, ppm, TMS, CCl_4): 4.61 (d, 2H, CH_2), 6.99–7.87 (m, 11H, *o*-I-$C_{10}H_6$, C_6H_5). Found: C, 54.23; H, 2.82; Fe, 22.12; N, 2.82. $C_{23}H_{13}Fe_2NO_6$ calcd.: C, 54.05; H, 2.57; Fe 21.86; N, 2.74%.

The mass spectra of compounds I–VII were recorded on an LKB-2091 instrument operating at 70 and 12 eV electron energy and 50 mA trap current. The samples were introduced using a direct insertion system, with sample evaporation temperature between 50 to 70°C and ion chamber temperature of 200°C.

References

1 N.S. Nametkin, V.D. Tyurin, V.V. Trusov and A.M. Krapivin, J. Organomet. Chem., 254 (1983) 243.
2 A.N. Nesmeyanov, M.I. Rybinskaya and L.V. Rybin, Uspekhi Khim., 48 (1979) 393.
3 V.V. Trusov, N.A. Nechitaylo, V.D. Tyurin, M.A. Dzyubina and N.S. Nametkin, Izv. Akad. Nauk SSSR, Ser. Khim., (1982) 692.
4 Yu.S. Nekrasov, V.A. Puchkov and N.S. Vulfson, Izv. Akad. Nauk SSSR, Ser. Khim., (1968) 1527.
5 J.H. Bowie, R.G. Cooks, J.W. Fisher and T.McL. Spotswood, Austr. J. Chem., 21 (1968) 2021.
6 M.M. Bagga, W.T. Flannigan, G.R. Knox, P.L. Pauson, F.J. Preston and R.I. Reed, J. Chem. Soc. C, (1968) 36.
7 F.J. Preston, W.T. Flannigan, G.R. Knox, P.L. Pauson and R.I. Reed, Int. J. Mass. Spectr. Ion Phys., 3 (1969) 63.
8 S.E. Scheppele, R.D. Grigsby, K.F. Kinneberg, E.D. Mitchell and C.A. Mannan, Org. Mass Spectrom., 3 (1970) 557.
9 S.E. Scheppele, R.D. Grigsby, E.D. Mitchell, D.W. Miller and G.R. Waller, J. Amer. Chem. Soc., 90 (1968) 3521.
10 N.P. Buu-Hoi and G. Saint-Ruf, Bull. Soc. Chim. France, (1970) 343.
11 S. Otsuka, T. Yoshida and A. Nakamura, Inorg. Chem., 6 (1967) 20.
12 N.S. Nametkin, V.D. Tyurin, A.I. Nekhaev, Yu.P. Sobolev, M.G. Kondrat'eva, A.S. Batsanov and Yu.T. Struchkov, J. Organomet. Chem., 243 (1983) 323.
13 N.S. Nametkin, V.D. Tyurin, V.V. Trusov, L.A. Nekhaeva and A.A. Popal, Izv. Akad. Nauk SSSR, Ser. Khim., (1982) 418.
14 N.S. Nametkin, V.D. Tyurin, V.V. Trusov, A.S. Batsanov and Yu.T. Struchkov, J. Organomet. Chem., 219 (1981) C 26.