Mass Spectrometry of Transition-metal π-Complexes. Part I. Studies on Derivatives of Cyclo-octatetraenetricarbonyliron

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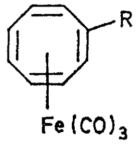
The mass spectra of the cyclo-octatetraenetricarbonyliron derivatives $(C_8H_7R)Fe(CO)_3$ [R = CHO, CH_2OH, CH(Me)OH, and CH_2OMe] have been examined and compared with those of the free organic ligands. Fragmentation routes have been elucidated by means of high-resolution measurements and deuterium labelling of two of the complexes. The results are discussed in terms of metal-atom control on the fragmentation of the organic ligands.

MASS spectrometry is a widely established technique in structural studies on metal carbonyl and organometallic compounds. The major application has been in the determination of molecular weights, but more recently the availability of many fragmentation data for these types of compound has led to the building up of a more detailed picture of fragmentation routes and mechanisms.[1] Nevertheless there is still a large amount of work to be done before organometallic mass spectrometry is in the state of development that allows qualitative predictions of fragmentation behaviour in a manner similar to that now widely applied to organic compounds.

The role of the metal atom in influencing ligand fragmentation is now widely recognised and there is increasing evidence[1e,2] that the radical character of molecular ions and, by analogy, possibly that of metal-containing fragment ions, formed from transition-metal organometallic compounds is located in a molecular orbital that is of essentially metal character. On this basis, differences in the fragmentation behaviour of free and complexed organic compounds might be expected, as the organic moiety in the transition-metal organometallic molecular ion and some fragment ions would be essentially an even-electron species, as opposed to the radical character possessed by the molecular ion and some fragment ions formed from the free organic molecule. The stability of ionic and neutral fragments in mass spectral decompositions has been discussed by McLafferty[3] and he points out that the most useful initial indication of fragment-ion stability is classification as either an even-electron or odd-electron species, the former being the most stable in most cases. This classification applies to both ions and neutral fragments. Therefore, on this basis, one might expect the most favoured fragmentation of an organic ligand bonded to a transition metal to be loss of an even-electron neutral species (a neutral molecule) with concomitant formation of a metal-containing ion which can be classified as ' even-electron ' with regard to the metal-bonded organic fragment. Although, in the absence of extensive energetic data for all the systems under consideration, this approach may be considered as simply an ' electron bookkeeping ' exercise, it does provide a ready rationale for many of the fragmentations of metal-bonded organic moieties.

Further examples of the effect of the presence of a metal atom upon the fragmentation of organic ligands are presented in this study of some substituted cyclo-octatetraenetricarbonyliron compounds. The compounds studied are (I)—(IV).



R = CHO (I)
R = CHMe·OH (II)
R = CH_2OH (IIIa) R = CHDOH (IIIb)
R = CH_2OMe (IVa) R = CHDOMe (IVb)

EXPERIMENTAL

All reactions were carried out under dry nitrogen and all solvents were purified and dried before use. The unlabelled tricarbonyliron–cyclo-octatetraene derivatives were prepared by methods previously described.[4] However, in the case of compound (I) we have found the yield to be significantly improved by a slight modification of the preparation. Thus, consistently high yields (*ca.* 80%) were obtained when hydrolysis of the Vilsmeyer salt was allowed to proceed to completion during 15—20 h.

Tricarbonyl(hydroxymonodeuteriomethylcyclo-octatetraene)-iron (IIIb).—A solution of the aldehyde (I) (0·342 g) in absolute ethanol was cooled to 0 °C and powdered sodium $[^2H_4]$borohydride (1·0 g) slowly added during 15 min. The mixture was stirred for 5 min at 0 °C. The resulting suspension was hydrolysed with ice-water (100 ml) and extracted with ether until the aqueous layer became colourless. The ether extract was dried ($MgSO_4$) and the solvent removed under vacuum to give a red oil, which was chromatographed on silica gel. Elution with toluene gave a small amount of unchanged aldehyde and further elution with ethyl acetate, followed by removal of the solvent from the eluted solution, gave the alcohol (IIIb) as a red oil. The product was further purified by distillation on to a cold-finger (100 °C, 0·05 mmHg) (yield: 0·307 g, 89%).

Tricarbonyl(methoxymonodeuteriomethylcyclo-octatetraene)-iron (IVb).—The alcohol (IIIb) (0·22 g) was dissolved in anhydrous ether (25 ml) and aqueous 65% hexafluorophosphoric acid was added dropwise with stirring until precipitation was complete. The resulting hexafluorophosphate salt was filtered off, washed with anhydrous ether (3 × 10 ml),

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[1] (*a*) M. I. Bruce, *Adv. Organometallic Chem.*, 1968, **6**, 273; (*b*) D. B. Chambers, F. Glockling, and J. R. C. Light, *Quart. Rev.*, 1968, **22**, 317; (*c*) M. Cais and M. S. Lupin, *Adv. Organometallic Chem.*, 1970, **8**, 211; (*d*) R. B. King, *Fortschr. Chem. Forsch.*, 1970, **14**, 92; (*e*) J. Müller, *Angew. Chem. Internat. Edn.*, 1972, **11**, 653 and references therein.

[2] A. Hammett and A. F. Orchard, in ' Electronic Structure and Magnetism of Inorganic Compounds,' vol. 1, Chemical Society Specialist Report, Senior reporter, P. Day, 1972, p. 1.

[3] F. W. McLafferty, in ' Mass Spectrometry of Organic Ions,' Academic Press, New York, 1963, p. 309.

[4] B. F. G. Johnson, J. Lewis, and G. L. P. Randall, *J. Chem. Soc. (A)*, 1971, 422.

and dried *in vacuo*. The salt was then suspended in absolute methanol (25 ml) and the suspension stirred until a clear red solution was formed. Water (100 ml) was added to the resulting solution and the mixture extracted with ether (3 × 25 ml). The combined extracts were dried ($MgSO_4$), the ether removed under vacuum, and the resulting red oil chromatographed on silica gel. Elution with 10% ethyl acetate in toluene followed by removal of the solvent gave the ether (IVb) as a red oil. Further purification was achieved by distillation of the product on to a cold-finger (100 °C, 0·05 mmHg) (yield: 0·126 g, 60%).

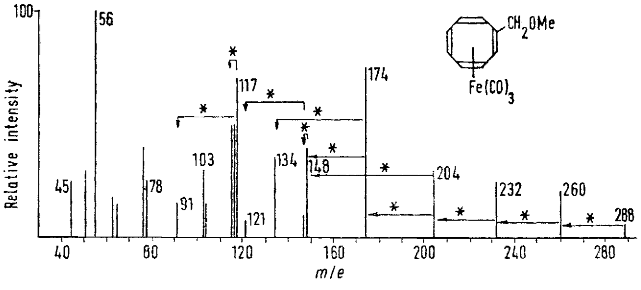


FIGURE 1

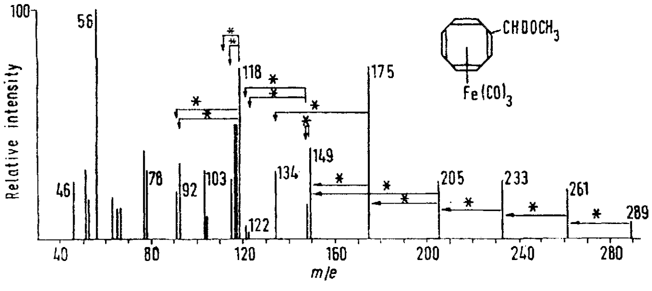


FIGURE 2

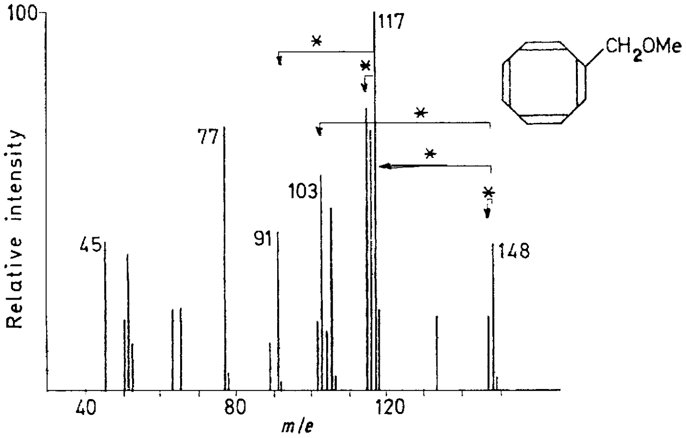


FIGURE 3

N.m.r. Data.—The n.m.r. spectra of all compounds were run as CS_2 solutions on a Perkin-Elmer R10 spectrometer operating at 60 MHz. The spectra of the unlabelled compounds were completely in accord with those reported elsewhere.[4] The deuterium-labelled compounds gave the following spectra: compound (IIIb): τ 4·8 (7H, multiplet; ring protons), τ 6·15 (1H, doublet, *J* 6 Hz; exocyclic CH), τ 6·60 (1H, doublet, *J* 6 Hz; OH); compound (IVb): τ 5·0 (7H, multiplet; ring protons), τ 6·3 (1H, singlet, exocyclic CH), τ 6·8 (3H, singlet; Me).

Mass Spectra.—The spectra were recorded on an A.E.I. MS9 spectrometer, the samples being introduced *via* the direct insertion probe. Electron beam energy was maintained at 70 eV and 100 μA trap current. Fragmentation patterns were obtained at 1000 resolution and mass measurements performed at 10,000 resolution by the peak-matching technique. The spectra are shown in barographic form in

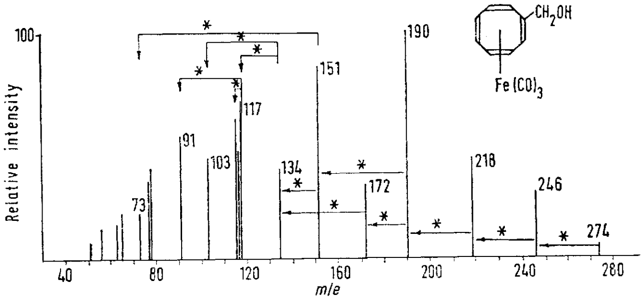


FIGURE 4

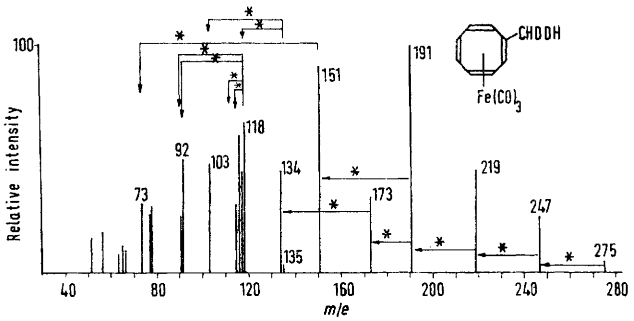


FIGURE 5

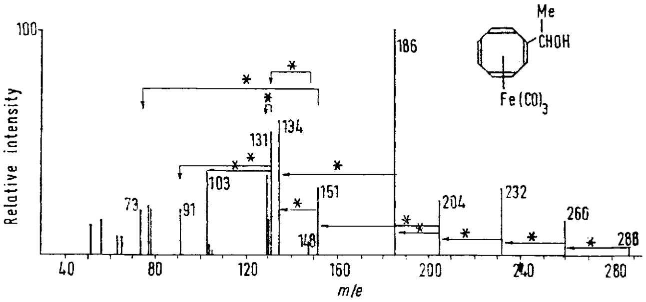


FIGURE 6

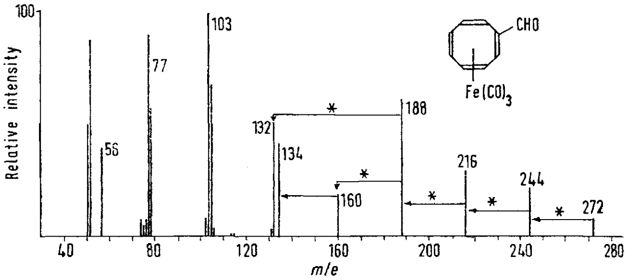


FIGURE 7

Figures 1—8. All spectra have been submitted to the Mass Spectrometry Data Centre, Aldermaston.

Analytical data for the compounds are in Table 1.

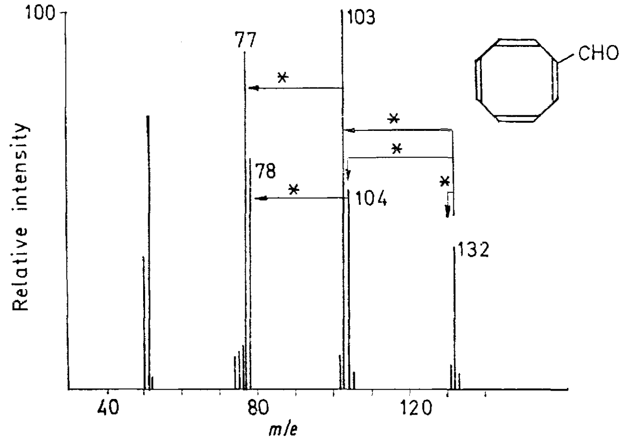


FIGURE 8

TABLE 1

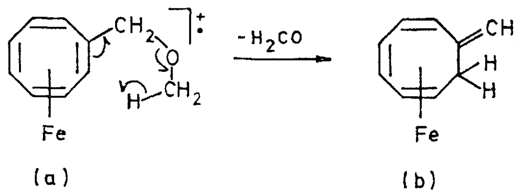
Analytical data

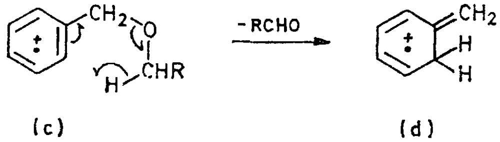
	Found			Calculated		
Compound	C (%)	H (%)	M^+	C (%)	H (%)	M *
(I)	53·1	2·75	277·998	53·0	2·90	271·9971
(II)	54·5	4·00	288·008	54·25	4·15	288·0084
(IIIa)	52·6	3·50	273·993	52·5	3·65	273·9928
(IIIb)	52·5	3·60	274·999	52·35	3·25	274·9991
(IVa)	54·0	4·15	288·009	54·25	4·15	288·0084
(IVb)	54·4	4·10	298·015	53·4	3·80	298·0147

* Calc. for ^{56}Fe.

RESULTS AND DISCUSSION

The mass spectra of all the compounds examined shows the presence of the ions $[(C_8H_7R)Fe(CO)_n]^{+\cdot}$ (n = 1—3), although in most cases these are of low relative abundance. In none of the complexes does fragmentation of the organic ligand provide an alternative mode of decomposition of the molecular ion to metal decarbonylation. The relative abundance of the carbonyl-free ions, $[(C_8H_7R)Fe]^{+\cdot}$ is found to vary with the nature of the side chain, but in all cases these are among the most intense peaks in the respective spectra. Fragmentation of the carbonyl-free ions proceeds either by metal–ligand bond cleavage, usually with charge retention on the ligand fragment, or by ligand fragmentation producing metal-containing fragment ions. Subsequent fragmentation of the species $[C_8H_7R]^{+\cdot}$ produced in the above manner directly parallels that of these ions produced directly from the free organic compound (R = CHO or CH_2OMe). Thus the ion $[C_8H_7{\cdot}CH_2{\cdot}OMe]^{+\cdot}$ (m/e 148), produced from either (IVa) or the free ligand, shows the usual α-cleavage decompositions of ethers forming the ions $[C_8H_7CH_2O^+{=}CH_2]$ (m/e 147)† and $[CH_2{=}^+OCH_3]$ (m/e 45) as well as loss of MeO$^\cdot$ yielding $[C_9H_9]^+$ (m/e 117) as its principal modes of decomposition. (Further discussion of the structure of the $[C_9H_9]^+$ ion is presented later.) In contrast, the ion $[(C_8H_7CH_2OMe)Fe]^{+\cdot}$ shows exclusive ligand fragmentation by loss of the elements of formaldehyde producing $[(C_9H_{10})Fe]^{+\cdot}$ (m/e 174). This decomposition can perhaps best be rationalised in terms of charge localisation on the metal atom in the parent ion, loss of a neutral molecule thus producing a daughter ion in which the organic moiety can be classified as an even-electron species. Such a fragmentation then fulfils the requirements suggested by McLafferty[3] for decomposition *via* a rearrangement process rather than a simple bond cleavage. Such a loss of formaldehyde can be formally represented as proceeding *via* a six-membered transition state [(a) ⟶ (b)] and is analogous to the McLafferty rearrangement reported for alkyl benzyl ethers[5,6] although in this case the process is not very significant when R = H [(c) ⟶ (d)]. However, at least two other mechanisms with their concomitant different ion structures for the daughter ion (m/e 174) can be postulated for this decomposition. These are: (i) elimination of H_2CO *via* a four-membered transition state, producing an ion that can be represented as $[(C_8H_7CH_3)Fe]^{+\cdot}$ and (ii) elimination involving direct hydrogen transfer to the metal atom giving the ion $[(C_9H_9)FeH]^{+\cdot}$. The direct involvement of the metal atom of the type (ii) has been postulated to explain similar losses from a range of substituted ferrocenes[1c] and such a mechanism is supported by the observation of the ions $[FeR]^+$ (R = OH, OMe, or NHMe) in the spectra of these compounds. Thus if mechanism (ii) were operating in the case of (IVa), then the appearance of one or both of the ions $[FeH]^+$ and $[C_9H_9]^+$ might be predicted. In practice, however, the former is not observed and the only precursor of the latter identified from metastable evidence is $[C_8H_7{\cdot}CH_2OMe]^{+\cdot}$. Although negative evidence of this type does not exclude mechanism (ii), we have no indication that such a mechanism





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† The ion of m/e 147 is written as $[C_8H_7CH_2O^+{=}CH_2]$ as the spectrum of compound (IVb) shows exclusive loss of protium from the ion of m/e 149.

[5] K. Biemann, ' Mass Spectrometry,' McGraw-Hill, New York, 1962, p. 124.

[6] J. K. MacLeod and C. Djerassi, *Tetrahedron Letters*, 1966, 2183.

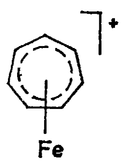
is being adopted. The ion $[(C_9H_{10})Fe]^{+\cdot}$ fragments by loss of acetylene to $[(C_7H_8)Fe]^{+\cdot}$ (*m/e* 148) *, which undergoes further decomposition to $[(C_7H_7)Fe]^+$ (*m/e* 147) * and the fragmentation of (IVb) follows a strictly analogous route, the deuterium atom being retained in the formation of $[(C_7H_6D)Fe]^+$ (*m/e* 148) * as the exclusive product of this route. $[(C_9H_9D)Fe]^{+\cdot}$ (*m/e* 175) also shows exclusive loss of C_3H_3D forming $[(C_6H_6)Fe]^{+\cdot}$. Although detailed discussion of the structures of $[(C_9H_{10})Fe]^{+\cdot}$ and the product ions of these two fragmentation pathways is not possible on this basis, the specific losses shown by (IVb) indicate that the α-methylene group in $[(C_8H_7\cdot CH_2\cdot OMe)Fe]^{+\cdot}$ maintains its identity with respect to hydrogen scrambling both on the loss of H_2CO and subsequent fragmentations and that it may possibly retain its exocyclic positional identity in the daughter ions produced by sequential loss of H_2CO and C_2H_2. However, there is no definite evidence to differentiate between a six- and a four-membered transition state for loss of formaldehyde.

TABLE 2

Mass-spectrometric measurements on some ions formed from compounds (IVa) and (IVb)

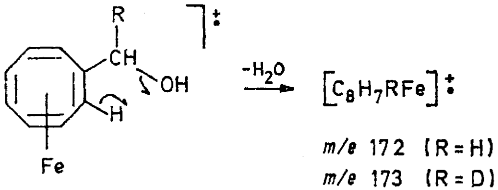
Structure	*m/e*	Formula	*M*, Found	*M*, Calc.
(IVa)	148	C_7H_8Fe	147·998	147·9975
		$C_{10}H_{12}O$	148·089	148·0888
	147	C_7H_7Fe	146·990	146·9897
		$C_{10}H_{12}O$	147·081	147·0810
(IVb)	149	C_7H_7DFe	149·003	149·0038
		$C_{10}H_{11}DO$	149·095	149·0951
	148	C_7H_6DFe	147·996	147·9960
		$C_{10}H_{10}DO$	148·088	148·0873

The ion $[C_7H_7Fe]^+$ (*m/e* 147) formed in the spectrum of (IVa) further fragments by loss of C_2H_2 to $[C_5H_5Fe]^+$ (*m/e* 121). The analogous fragmentation of $[C_7H_6DFe]^+$ formed from (IVb) produces $[C_5H_5Fe]^+$ and $[C_5H_4DFe]^+$. The relative intensities of these two ions (*m/e* 122 : *m/e* 121 = 5 : 2) are in accord with those predicted on the basis of complete hydrogen scrambling in the parent ion of this decomposition. The metastable daughter ions of this decomposition show similar relative intensities, although it was not possible to make accurate intensity measurements on these ions. On the basis of this evidence we infer that the organic moiety of the ion $[C_7H_7Fe]^+$ has a tropylium type structure (e). Similar results have been obtained from a study of the $[C_7H_7Fe]^+$ ion produced from 1,1′-divinylferrocene,[7] although in this case this is not the only structure contributing to high-energy $[C_7H_7Fe]^+$ ions (produced by 75 eV bombardment and undergoing normal fragmentation), it does appear to be the structure of low internal energy ions (produced at 18 eV and giving rise to metastable daughter ions), as would be expected.[8]

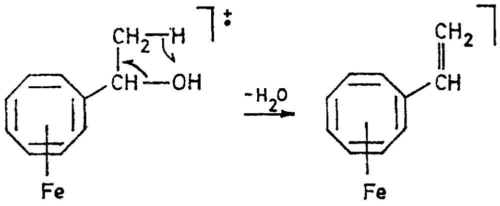


(e)

The decarbonylated ions $[(C_8H_7\cdot CH_2OH)Fe]^{+\cdot}$ (*m/e* 190) and $[(C_8H_7\cdot CHMeOH)Fe]^{+\cdot}$ (*m/e* 204) formed from (IIIa) and (II) respectively show loss of the elements of water as one of their principal modes of fragmentation. Direct comparison with the fragmentation of $[C_8H_7\cdot CHROH]^{+\cdot}$ (R = H or Me) (*m/e* 134 and 148 respectively) ion produced from the free ligands was not possible in this case, as no preparative condition has been found under which the ligands can be liberated from the metal complexes. However, these ions occur in the spectra of (II) and (IIIa) † and both show subsequent fragmentation quite different from that of the corresponding metal-containing species. Thus the metal-free ions show fragmentation by α-cleavage producing the ions $C_8H_7^+$ and $CHR{=}^+OH$ (R = H or Me) as well as hydroxyl radical loss to form $C_9H_9^+$. It therefore appears that in the case of (II) and (IIIa) ligand fragmentation is again modified in metal-containing ions such that loss of even-electron neutral species becomes a favourable process. The exclusive loss of H_2O from $[(C_8H_7\cdot CHDOH)Fe]^{+\cdot}$ (*m/e* 191) formed from (IIIb) indicates that a ring hydrogen (f) must be involved in dehydration of the primary alcohol, but the involvement of methyl hydrogens (g) ⟶ (h) cannot be excluded in the fragmentation of the secondary alcohol.



(f)



(g) (h)

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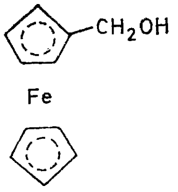
* The ions of *m/e* 148 and 147 in the spectrum of (IVa) and *m/e* 149 and 148 in the spectrum of (IVb) all occurred as doublets under high resolution. Mass measurements on both components of each doublet yielded the results shown in Table 2.

† The ion *m/e* 134 in the spectrum of (IIIa) is observed as a doublet under high resolution. Mass measurement of the principal component of the doublet showed it to be $[C_6H_6Fe]^{+\cdot}$ (Found: *M*, 133·982. Calc. for C_6H_6Fe: *M*, 133·9819). The low intensity of the second component precluded an accurate determination of its mass, but approximate measurements gave it as 134·1 (Calc., 134·0674).

[7] D. T. Roberts, W. F. Little, and M. M. Bursey, *J. Amer. Chem. Soc.*, 1968, **90**, 973.

[8] I. Howe, D. H. Williams, and R. G. Cooks, *Organic Mass Spectrometry*, 1969, **2**, 137.

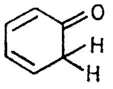
A similar mechanism, involving ring hydrogen atoms has been found to operate in the fragmentation of (i) by loss of H_2O.[9]



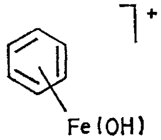
(i)

The daughter ions formed by loss of H_2O all show the unusual loss of C_3HR (R = H, D, or CH_3) giving rise to the ion $[C_6H_6Fe]^{+\cdot}$ (*m*/*e* 134). Conjecture on the structure of the parent ions of this decomposition or the mechanisms of the reactions is unwarranted, but we believe the driving force for this process to be the formation of the 6π-Fe^I ion $[C_6H_6Fe]^{+\cdot}$. Similar arguments have been advanced for the ready formation of ions of the type $[C_6H_6Fe(CO)_n]^{+\cdot}$ in the fragmentation of cyclohexadienetricarbonyliron.[10]

The ions $[(C_8H_7{\cdot}CHR{\cdot}OH)Fe]^{+\cdot}$ also show a common decomposition process by loss of $C_3H_2R\cdot$ (R = H, D, or CH_3) yielding the fragment ion $[C_6H_7OFe]^+$ (*m*/*e* 151)



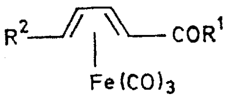
(j)



(k)

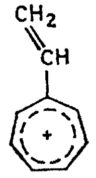
and the structural analogy can be drawn between this ion and that widely ascribed to the decomposing molecular ion of phenol[11] (j). However, the fragmentation of the metal-containing species by loss of OH· rather than CO suggests that this ion has a structure different from (j). This ion also fragments by loss of C_6H_6 forming $Fe(OH)^+$ (*m*/*e* 73) and this leads us to suggest it probably has the structure (k) similar to the ion $[(C_5H_5)Fe(OH)]^+$ formed from some primary alkanols of ferrocene.[9] Again the driving force for loss of C_3H_2R from the decarbonylated ions of (II), (IIIa), and (IIIb) is probably the formation of a 6π organic moiety within the metal-containing fragment ion.

Compound (I) shows the stepwise decarbonylations yielding the ion $[(C_8H_7{\cdot}CHO)Fe]^{+\cdot}$ (*m*/*e* 188). Surprisingly, further decarbonylation of this ion is observed yielding $[C_8H_8Fe]^{+\cdot}$ (Found: *M*, 159·997. Calc. for C_8H_8Fe: *M*, 159·9975). The related ketone $(C_8H_7{\cdot}COMe)Fe(CO)_3$ also shows four stepwise losses of carbon monoxide from the molecular ion yielding the ion $[C_9H_{10}Fe]^{+\cdot}$.[12] Further fragmentation of this ion to $FeMe^+$ (metastable ion observed) suggests that direct metal interaction is again taking place and that ligand decarbonylation of the ketone complex is analogous to that reported for some monosubstituted ferrocenes of the type $(C_5H_5)Fe(C_5H_4COR)$ (R = Me, OH, OMe, or NHMe)[13] and substituted butadiene–tricarbonyliron complexes (l).[14] However, in the case of the formyl compound (I) there is no evidence for formation of the ion FeH^+ and the observation that the free ligand also shows fragmentation by loss of CO from the molecular ion {such a decomposition is not observed from the ion $[C_8H_7COCH_3]^{+\cdot}$ formed from $(C_8H_7{\cdot}COMe)Fe(CO)_3$} suggests that a different mechanism may operate in this case.



(l) R^1 = OH, NH_2
R^2 = Me

The ion $C_9H_9^+$ is observed in the mass spectra of both (IVa) and free organic compound $C_8H_7{\cdot}CH_2{\cdot}OCH_3$ and is produced by loss of MeO· from the ion $[C_8H_7{\cdot}CH_2{\cdot}OMe]^{+\cdot}$. An analogous loss of OH· from the ion $[C_8H_7{\cdot}CH_2OH]^{+\cdot}$ in the spectrum of (IIIa) also gives rise to this ion. Bowie *et al.*[15] have made a detailed study of the fragmentation of the $C_9H_9^+$ ion and on the basis of the decomposition of ^{13}C- and ^2H-labelled ions have suggested that loss of C_2H_2 and H_2 probably occurs from this ion of structure (m) and that scrambling of both



(m)

carbon and hydrogen atoms occurs *via* a ring expansion–contraction cycle before loss of these molecules in metastable transitions. The decomposition of $C_9H_8D^+$ formed from either (IIIb) or (IVb) involves the loss of H_2 and HD and C_2H_2 and C_2HD. The results of these

TABLE 3

Fragmentation of the ions $C_9H_8D^+$

Compound	Loss	Daughter ions [a]	Intensity [b]
(IIIb)	$H_2 : HD$	$C_9H_6D^+ : C_9H_7^+$	78 : 22
(IIIb)	$C_2H_2 : C_2HD$	$C_7H_6D^+ : C_7H_7^+$	*c*
(IVb)	$H_2 : HD$	$C_9H_6D^+ : C_9H_7^+$	78 : 22
(IVb)	$C_2H_2 : C_2HD$	$C_7H_6D^+ : C_7H_7^+$	*c*

[a] Total intensity of daughter ions normalised to 100. Complete hydrogen randomisation requires 78 : 22. [b] Metastable daughter ions. [c] Metastable ions too weak for accurate intensity measurements.

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fragmentations in metastable decomposition processes are given in Table **3**. These data show that hydrogen scrambling is complete for the metastable process (1) but

$$C_9H_9^+ \longrightarrow C_9H_7^+ + H_2 \qquad (1)$$

the metastable ions corresponding to the transition (2)

$$C_9H_9^+ \longrightarrow C_7H_7^+ + C_2H_2 \qquad (2)$$

were too weak for accurate integrated intensity measurements to be made.

These studies are therefore in accord with the results of Bowie *et al.* and further extend the range of precursors giving rise to $C_9H_9^+$ ions which undergo metastable decompositions of this type.

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