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Pyrolysis - Mass Spectral Studies on Ferrocenyl Compounds : Evidence for the Norbiphenylene Cation

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Abstract: Mass spectra of 1,1'(2,4-dichlorobenzoyl) ferrocene (1,1'DCBF) and 1,4,5,6,7,7 hexachloro-5 norbornene-2,3-dicarboxylic anhydride ferrocene (HNDAF) have been obtained using temperature - programmed pyrolysis mass spectrometry. HNDAF fragmentation is characterised by the elimination of a hexachlorocyclopentadiene fragment. 1,1'DCBF yields an intense peak at m/z 139. attributed to $C_{11}H_7^+$, which is also formed in the fragmentation of the mono substituted 3,4-dichlorobenzoyl ferrocene, and is assigned to the norbiphenylene (cyclopenta [3,4] cyclobuta [1,2] benzenylium)cation. This appears to be the first reported experimental observation of this ion.

Ferrocene and its derivatives have been demonstrated to have potential as smoke suppressants and flame retardants for polymers, particularly for PVC formulations[1,2]. Some of the compounds synthesised during these investigations have proved useful model compounds for the study of target factor analytical applications in pyrolysis-mass spectrometry [3,4].

Metallocene derivatives have been widely studied by mass spectrometry, notably by Zagorevskii and co-workers[5,6], but little work has been reported on halogenated benzoyl ferrocenes, although Dang et al [7] have reported mass spectra for 1,2-diferrocenyl-1,2-diarylethenes and 1,2-diferrocenyl-1,2-diarylethanes, including 3,4 dichlorobenzoyl substitution. We have reported earlier the preparation and crystal structure of HNDAF (1,4,5,6,7,7 hexachloro-5-norbornene-2-3 dicarboxylic anhydride ferrocene)[8] but its mass spectrum has not been reported previously.

Pyrolysis-mass spectrometry was felt to be a suitable method for analysis of these ferrocene derivatives which, although rather involatile, are often characterised by high thermal stability.

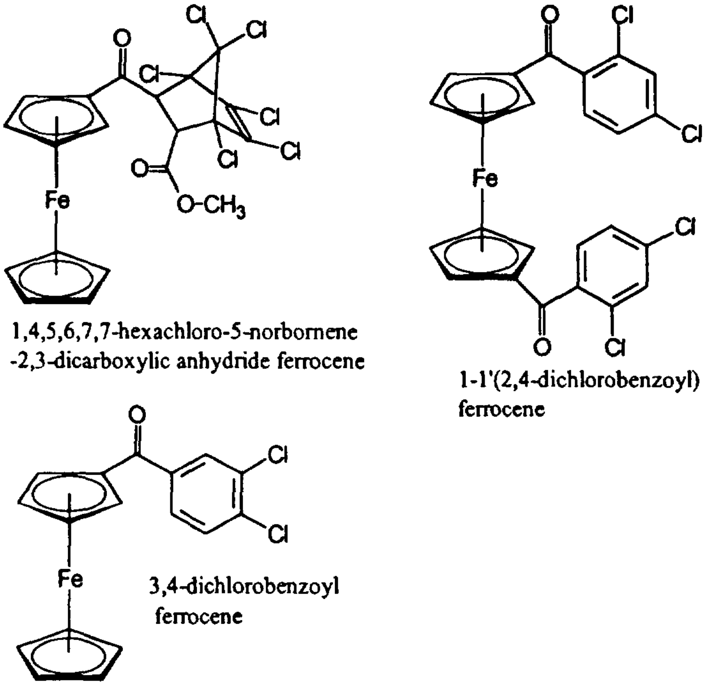
During the course of this work some unusual features were noted, particularly the occurrence of an intense fragment ion peak at m/z 139, for dichlorobenzyl ferrocenes and in this work we report the spectra and propose the main fragmentation processes including the formation of the m/z 139 peak.

EXPERIMENTAL

A VG Analytical 70-70HS dual focusing, forward geometry (EB) mass spectrometer was used with a variable rate temperature controller and direct insertion probe, electron impact ionisation, and accelerating potential of 4kV. The source temperature was maintained at 180°C, and samples (< 1 mg) placed in a 20 mm x 1 mm ID quartz tube in the direct insertion probe, which was temperature programmed, from 20°C at 60°C/min to around 500°C. Mass spectra were recorded from 10 - 650 amu (exponential down scan) with 6.6 sec/scan.

The ferrocene derivatives[2] are described in Figure 1. Perfluoro-kerosene was used for calibration of the spectrometer and for accurate mass determination.

Fig 1 The structures of the 3 ferrocenes used



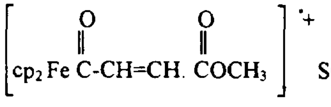
1,4,5,6,7,7-hexachloro-5-norbornene -2,3-dicarboxylic anhydride ferrocene

1-1'(2,4-dichlorobenzoyl) ferrocene

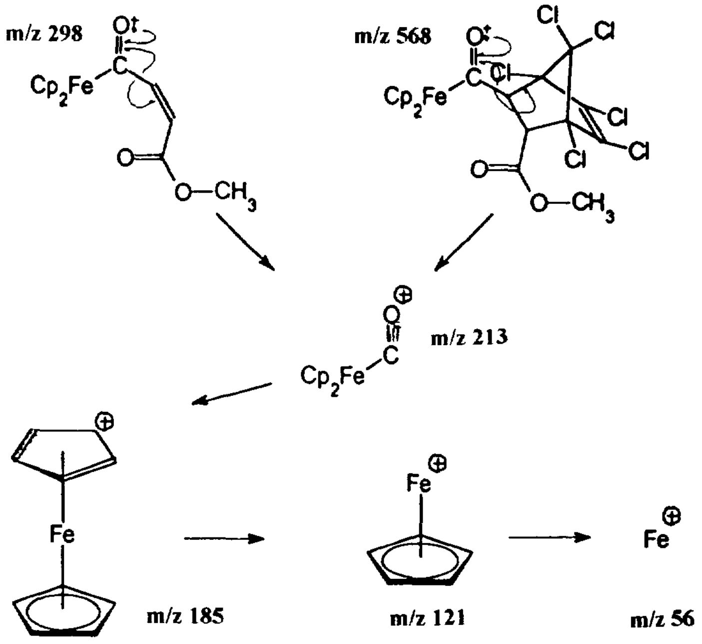
3,4-dichlorobenzoyl ferrocene

RESULTS AND DISCUSSION

Volatilisation occurred in the range 200 - 260°C for HNDAF and 300 - 410°C for 1,1'DCBF and 28 and 38 scans respectively were factor analysed to aid interpretation[4]. The first two dominant factors, accounting for over 99% of the variance were the background, and the sample spectra. Additional minor factors due to bias in scanning, to a small HCl loss from associated thermal degradation in the probe and a trace of solvent ($CDCl_3$) were identified and will be discussed more fully elsewhere. These additional factors had only a small effect on the observed spectra, and could be removed by use of target testing [3].

The spectra obtained for HNDAF and 1,1'DCBF are shown in fig 2, together with the spectrum obtained for 3,4 dichlorobenzoyl ferrocene, for comparison. In all cases the molecular ion was observed demonstrating that these molecules can be volatilised successfully with little thermal degradation. Thermogravimetric studies in a nitrogen atmosphere show that HNDAF degrades at around 350°C, but loses a significant amount of weight (~ 10%) by volatilisation at 250° - 350°C, while 1,1'DCBF is thermally stable to around 400°C but shows small volatilisation losses below this temperature [2]. These observations are entirely consistent with the mass spectroscopic observations with sample volatilisation occurring at somewhat lower temperatures under the vacuum in the direct insertion probe. The HNDAF spectrum shows the expected molecular ion at m/z 568 with the associated chlorine isotope peaks, and is dominated by the base peak at m/z 298 which is readily attributable to the elimination of the stable neutral molecule C_5Cl_6 to form the ion  $\left[\mathrm{cp_2Fe\ \overset{\overset{O}{\|}}{C}\text{-}CH{=}CH.\ \overset{\overset{O}{\|}}{C}OCH_3}\right]^{\cdot+}$ Successive fragmentation of this ion leads to the formation of ions m/z 213, 185, 121 and 56 as indicated in Scheme 1. Direct formation of m/z 213 from the molecular ion is also possible as shown in the scheme.

Scheme 1 Proposed fragmentation pathway for HNDAF.



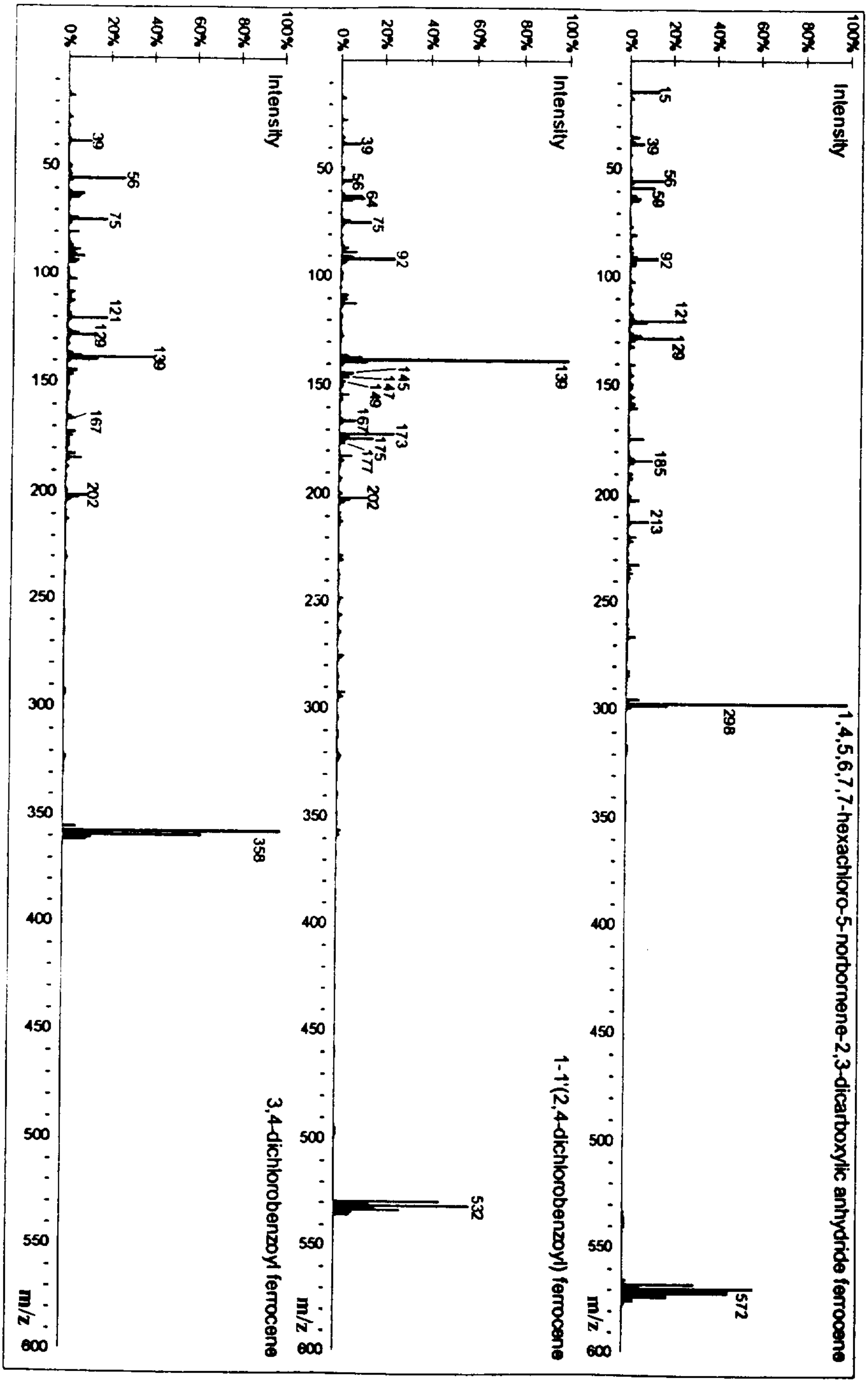
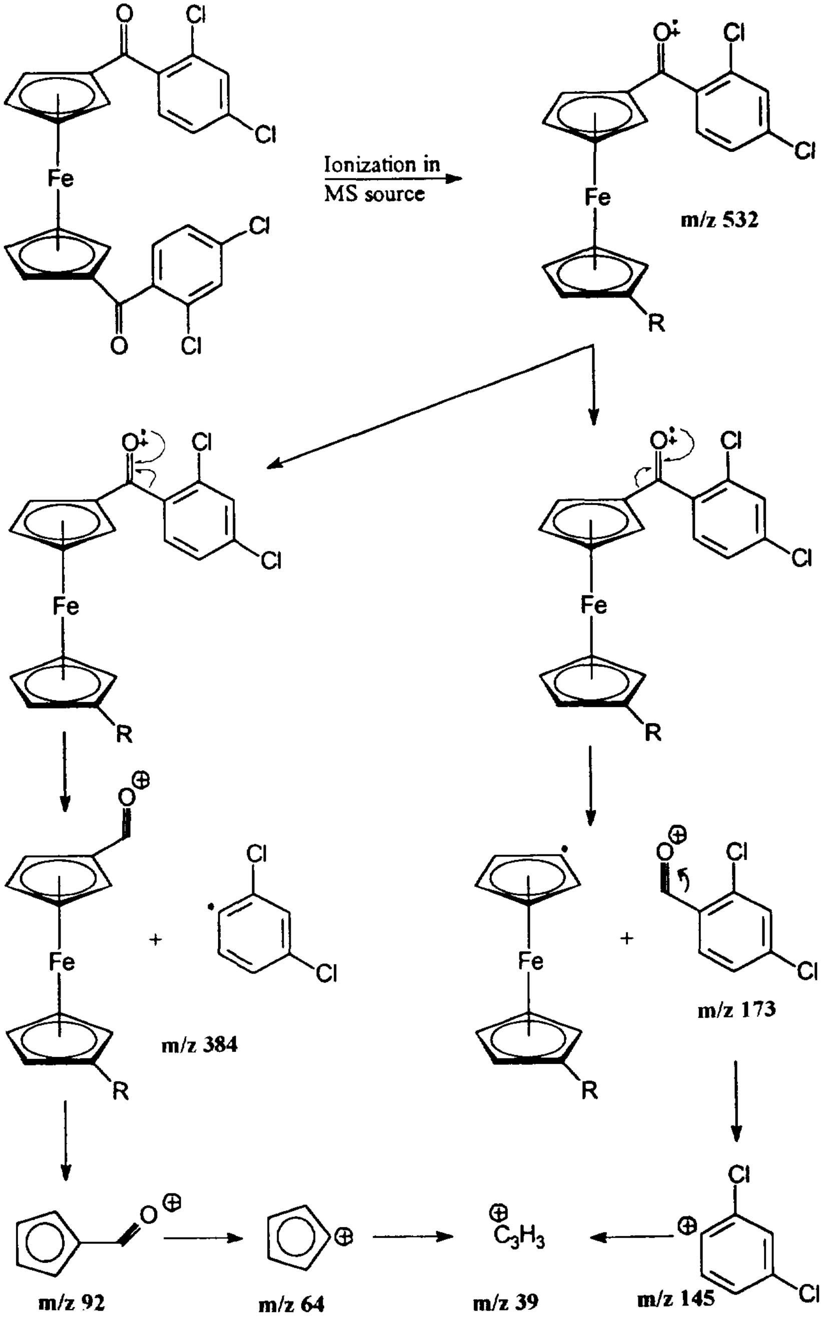


Fig 2. Mass spectra of HNDAF, 1,1'-DCBF and DCBF.



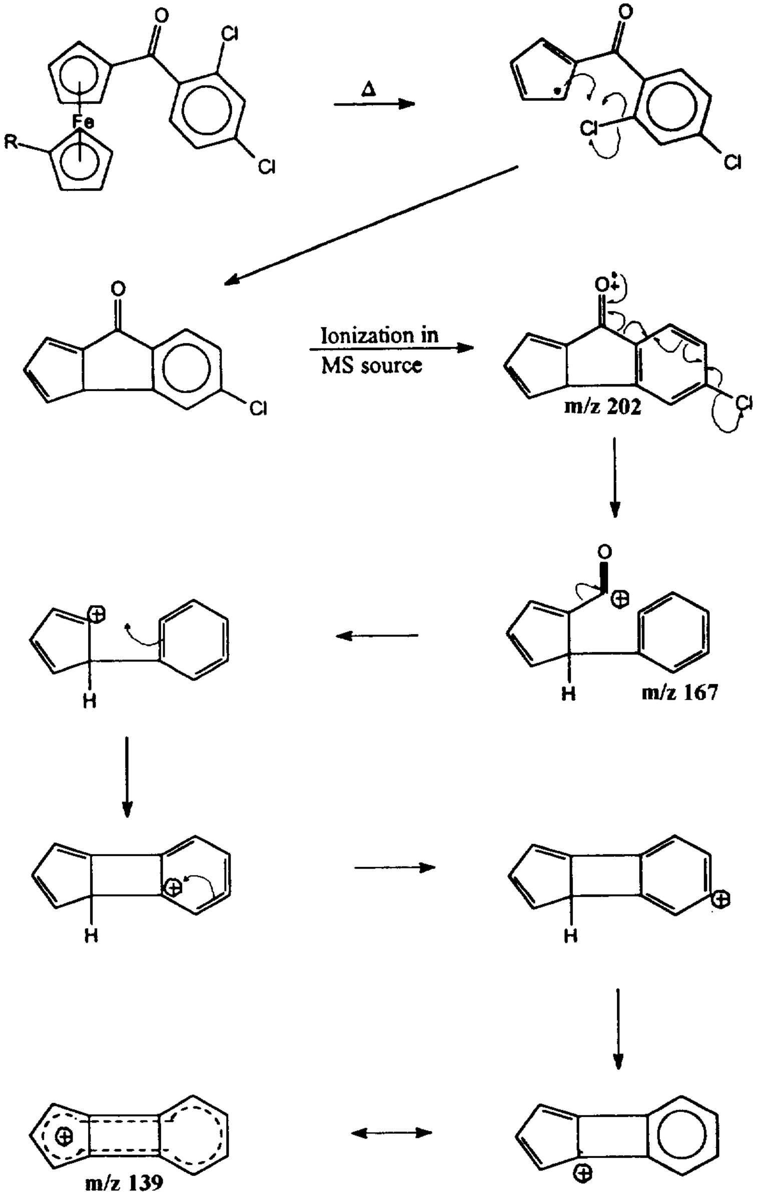
Scheme 2 Proposed fragmentation pathway for 1,1′-DCBF.

The 1,1′ DCBF spectrum also shows the expected molecular ion at m/z 532 and subsequent α-cleavage may lead to either the sequence m/z 173 and 145 or m/z 92 and 64 as shown in scheme 2. These routes do not explain, however, the base peak at m/z 139 and the further low intensity peaks at m/z 167 and 202. In order to ascertain the origins of these peaks, the spectrum of 3,4-dichlorobenzoyl ferrocene (DCBF) was studied and was also found to contain the peaks at m/z 139, 167 and 202. The accurate mass of the peak at m/z 139 was found to be 139.0554 (average of six spectra, standard deviation = 0.0030) corresponding to an elemental formula of $C_{11}H_7^+$ (exact mass 139.05478) and sufficiently different for the next nearest possible match, $C_8H_{11}O_2$ (exact mass 139.07590), to be rejected. $C_{11}H_7^+$ ions of structure $C_6H_5\text{-}C \equiv C\text{-}C \equiv C\text{-}CH_2^+$ have been identified previously in fuel-rich and sooting acetylene and benzene flames[9], but such ions are unlikely to be observed here. While there have been studies on the related anion [10], which appears to have been obtained only in solution, there appear to be no experimental reports of $C_{11}H_7^+$ ions with the structure assigned to the cyclopenta [3,4], cyclobuta [1,2] benzenylium, or norbiphenylene, cation. However, a theoretical MNDO study suggests that this structure should be viable in view of its aromatic stability[11], as it is an analogue of the 10-π-electron molecule naphthalene, and mechanistic considerations suggest that this is the isomer most likely to be formed in the fragmentation of the ferrocenyl derivatives in this study.

The proposed fragmentation mechanism shown in scheme 3, which assumes that the ferrocene derivatives lose a substituted cyclopentadienyl ring, either by thermal decomposition in the source or by fragmentation of the molecular ion, accounts for the appearance of peaks of low intensity at m/z 202 and 167 and the intense peak at m/z 139 due to the $C_{11}H_7^+$ ion. This mechanism would be expected to occur for any dichlorobenzoyl substituted ferrocene, particularly if one of the chlorine atoms is in the ortho position, although formation of $C_{11}H_7^+$ from DCBF suggests it can also occur for chlorine atoms in the meta position. No peaks at m/z 139 were reported by Dang[7], presumably reflecting the need for the presence of the carbonyl group in the fragmentation pathway in Scheme 3, or by Sheley and Fishel[12] who studied simple 1,1′ diacetyl and 1,1′ dipropionyl ferrocenes which do not have an arone substituent. No suitable m/z 139 base peak or fragment ions were found in the NIST Library [13], or in Chemical Abstracts and consequently these appear to be the first observations consistent with the norbiphenylene cation. Further work will be directed at studying a wider range of substituted halogenobenzoyl ferrocenes and model chlorobenzoyl compounds in order to confirm the proposed mechanism for the thermal degradation of these compounds.

SUMMARY

Temperature-programmed pyrolysis is a suitable method for the determination of mass spectra of highly substituted chlorinated ferrocenes. Relatively simple mass spectra are readily obtained and all the major features for HNDAF, 1,1′-DCBF and DCBF have been explained. Of particular interest are the facile



Scheme 3 Formation of the m/z 139 ion from 1,1'DCBF and DCBF.

elimination of C_5Cl_6 by chlorendic acid derivatives of ferrocene such as HNDAF, and the detection of the norbiphenylene ion $C_{11}H_7^+$ in the spectra of dichlorobenzoyl substituted derivatives of ferrocene.

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