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MÖSSBAUER STUDIES ON FERROCENE COMPLEXES

III *. STRUCTURE OF FERROCENYL CARBENIUM IONS

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Summary

Mössbauer and NMR spectra are reported for ferrocenyl (Fc) carbenium ions, $FcCH_2^+$ (III^+) and FcC^+Me_2 (II^+) in frozen acidic media. ^{1}H-NMR spectra showed no evidence of Fe—H bonded species. Mössbauer parameters for II^+ were identical within experimental error to those obtained for the carbenium ion precursors and to ferrocene itself, whereas quadrupole splittings for III^+ were significantly larger. The results for the latter species are interpreted in terms of stabilisation via orbital overlaps with the central iron atom.

The structure of ferrocenyl carbenium ions has long been problematical. The controversy centres around how the ion is stabilised, and has led to a number of different structures being proposed.

The ferrocenyl group acts as a very strong electron releasing substituent which results in exceptionally stable carbenium ions [2]. Richards [3] has suggested that the iron atom is not located symmetrically between the rings but is displaced towards the *exo* carbon atom (C_{exo}), a phenomenon known as ring slip (A). Cais [4] invoked the deformation of the cyclopentadienide ring which should result in better overlap between the iron atom ϵ_{2g} orbital and the empty *p* orbital on C_{exo}(B). Extended Hückel calculations [5] suggest that a ring-tilted structure (C) represented an energy minimum formulation. In all these structures bonding is postulated between the Fe atom and C_{exo}. However, other authors [6a,b] prefer the view that stabilisation occurs via resonance with the cyclopentadienide rings (D ⟷ E). Hyperconjugation by iron-ring orbitals has also been advanced [7a,b,8]. More recently, in an extensive investigation of ferrocenylalkylium ions, Watts [9] has shown from a study of restricted rotation about the

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[*] For part II see ref. 1.

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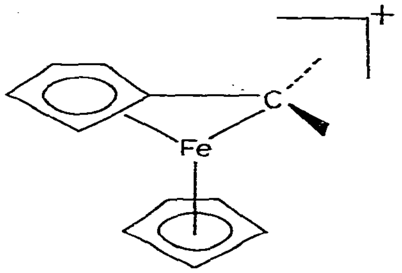
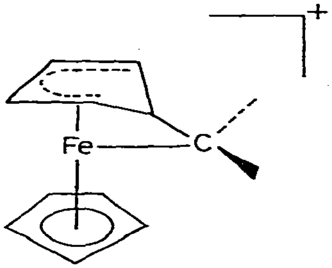


(A)



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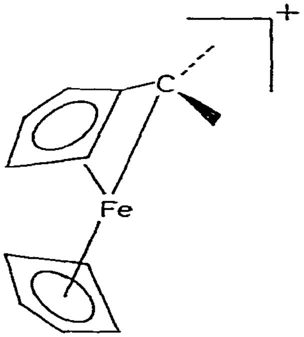

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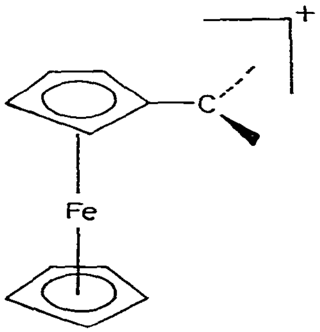

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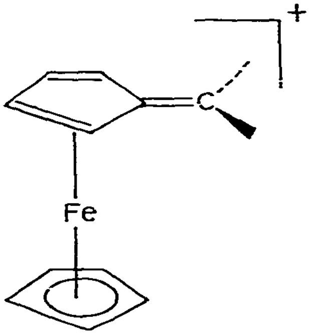


(E)

C_{exo}—ring bond that there is no marked double bond character, and also little, if any, Fe—C_{exo} bonding. The ring slip structure (A) has also been criticised in a study of pK_{R^+} values which indicated that the introduction of a three methylene bridge increases the thermodynamic stability of the carbenium ion, a situation where overlap of Fe—C_{exo} orbitals would be less due to ring tilt [9]. The crystal structure of α,α-diferrocenylmethylium tetrafluoroborate has revealed that the C_{exo} lies somewhat out of the plane of the cyclopentadienide rings but not sufficiently close to the Fe atom to cause any strong bonding [10]. In addition, rotation about the ring—C_{exo} bond was not greatly hindered.

ESCA and Mössbauer spectra [11] indicate that the positive charge on the iron atom did not differ significantly from that of ferrocene itself. Dannenberg and Richards [3,12] have also reported Mössbauer data on frozen solutions of the ferrocenylmethylium ion in solvent sulphuric acid, and compared the parameters with those of the precursor carbinol in benzene. The isomer shifts (IS) were identical within experimental error but the quadrupole splitting (QS) differed very significantly. However, the interpretation is flawed by a misquotation of QS values for ferrocene itself from previous work, which renders their conclusions invalid. Because of this confusion, and because Mössbauer spectroscopy offers a useful probe of electron density around the iron atom, we have used this technique to study ferrocenylcarbenium ions in frozen acidic solutions. 2-Ferrocenylpropan-2-ol(I), 2-ferrocenylprop-2-ene(II) and ferrocenylcar-

TABLE 1

NMR DATA FOR FERROCENYL CARBENIUM IONS AND THEIR PRECURSERS

Compound	Solvent	Chemical shifts (δ, ppm)				
		Cp	CH_2	H_α	H_β	Me
I	CF_3SO_3H	4.27	—	4.27	5.67	1.67
II	CCl_4	3.93	—	4.08	4.22	—
II	CH_3CO_2H	4.67	—	3.77	4.00	—
II	CF_3CO_2H	3.97	—	4.03	5.37	1.38
II	CF_3SO_3H	4.25	—	4.25	5.67	1.67
III	CCl_4 [a]	4.10	~4.1 [a]	4.15	4.23	—
III	CF_3CO_2H	4.73	5.37	4.23	5.70	—
III	H_2SO_4 [b]	4.86	5.30	4.21	5.66	—

[a] Underlying the C_5H_5 resonance. [b] 98.0% Analar H_2SO_4.

binol(III) were prepared by standard methods and their ^{1}H-NMR spectra run in CF_3CO_2H and trifluoromethanesulphonic acid (triflic acid), CF_3SO_3H.

NMR Spectroscopy

Compounds I and II had identical spectra in CF_3CO_2H which corresponded quite closely to those previously reported [13] and showed no metal-bound proton resonances. Iron protonation was also absent in the much stronger acid CF_3SO_3H. In this medium, three slightly broadened peaks appear at 1.67 (6 H), 4.25 (7 H) and 5.67 ppm (2 H). The upfield resonance is clearly assigned to the *gem* dimethyl group in the carbenium ion. The centre resonance contains the five cyclopentadienide protons together with two H_α protons and the downfield absorption is due to the two H_β protons. The corresponding shifts in CF_3CO_2H appear in Table 1. It was noticeable that in CF_3SO_3H, lines were much broader, probably due to some oxidation (vide infra).

The spectra of ferrocenylcarbinol in CF_3CO_2H and H_2SO_4 (98%) were virtually identical and showed considerable deshielding of the protons relative to those in CCl_4. As for II, the H_β (5.7 ppm) protons were strongly deshielded with respect to the α protons (4.2 ppm) and is typical of such carbenium ions.

TABLE 2

MÖSSBAUER PARAMETERS FOR FERROCENYL CARBENIUM IONS

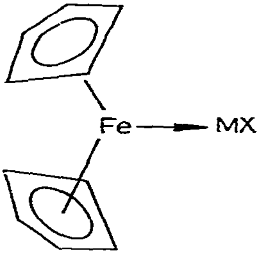
	Temp. (°C)	Isomer shift (mm sec^{-1})	Quadrupole splitting (mm sec^{-1})
$Fe(C_5H_5)(C_5H_4C(CH_3)_2OH)$	80	0.53(2)	2.40(2)
	300	0.49(2)	2.40(2)
$Fe(C_5H_5)(C_5H_4C(CH_3)_2OH)/CF_3SO_3H$ [a]	80	0.53(2)	2.38(2)
		0.63(3)	—
$Fe(C_5H_5)(C_5H_4C(CH_3)_2OH/CF_3COOH$ [a]	80	0.52(2)	2.40(1)
		0.61(1)	—
$Fe(C_5H_5)(C_5H_4C(CH_3)_2OH/H_2SO_4$	80	0.51(2)	2.41(2)
$Fe(C_5H_5)(C_5H_4CH_2OH)/H_2SO_4$	80	0.48(2)	2.70(2)
$Fe(C_5H_5)(C_5H_4CH_2OH/CF_3SO_3H$	80	0.47(2)	2.67(2)
$Fe(C_5H_5)(C_5H_4CH_2OH/CH_3COOH$	80	0.50(1)	2.40(1)

[a] These spectra show single peaks of oxidised product.

Again, no signals for iron-bound protons were observed in the range 0 to —5 ppm. The resonances in sulphuric acid were somewhat broader than in CF_3CO_2H, probably due to slight oxidation.

Mössbauer spectroscopy

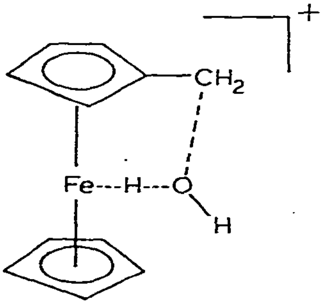
The Mössbauer parameters for the compounds studied appear in Table 2. In some cases, small amounts of oxidised ferrocenes appeared in accordance with the NMR observations. The principle feature of the results is that, for II, both IS and QS values are almost identical with those of ferrocene itself, whereas for ferrocenylcarbinol (III) a marked increase in QS was found both in sulphuric acid and triflic acid frozen solutions compared with values in frozen acetic acid where no carbenium is formed. Our results therefore differ significantly from those of Dannenberg and Richards [3,12]. The discrepancies in QS cannot be explained by the somewhat different experimental conditions employed since the room temperature QS value obtained by us for solid II was very similar to those reported for solid ferrocene itself [14,15,16] which are significantly larger than that reported by Dannenberg and Richards. We have recently reported Mössbauer data [1,17] on complexes where the iron atom is bonded to an electropositive group as depicted below.



(IV, $M = Hg$, $X = [Cl_2(HgCl_2)_6]$;

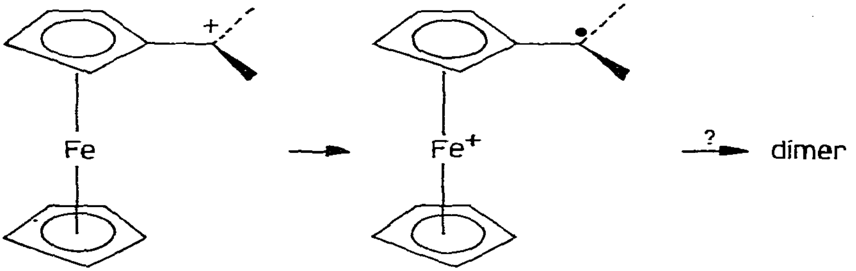
V, $M = H^+$, $X = [AlCl_4]^-$)

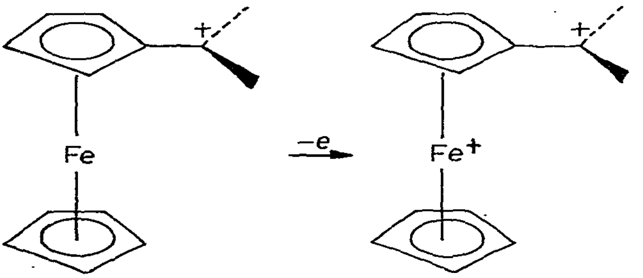
Such complexation results in a large distortion of the charge on the iron atom together with ring tilting. Anomalously high values of QS were found for these systems (IV 3.09, V 2.72 mms^{-1}). These values were interpreted as arising mainly from the transfer of charge from the iron since ring tilting generally causes a lowering of QS values [15]. If the e_{2g} or a_{1g} orbitals participate in the stabilisation of the positive charge on C_{exo} then the QS values should be greater than those of ferrocene and the precursors themselves. Such in the case for carbenium ion III^+. The values of QS for the latter ion are also consistent with the iron—hydrogen bonded structure;



(cf. a QS value of 2.59 mms^{-1} for ferrocene is CF_3SO_3H [1]) However, NMR spectra of solutions of III^+ show no evidence of such bonding and thus it is concluded that charge is transferred from the iron atom to the carbenium ion centre and not to solvent protons in this case. One cannot completely rule out the possibility of hyperconjugative stabilisation as proposed by Traylor [7], though it is rather difficult to assess what effect, if any, this would have on QS values. In contrast, the ferrocenyldimethyl carbenium ion (II^+) generated from II showed no such exalted QS value, and parameters were, within experimental error, identical with that of solid ferrocene at 80°K and those of frozen solutions of ferrocene in solvents CH_3OH, $CHCl_3$, and CH_3CO_3H [1]. This implies little change in the electronic environment of the iron nucleus on forming the carbenium ion. Our interpretation of the data is that for the tertiary carbenium ion, II^+, enough stabilisation is achieved from inductive/hyperconjugative electron release from the methyl groups plus resonance contributions from the cyclopentadienide ring such that additional participation by the iron orbitals is unnecessary. For III^+ the case is rather different since it is formally a primary carbenium ion, and hence requires some additional stabilisation. This is now provided at least in part by the iron atom. Although participation by iron appears to be excluded for tertiary systems such as II in the highly acidic media described above, one cannot discount such interactions for secondary systems used in S_N1 solvolysis reactions [18,19].

Oxidation of the carbenium ions has already been referred to and raises an interesting point with regard to the structure of the product. Two possibilities exist, one where the electron is transferred to the C_{exo} site or where the electron is transferred directly to oxygen to form a doubly charged ion.





The Mössbauer spectra of the ferrocenylcarbenium ions in trifluoromethanesulfonic and trifluoroacetic acid showed, in addition to the doublet due to the ferrocene structure, a single peak with an isomer shift of 0.62 mm sec^{-1}; this isomer shift is similar to those reported by other workers and ourselves

[1,17] for ferricinium species and is obviously the oxidation product from the ferrocenylcarbenium ion. As the isomer shift is so similar for this species to those of other reported ferricinium species, then if indeed a doubly charged ion is formed the Mössbauer data gives no indication of this. Additionally, UV spectra of these oxidised solutions showed a λ_{max} at 610 nm typical of simple ferricinium derivatives.

Experimental

Trifluoromethanesulphonic acid and trifluoroacetic acid were distilled from a small quantity of P_2O_5 prior to use.

2-ferrocenyl propene and 2-ferrocenyl propan-2-ol were synthesised by the method of Horspool et al. [22], from the reaction of acetyl ferrocene with methyl magnesium iodide. The products were separated on neutral alumina eluting with pet. ether. The first and major product to elute was the olefin followed by very small quantities of the alcohol. Ferrocenyl carbinol was prepared by reaction of $[C_5H_5FeC_5H_4CH_2N^+Me_3]I^-$ with NaOH. NMR spectra were run on a Varian EM-360 spectrophotometer housed in a constant temperature room with a probe temperature of 28°C.

Mössbauer spectroscopy

The Mössbauer spectra were from frozen solutions, and typically made up as follows.

The solution was prepared by adding enough solid 2-ferrocenylpropene to the required acid to give a 0.2 *M* solution. Part of each of the resulting dark brown solutions was then transferred to a Teflon cell which was quench cooled in liquid nitrogen and loaded into a liquid nitrogen cryostat. The Mössbauer studies on the ferrocenylcarbinol were on a solid absorber thickness 0.5 mm. The Mössbauer spectrometer has been previously described [23] and spectra were fitted as previously reported (17). The velocity scale was calibrated with a 25 μm thick natural iron reference absorber. All isomer shifts are referred to this as zero shift.

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