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MÖSSBAUER STUDIES ON FERROCENE COMPLEXES

VI *. BRIDGED FERROCENYL CARBENIUM IONS AND RELATED PROTONATED KETONES

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Summary

^{57}Fe Mössbauer data are reported for [3]-ferrocenophan-6-one (I) and -6-ol (II), and [4]-ferrocenophan-7-one (III) and -7-ol (IV) both as solids and in frozen solid solutions in CF_3CO_2H and 80% H_2SO_4. Solid I showed QS values typical of a ring-tilted ketone (2.22 mms^{-1}) whereas III has a lower QS value (2.30 mms^{-1}) than anticipated, probably due to specific interaction of the carbonyl with the central iron atom. The QS value of the protonated ketone I (2.14 mms^{-1}) lay in the normal range for such species. Contrary to previous work no evidence was found for protonation of III in CF_3CO_2H or 70% H_2SO_4. Solid II had a QS value typical of a ring-tilted bridged alcohol (2.28 mms^{-1}). Solid IV gave Mössbauer parameters close to those of ferrocene. The carbenium ion derived from II in strongly acid media showed an exalted QS value of 2.53 mms^{-1} comparable to non-bridged ferrocenyl cations. IV, however, showed a very significantly larger QS of 2.79 mms^{-1}, the highest QS value yet reported for such carbenium ions. The result is interpreted in terms of iron participation via metal-based orbitals (e_2).

Introduction

We very recently reported on ^{57}Fe Mössbauer data of protonated ferrocenyl ketones [1] and the corresponding carbenium ions [2]. These studies revealed that for the former series, quadrupole splittings (QS) were generally significantly lower than those of the unprotonated species, which in turn are considerably lower than ferrocene itself. In the latter series QS values were much larger. The results have been interpreted in terms of involvement of ligand-based orbitals (e_1) in the

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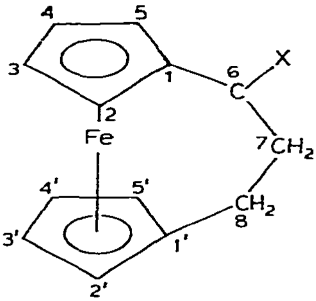
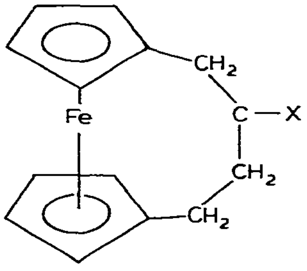
stabilisation of the ketones, and of metal-based orbitals (e_2) in the stabilisation of the carbenium ions. In order to test this hypothesis further, we now report NMR and Mössbauer data for a series of bridged ferrocenes in which the position of the ketone or carbenium ion centre is varied with respect to the ligand planes and the central iron atom.

The systems investigated were [3]-ferrocenophane-6-one (I) and -6-ol (II) and [4]-ferrocenophane-7-one (III) and -7-ol (IV). [3]-Ferrocenophanes possess a ring-tilted structure in which the dihedral angles between the planes of the cyclopentadienyl rings lie between 9 and 10° [3,4,5]. For the one [4]-ferrocenophane of known crystal structure ([4]-ferrocenophane-6-one [6]), the rings show a small tilt of about 4°.



(I, X = (=O);
II, X = H, OH)



(III, X = (=O);
IV, X = H, OH)

Results and discussion

NMR spectroscopy

The ^{1}H NMR spectrum of I in CCl_4 agreed with the previously reported data [7], the most notable feature being the sharp four-proton singlet for the methylene protons, indicating rapid conformational changes of the bridging carbon chain. In CF_3CO_2H, I showed broad singlets at 3.00 (4H), 3.78 (2H), 4.75 (4H) and 4.95 ppm (2H). The upfield four-proton signal is clearly assigned to the bridging methylenes which are deshielded 0.2 ppm relative to the unprotonated ketone. The downfield two-proton signal is assigned to H(2,5). The remaining two and four proton singlets are due to H(2',5') and H(3,4), H(3',4') respectively. The spectra of III and IV in CF_3CO_2H agreed well with previous work [8], though the assignments of the H(2,5) and H(3,4) are not entirely straightforward since there cannot now be conjugation between the Cp ring and the carbenium ion/carbonyl groups. Any participation by the central iron atom would alter its anisotropy in a manner difficult to predict. β-Ferrocenylcarbenium ions were found to be unusually stable and have been studied in solvent CF_3CO_2H [9]. One of the most interesting features of their PMR spectra is the very large upfield shift of the carbenium ion methine proton (4.6 ppm) of the C(7) ion compared with that of the C(6) ion (8.10 ppm). This strongly suggests pronounced shielding by the central iron atom with presumably concommitant deshielding of H(3,4), H(3',4'). The stability of carbenium ions of bridged ferrocenes has also been measured spectrophotometrically in aqueous sulphuric acid [8,10]. The

pK_{R^+} values of [4]-ferrocenophan-6- and -7-ol were reported as 0.15 and 0.1, respectively, compared with a value of -3.2 for [3]-ferrocenophan-6-ol. These striking results show that the C(6) and C(7) carbenium ions for the four-carbon bridged series have almost identical stabilities. For the C(6) carbocation, there will be some conjugation between the carbenium ion centre and the Cp ring orbitals. Such conjugation is however ruled out for the C(7) carbenium ion due to the interposed methylene group. This result therefore strongly suggests participation by the iron atom. [3]-Ferrocenophan-6-ol generates a much less stable ion due presumably to distortion of the empty *p* orbital out of coplanarity with the Cp ring. The apparent enhanced stability of the C(7) cation raises an important question. Recent kinetic studies of the hydrolysis of ferrocenophan-1-yl acetates indicates than an S_N1 mechanism operates [11] with rate-determining formation of ferrocenyl carbenium ions. However, [4]-ferrocenophan-2-yl acetate was completely inert under the conditions used (80% aqueous acetone) [12]. This result is puzzling and is in direct contradiction of the measured carbenium ion stability. The pKa values of the corresponding protonated ketones reportedly show similar trends [8]. [4]-Ferrocenophan-6-one (V) and -7-one (III) have values of -2.5 and -4.0 respectively, indicating much greater basicity than acetone ($pKa = -7.9$ [13]). However, we have found that III is only very slightly soluble in 70% H_2SO_4 ($H_0 = -5.6$) [14] but quite soluble in 80% H_2SO_4 ($H_0 = -7.2$) [14]. This implies that the pK_a of III is between -6 and -7 i.e. III is a much weaker base than claimed. Moreover, 80% H_2SO_4 solutions of III have a marked tendency to oxidise at room temperature as shown by the absence of PMR signals for freshly prepared solutions. The reported basicity of III must therefore be called into question. Further evidence on this point will be presented in the Mössbauer section. The carbonyl stretching frequencies of I, III and V are reported as 1681 [15], 1710 [8] and 1650 [8] cm^{-1}, respectively. These are indicative of significantly reduced conjugation for [3]-ferrocenophan-6-one (I) due to reduced coplanarity with the Cp ring, and complete lack of conjugation in the case of III. Even for V there is reduced conjugation due to a dihedral angle of about 18° between the Cp ring and carbonyl plane [6].

Mössbauer spectroscopy

The Mössbauer spectra of frozen solid CF_3CO_2H or 80% H_2SO_4 solution of the ferrocenyl ketones and alcohols were run and compared with those of the solid ketones or alcohols. The results appear in Table 1. There were no significant differences in isomer shifts for all the compounds studied.

For compound I (solid) the Mössbauer data are identical within experimental error to those obtained from a frozen solution of the material in CF_3CO_2H, showing no changes on solution have occurred. However, when I is protonated in 80% sulphuric acid a decrease in QS of about 0.1 mms^{-1} is observed.

These results are comparable with those for the mono ketones reported previously where the QS range in 2.24–2.27 mms^{-1} for the solids [1,16].

The crystal structure of I shows that the molecule has a ring tilt of 9°. A carbonyl adjacent to the rings causes a reduction in QS of 0.13 mms^{-1} due to electron withdrawal from the Cp rings, where there is no restriction to Cp ring-carbonyl coplanarity. The observed QS for I is 2.22 mms^{-1}, which is somewhat lower than predicted for a carbonyl substituent. The carbonyl in I is distorted out of the Cp ring plane which would decrease the π conjugation and give a QS value close to

TABLE I

^{57}Fe MÖSSBAUER PARAMETERS FOR SOME [3]- AND [4]-FERROCENOPHANES IN SOLID PHASE OR FROZEN SOLUTIONS IN STRONGLY ACIDIC MEDIA AT 80 K

Compound	Phase	QS(mm s^{-1})	IS(mm s^{-1})
Ketones			
I	solid	2.22(2)(2.22(1))^a	0.52(1)(0.48(1))^a
I	CF_3CO_2H	2.21(2)	0.51(1)
I	80% H_2SO_4	2.14(4)	0.50(2)
III	solid	2.30(2)	0.54(2)
III	CF_3CO_2H	2.34(1)	0.53(1)
III	80% H_2SO_4	2.34(1)	0.54(1)
Alcohols			
II	solid	2.28(2)(2.31(1))^a	0.53(2)(0.48(1))^a
II	CF_3CO_2H	2.53(1)	0.50(1)
IV	solid	2.39(3)	0.51(1)
IV	CF_3CO_2H	2.79(2)	0.52(1)

^{a} Values from ref. 16.

ferrocene. The other change in molecular geometry is that of ring tilt [16] which appears to decrease the QS by about 0.1 mms^{-1} for a 9° tilt angle. The observed QS can thus be explained by a combination of the above two effects. Protonation of I leads to a small but significant further decrease in QS relative to I (or relative to ferrocene of 0.24 mms^{-1}). This decrease in QS is again smaller than those observed for non-bridged ketones, and further reflection of the lack of coplanarity of the carbonyl function and the Cp rings.

Solid III shows Mössbauer parameters very close to those of ferrocene itself. This is to be expected for a ketone derivative in which conjugation with the Cp ring is prevented by an intervening methylene group. Ring tilt is likely to be ~ 4°. For [3]-ferrocenophanes, bridge substituents other than α carbonyls have no significant effect on QS, viz. [3]-ferrocenophane and [3]-ferrocenophane-6-ol with QS = 2.30 and 2.31 mms^{-1} respectively [16]. Thus the alcohol function in [4]-ferrocenophan-6-ol should have no appreciable effect on QS as indeed is shown by the value of 2.38 mms^{-1} which is identical to that of ferrocene. Our value for [4]-ferrocenophane-7-one is 2.30 mms^{-1}, significantly lower than anticipated which indicates some interaction with Fe-based orbitals (e_2), as the change in QS expected from such a small ring tilt would not account for this decrease.

Mössbauer parameters of III show no appreciable variation for the solid and solid frozen solutions in CF_3CO_2H and 80% H_2SO_4. It was noted that the typical purple-blue colour of protonated ferrocenyl ketones was not observed in trifluoroacetic acid. This again suggests that III is not protonated. The fact that no observable decrease in QS is found further demonstrates the lack of protonation in this medium.

Solid II shows a QS of 2.28 mms^{-1} which is lower than that expected for a ferrocenyl alcohol (2.36–2.41 mms^{-1}) and is due to ring tilt (~ 9°) [3]. On forming the corresponding carbenium ion, the QS is markedly increased to 2.53 mms^{-1}, a ΔQS (= QS acid − QS solid) of 0.25 mms^{-1}. This compares well with the ΔQS of 0.25 mms^{-1} for the methylferrocenyl cation [2], and is strongly suggestive of iron participation via iron-based orbitals e_2.

Solid IV has Mössbauer parameters very close to those of ferrocene. On solution in CF_3CO_2H and freezing, a QS of 2.79 mms^{-1} ($\Delta QS = 0.40$ mms^{-1}) was found. This is the largest value yet recorded for a ferrocenyl carbenium ion. Here, as the charge cannot be delocalised via the rings, only direct iron participation via e_2 orbitals can take place. It is noticeable that this value of 2.79 mms^{-1} is larger than the largest (2.7 mms^{-1}) found by us previously [2], in which we suggested that this might be a maximal iron participation for that position due to the large Fe–C *exo* distance involved. In this context, it is pertinent to consider the relevant iron–carbon bond distances. The known crystal structures of the [3]-ferrocenophanes, 2-(α-phenyl, α-hydroxypropyl) [3]-ferrocenophane [5] and [3]-ferrocenophan-6-one [3], revealed some interesting differences. The former shows an average Fe–C(6) bond distance of 3.13 Å whereas in the latter this distance is much reduced for Fe–CO to 2.93 Å. This cannot be wholly due to strain since the Fe–C(8) distance remains the same at 3.13 Å. For [4]-ferrocenophan-6-one, which is less strained, the Fe-carbonyl distance of 2.88 Å is even shorter than that of the three-carbon-bridged analogue. This suggests some attractive interaction with the iron atom. The Fe–C(7),C(8) distances in 4-ferrocenophan-6-one are in the range 3.58–3.67Å (calculated from atom position data given in ref. 6).

A scale molecular model of the carbenium ion (positive charge on C(7)) derived from IV and based on bond lengths reported in ref. 6 using tetrahedral bond angles, gives an Fe–C(7) distance of about 2.9 Å. The C(7) atom lies almost in the plane of the e_2 orbitals with the empty carbon p orbital directed at the iron centre suggesting a σ-type of overlap. Such an overlap would be in keeping with the e_2 participation reflected in the exalted QS previously described for protonated ferrocenes [17] and the ferrocene-mercuric chloride complexes [18]. It is worth noting that the order of increasing QS is as follows: Fe–H < Fe–C < Fe–Hg.

Experimental

[3]-Ferrocenophane-6-one (I) was prepared using the simplified procedure of Turbitt and Watts [19] by reaction of acryloyl chloride with ferrocene in the presence of aluminium trichloride in CH_2Cl_2 at −78°C. [4]-Ferrocenophan-7-one(III) was synthesised from I by reaction with diazomethane [20]. The corresponding alcohols were made by $NaBH_4$ reduction as previously described [2].

NMR and Mössbauer spectra were obtained as reported previously [2,17,18].

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