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MÖSSBAUER STUDIES ON FERROCENE COMPLEXES

V *. PROTONATION OF FERROCENYL KETONES

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Summary

The structure of protonated ferrocenes has been investigated using ^{1}H NMR and ^{57}Fe Mössbauer spectroscopy. The ketones were fully protonated in CF_3CO_2H and in 70% H_2SO_4/H_2O. In more concentrated sulphuric acid (>90% H_2SO_4/H_2O) rapid heteroannular sulphonation occurred.

No evidence was obtained of any iron protonation in these systems. For the *para* substituted aromatic derivatives $C_5H_5FeC_5H_4COC_6H_4X$ the NMR data indicates steric inhibition to resonance. 1,1′-Diketones are doubly protonated in strongly acid media (98% H_2SO_4, CF_3SO_3H).

Mössbauer data on the solid ketones showed a decrease in quadrupole splitting (QS), relative to ferrocene itself, of about 0.12 mm s^{-1} for each successive acyl function added. For solid solutions of the protonated ketones in CF_3CO_2H this decrease (ΔQS) was much larger at about 0.28 mm s^{-1}. The results are interpreted as involving electron withdrawal from ring-based orbitals (ϵ_1), rather than the iron-based orbitals (ϵ_2). In the aromatic series, ΔQS was significantly smaller for electron withdrawing substituents.

We have recently reported detailed studies of ferrocenyl carbenium ions in which evidence for iron participation in stabilisation of these ions was obtained from Mössbauer spectroscopy [1,2]. These studies have now been further extended to protonated ferrocenyl ketones, as part of a programme devoted to the investigation of the role of iron in complexes of ferrocene.

The ease with which ferrocenyl ketones protonate was first noted by Pauson et al. [3], and led to a detailed examination of these protonated species by infrared spectroscopy [4]. The principle finding of this study of the HCl com-

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* For part IV see ref. 1.

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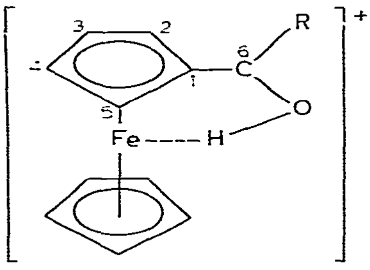
plexes was the absence of the $\nu(C{=}O)$ band at 1670 cm^{-1}, and the appearance of a new band at 1550 cm^{-1}. Also a highly perturbed $\nu(OH)$ band at 2200 cm^{-1} was observed. The results were interpreted in terms of structures Ia and Ib, in which the proton is held by both oxygen and iron atoms, and the carbonyl has only partial double bond character. 1,1′-(α-ketotrimethylene)-ferrocene, by contrast, was not readily protonated due, it was presumed, to steric hindrance to the formation of the Fe—H bond *. One consequence of Fe—H bonding is that the carbonyl group would be almost orthogonal to the cyclopentadienyl ring (Cp) which would cause a loss of resonance stability. It is also apparent that, if Fe—H bonds are formed, then the protons should absorb in the highly characteristic region of the ^{1}H NMR spectrum at ~—2.0 to —2.5 ppm. Such resonances have not been observed for any of the protonated ketones.



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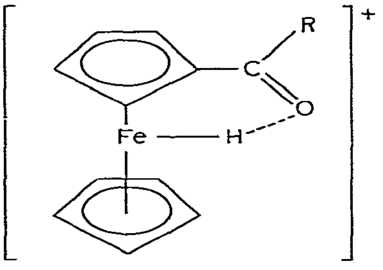

(Ib)

More recently, detailed spectrophotometric studies of protonated ferrocenyl ketones have appeared in which the ketones were found to behave as excellent Hammett bases [5,6]. The pK(BH$^+$) values obtained for a series of heteroannularly substituted ketones gave a good correlation with σ_m (ρ = 3.11) but a much poorer one with σ_p. Resonance effects appear to be rather small and the results were interpreted in terms of inductive effects operating possibly through space. Reservations however must be made on the use of σ constants for a system which is far removed from normal benzenoid structures.

1-Acetyl-2-ethylferrocene was found to be less basic then acetylferrocene itself whereas the heteroannularly substituted 1-acetyl-1′-ethylferrocene was more basic. It is difficult to rationalise these results in terms of a simple inductive effect, since the homoannularly substituted ethyl group should give rise to an enhanced basicity. It is also not easy to see how the 1′-ethyl substituent could act in a direct field sense. One cannot discount steric effects in the 2-ethyl derivative. Clearly a more detailed and systematic examination of substituent effects on basicity of ferrocenyl ketones is required before definitive answers to these anomalies can be given. Olah [7] has studied the protonation of acylferrocenes in strongly acidic media (FSO_3H-SO_2ClF-SO_2), and has concluded that protonation occurs on the oxygen atom, as shown by the appearance of broad one-proton resonances at 11.2 ppm at —101°C. The low temperature spectrum of protonated acetyl ferrocene was very similar to that of the ferrocenyl methyl

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* More recent studies in aqueous H_2SO_4 have shown that the bridged ketone has almost the same basicity as acetyl ferrocene [6].

methylium ion [1,8] in CF_3CO_2H at room temperature, the major difference being that the H_5 proton was significantly more deshielded for the protonated ketone. When the temperature was increased the spectrum of the former ion broadened and eventually underwent reaction at 20° C to give unidentified products. Protonated benzoylferrocene showed a broadened aromatic multiplet at —105° C in contrast to the well separated proton absorptions in protonated acetophenone at —100° C. This was taken to indicate a smaller degree of charge delocalisation into the phenyl ring than for the former ion.

The above results strongly suggest that the barrier to rotation about the C_1—C_6 bond is very much lower for the protonated ketones than for the corresponding carbenium ions. We have studied a series of ferrocenyl ketones in strongly acidic media (CF_3CO_2H, and aq H_2SO_4) using ^1H NMR spectroscopy and Mössbauer spectroscopy (frozen solid solutions).

Though basicity of ferrocenyl ketones is remarkably high, ($pK(BH)$'s for acetyl and benzoylferrocene —2.80, and —3.31 respectively compared with —7.82 for acetophenone) trifluoroacetic acid has a H_o value variously reported between —2.77 and 4.4 [9] and this raises the question of the degree of protonation of the above ketones. The highest value of H_o (—4.4) was obtained using benzalacetophenone as the Hammett indicator [10], and thus is the most appropriate value for use in the present work. The ferrocenyl ketones should therefore be fully protonated in CF_3CO_2H. This is supported by the fact that NMR spectra of the ketones in 70% H_2SO_4/D_2O ($H_o \sim$ —5.9) [11] were qualitatively very similar to those in CF_3CO_2H (vide infra).

The NMR data for both CF_3CO_2H and 70% (by weight) sulphuric acid appear in Tables 1 and 2.

The spectra of acetyl- and benzoyl-ferrocene agree fairly well with those reported previously [8], the small differences in chemical shift (δ) being probably due to the use of external and internal TMS references.

Acetylferrocene in 98% H_2SO_4 after 2 min showed very broad resonances at 5.0 and 2.0 ppm. After 1 h four singlets (each 2H) were observed in the Cp

TABLE 1

CHEMICAL SHIFTS (δ in ppm from external TMS) FOR PROTONATED FERROCENYL KETONES, $C_5H_5FeC_5H_4\overset{+}{C}OHR$ at 0.5 *M* (A, CF_3CO_2H; B, 70% H_2SO_4)

R	Acid	H(3,4)	H(2,5)	Cp	H_A	H_B	others	
CH_3	A	4.67	5.00	4.10	—	—	CH_3	2.00
CH_3	B	5.12	5.63	4.55	—	—	CH_3	2.47
C_6H_5	A	4.77	5.12	4.00	—	—	—	
C_6H_5	B	5.28	5.90	4.53	—	—	—	
p-$CH_3C_6H_4$	A	4.83	5.17	4.05	7.30	6.90	CH_3	1.92
p-$CH_3C_6H_4$	B	5.50	6.07	4.75	8.03	7.65	CH_3	2.63
p-$CH_3OC_6H_4$	A	4.83	5.13	4.00	7.55	6.65	CH_3O	3.50
p-$CH_3OC_6H_4$	B [a]	—	—	—	—	—	CH_3O	3.95
p-ClC_6H_4	A	4.67	4.95	3.93	7.37	7.05	—	
p-ClC_6H_4	B	5.28	5.95	4.58	7.95	7.62	—	
p-CNC_6H_4	A	4.0	4.63	3.93	7.53	7.53	—	
p-CNC_6H_4	B	5.33	6.10	4.67	8.12	8.12	—	

[a] Underwent rapid sulphonation.

TABLE 2

CHEMICAL SHIFTS (δ in ppm from external TMS) FOR PROTONATED FERROCENYL 1,1′-DIKETONES $Fe(C_5H_4COR)_2$ (A, CF_3CO_2H; B, 70% H_2SO_4; C, CF_3SO_3H)

R	Acid	H(3,4)	H(2,5)	Others	
CH_3	A	4.33	4.50	CH_3	2.03
CH_3	B	5.51	5.70	CH_3	2.75
C_6H_5	A	4.47	4.55	C_6H_5	7.2—7.6
C_6H_5	B	5.35	5.52	C_6H_5	7.2—8.0
C_6H_5	C	5.53	5.63	C_6H_5	7.2—8.0

region at 4.70, 4.95, 5.23 and 5.62 ppm whilst the methyl signal appeared as a sharp singlet at 2.53 ppm. This is in keeping with moderately rapid sulphonation of the unsubstituted ring. Sulphonation was observed in 90% H_2SO_4 but did not occur at lower acid concentrations. The spectrum of acetylferrocene in 60% H_2SO_4 was largely unchanged after 3 days. The δ values of the sulphonated product were found to be acid concentration dependent, (cf. Ref. 7). Thus when a solution of acetylferrocene in 98% H_2SO_4 was equilibrated for 1 h then cooled in ice and diluted with D_2O to give 60% H_2SO_4, the spectrum showed singlets at 2.37 (3H), 4.43 (2H), 4.57 (2H) and 4.97 ppm (4H). Benzoylferrocene was sulphonated in less than 5 min at room temperature, with resonances at 4.85 (2H), 5.01 (2H), 5.55 (2H) and 5.87 ppm (2H). The spectrum of acetylferrocene in 60% H_2SO_4 comprises four singlets: 2.47 (CH_3), 4.55 (C_5H_5), 5.12 (H(3,4)), and 5.63 ppm (H(2,5)). The latter two resonances were assigned by reference to the assignments made for the unprotonated ketones [12] which were deduced unambiguously from the spectrum of 2,5-dideuteroferrocenecarboxaldehyde. The result suggests that the major factor which determines the chemical shift is the anisotropy of the carbonyl function, and not charge delocalisation onto the oxygen atom which would cause deshielding of the H(3,4) protons, as is the case for the corresponding carbenium ions [8]. Thus resonance effects from the Cp ring appear to be rather small, a conclusion supported by the evidence cited earlier from $pK(BH^+)$ measurements. For the aromatic series, Cp Fe $C_5H_4CO\text{-}C_6H_4\text{-}X$, the chemical shifts in CF_3CO_2H are uniformly between 0.5 and 0.6 ppm upfield from those in 70% H_2SO_4. This is possibly a simple medium effect but could also be due to ion pairing in CF_3CO_2H which has a very much lower dielectric constant. Comparison of this NMR data with those of the corresponding carbenium ions reveals some interesting trends. For the latter the H_3 and H_4 protons are systematically more strongly deshielded as the *para* phenyl substituent becomes more electron withdrawing whereas the opposite trend is found for the protonated ketones. A similar though less marked relative behaviour is apparent with H_2 and H_5 protons. For the carbenium ions the deshielding of the H_3, H_4 protons is due in part to the conjugate withdrawal of Cp ring electron density. The geometry of the carbenium ions and protonated ketones is very similar, in particular both systems suffer H_2, H_5—H_A compressions which necessitate the rotation of one or both ring systems out of coplanarity [1]. Steric inhibition to resonance was also observed in protonated benzophenones. Hammett plots of pK_a values for substituted acetophenones [13] and benzaldehydes yielded ρ values of 2.17

and 1.85 respectively [14]. For benzophenones however a value of 1.09 was obtained indicating greatly reduced overlap of ring and carbonyl orbitals. In view of the evidence against a large resonance contribution from the Cp ring, it is tempting to postulate a large dihedral angle, ϕ, between the Cp ring and the carbonyl plane, the protonated ketone then being stabilised by the phenyl ring. However, this in no way explains the fact that ferrocenyl ketones are some five orders of magnitude more basic than their acetophenone analogues. Nor does the answer to the problem lie in coordination of the acidic proton on the carbonyl to the central iron atom since the chemical shift of a proton in this environment is —2.0 ppm as opposed to the observed value of about 12 ppm. It seems likely that a compromise is arrived at as in the case of the carbenium ions, where both ring systems incline to the central sp^2 plane. It is interesting in this context to compare the chemical shift difference (δ(AB)) between the aromatic protons *ortho* (H_A) and *meta* (H_B) to the carbonyl group for the protonated ferrocenyl ketones and the ferrocenyl carbenium ions with those for the corresponding acetophenones [15] (Table 3).

In the latter seires, the full resonance effect of *para* substituents can operate. It is clear from the data in Table 3 that δ(AB) is independent of the acidic medium. Also δ(AB) values for the ferrocenyl carbenium ions and protonated ferrocenyl ketones are very similar but significantly smaller than those for the acetophenones. This again points to a degree of non-coplanarity between the phenyl ring system and carbonyl orbitals. In all three systems δ(AB) correlate reasonably well with σ^+ values but the slope of the plot for the acetophenones

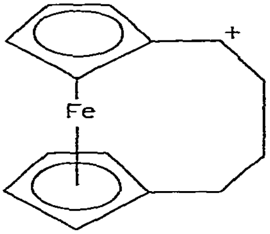
TABLE 3

CHEMICAL SHIFTS (δ in ppm) OF H_A AND H_B PROTONS FOR *para* SUBSTITUTED FERROCENYL PHENYL KETONES $C_5H_5FeC_5H_4COC_6H_4X$, CARBENIUM IONS $C_5H_5FeC_5H_4\overset{+}{C}HC_6H_4X$ AND THE CORRESPONDING ACETOPHENONES IN STRONGLY ACIDIC MEDIA (A, CF_3CO_2H; B, 70% H_2SO_4; C, FSO_3H)

p-X	Acid	H_A	H_B	δ(AB)
Ferrocenyl ketones				
MeO	A	7.55	6.65	0.90
Me	A	7.30	6.90	0.40
Me	B	8.03	7.65	0.38
Cl	A	7.37	7.05	0.32
Cl	B	7.95	7.62	0.33
CN	A	7.53	7.53	0.00
CN	B	8.12	8.12	0.00
Ferrocenyl carbenium ions [a]				
MeO	A	7.40	6.60	0.80
Me	A	7.22	6.83	0.39
Cl	A	7.18	6.92	0.26
CN	A	7.33	7.33	0.00
Acetophenones [b]				
MeO	C	8.80	7.56	1.24
Me	C	8.58	7.78	0.80
Cl	C	8.57	7.90	0.67

[a] Ref. 1. [b] Ref. 15.

(—0.65) is significantly greater than that of either the ferrocenyl carbenium ions (—0.46) or the protonated ferrocenyl ketones (—0.50). δ Values for the cyclopentadienyl protons in the latter series are almost independent of the nature of the substituent, whereas for the carbenium ions a systematic trend to lower field was found as electron withdrawal increased. Thus resonance effects between the phenyl ring and the carbonyl function appear small, and the origins of the enhanced basicity of the ferrocenyl ketones remain unclear. Ortaggi and coworkers [16] have recently reported on the stability of [4]-ferrocenophane 6-, and 7-carbenium ions and their corresponding protonated ketone analogues.



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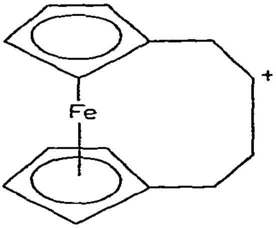
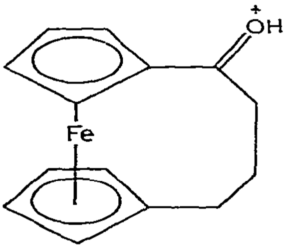


(III)

The pK(R$^+$) values of II and III were found to be very similar (0.15 and 0.10 respectively). No isomerisation of III to II was observed. For the corresponding protonated ketones IV and V the difference in pK_a is relatively small (IV —2.5, V —4.0). In both systems the authors conclude that the positive charge is extensively delocalised into the ferrocenyl group via iron participation. For a coplanar ferrocenyl carbenium (ϕ = o) overlap can occur with either ring based (ϵ_1) or iron based (ϵ_2) orbitals. As ϕ increases due to steric hindrance from the *ortho* protons of the phenyl ring for the aromatic derivatives, ϵ_2 overlaps will decrease much more rapidly than the ϵ_1 overlaps which use d_{xz}, d_{yz} orbitals of the iron atom and are stereoelectronically much better placed to maintain overlap. This point will be returned to in the discussion of the Mössbauer results. 1,1′-Ferrocenyl diketones monoprotonate readily to form a species in which the added proton is probably held by hydrogen bonding between the two acyl groups in a *syn* conformation. Addition of a second proton is consequently difficult (p$K_a < -9$) [6]. The NMR spectrum of diacetylferrocene in CF_3CO_2H shows a sharp singlet (6H) at 2.03 ppm for the methyl groups and two triplets at 4.33 and 4.50 ppm. The corresponding dialcohol in CF_3CO_2H shows two separate methyl resonances (doublets) at 1.13 and 1.83 ppm corresponding to mono-



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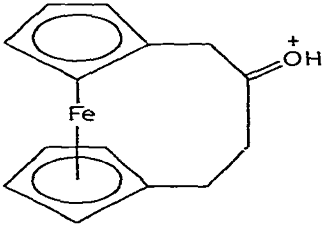


(V)

carbenium ion formation. Trifluoroacetic acid is far too weak to double protonate diacetylferrocene. The appearance of only one methyl resonance supports the hydrogen bonded structure described above. Further evidence supporting such a species comes from Mössbauer data (vide infra).

In 98% H_2SO_4, diacetylferrocene gives a sharp singlet at 2.75 ppm (6H) and two rather broad singlets at 5.51 and 5.70 ppm which represents a downfield shift of 1.3 ppm compared with δ values in CF_3CO_2H. This is too great to be a medium effect, and is likely to be due to diprotonation. 98% sulphuric acid has a H_o value of —10.2 [11] and is probably strong enough to effect diprotonation. Dibenzoylferrocene in CF_3SO_3H gives very similar Cp ring resonances to those in 98% H_2SO_4. Trifluoromethanesulphonic acid ($H_o = -14.6$ [17]) is a much stronger acid than sulphuric acid and thus diprotonation is confirmed. Clear supportive evidence comes from the Mössbauer data discussed in the following section.

Mössbauer spectroscopy

Mössbauer spectra of frozen solid CF_3CO_2H solutions of the ferrocenyl ketones were run and compared with those of the solid ketones or frozen acetic acid solutions of the ketones. The results appear in Table 4. There were no significant differences in isomer shifts for all the compounds studied. No major

TABLE 4

^{57}Fe MÖSSBAUER PARAMETERS FOR SOME SOLID FERROCENYL KETONES ($C_5H_5FeC_5H_4COR$, $Fe(C_5H_4COR)_2$) AND FOR THEIR FROZEN SOLUTIONS IN STRONGLY ACIDIC MEDIA (at 80°K)

R	Solvent	QS (mm s^{-1})	IS (mm s^{-1})	ΔQS [a]
Monoketones				
CH_3	solid	2.27(1)	0.54(1)	—
CH_3	H_2SO_4 [b]	2.08(2)	0.53(1)	0.15
CH_3	CF_3CO_2H	2.10(1)	0.54(1)	0.17
C_6H_5	solid	2.26(1)	0.54(1)	—
C_6H_5	CH_3CO_2H	2.24(1)	0.54(1)	—
C_6H_5	CF_3CO_2H	2.15(1)	0.55(1)	0.11
p-CH_3-C_6H_4	solid	2.23(1)	0.56(1)	—
p-CH_3-C_6H_4	CF_3CO_2H	2.08(2)	0.55(1)	0.17
p-CH_3O-C_6H_4	solid	2.24(1)	0.53(1)	—
p-CH_3O-C_6H_4	CF_3CO_2H	2.10(1)	0.53(1)	0.14
p-Cl-C_6H_4	solid	2.25(1)	0.53(1)	—
p-Cl-C_6H_4	CF_3CO_2H	2.10(1)	0.56(1)	0.15
p-CN-C_6H_4	solid	2.26(2)	0.52(1)	—
p-CN-C_6H_4	CF_3CO_2H	2.22(3)	0.54(2)	0.04
Diketones				
CH_3	solid	2.14(5)	0.54(1)	—
CH_3	CF_3CO_2H	2.09(1)	0.52(1)	—
CH_3	H_2SO_4	1.79(1)	0.55(1)	0.35
CH_3	CF_3SO_3H	1.78(2)	0.52(1)	—
C_6H_5	solid	2.17(1)	0.53(1)	—
C_6H_5	CF_3CO_2H	2.08(2)	0.53(1)	—
C_6H_5	H_2SO_4	1.85(2)	0.55(1)	0.32

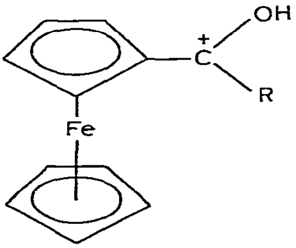
[a] ΔQS = QS(solid) — QS(strong acid). [b] 98% Analar H_2SO_4.

difference in quadrupole splitting (QS) was observed between solids and frozen solutions of weakly acidic media (acetic acid). The QS values for acetylferrocene in CF_3CO_2H and 98% H_2SO_4 are identical within experimental error showing that protonation in CF_3CO_2H was complete.

The monoketones as a whole show significantly lower QS (2.24—2.27 mm s^{-1}) than ferrocene (2.40 mm s^{-1}) [18,19]. This phenomenon is commonly exhibited by conjugated electron withdrawing substituents. The unprotonated diketones display even lower QS values (2.14—2.17 mm s^{-1}). The effect can be seen to be roughly additive, a lowering of about 0.12 mm s^{-1} occurring for each carbonyl substituent. On protonation these effects become more pronounced, with an average lowering of QS per protonated carbonyl of about 0.28 mm s^{-1}. Again the effect is approximately additive which is evidence supporting diprotonation. The QS values (1.78—1.85 mm s^{-1}) for the diprotonated species are the lowest yet reported for ferrocene derivatives. In view of the lower QS values observed, withdrawal of the electron density is unlikely to occur via iron-based orbitals ϵ_2, since it has been amply demonstrated that such withdrawal results in substantial increases in QS values; (viz. 3.09 mm s^{-1} for ferrocene—$HgCl_2$ complexes [20], 2.6—2.8 mm s^{-1} for iron-protonated ferrocenes [18]). The lower QS values observed for the protonated ferrocenyl ketones also rules out any interactions between the oxygen-bound proton and the central iron atom.

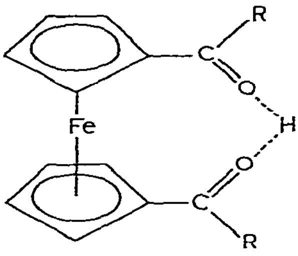
Any electron withdrawal therefore seems to occur via ring-based orbitals (ϵ_1) which, if such is the case, makes Mössbauer spectroscopy a valuable probe for investigating subtle electron redistributions in substituted ferrocenes and related derivatives. The ΔQS values (= QS(solid) — QS(protonated ketone)) tend to decrease with increasing electron withdrawing power of the *para* substituents in the aromatic derivatives. This could be accounted for by some participation by iron-based orbitals when the aromatic ring can no longer provide any resonance stabilisation. The effect is particularly noticeable for the *para* cyano derivative.

The low QS values also rule out carbenium ion structures such as VI since these ions have been shown to have QS values greater than ferrocene itself.



(VI)

This is further substantiated by the observation that at room temperature the H_2, H_5 protons are magnetically equivalent whereas separate resonances occur for the corresponding carbenium ions [2]. Thus the barrier to partial rotation about the Cp—C_{exo} bond must be very much lower than that of the corresponding carbenium ion such that the "tick-tock" motion is extremely rapid on the NMR time scale. At 80°K this motion will be frozen out but Mössbauer spec-



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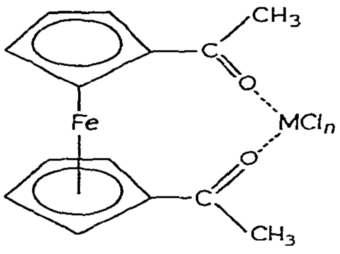

(M = Ti, Fe; n = 4 or 3)

(VIII)

troscopy cannot distinguish between the resulting conformers. The structure put forward for monoprotonated ferrocenyl diketones (VII) receives some justification from the Mössbauer spectra of metal complexes of the type VIII [21] where the diketone acts as a bidentate ligand. QS values of 2.04—2.08 mm s^{-1} have been found [22] which are almost identical to that of diacetylferrocene in CF_3CO_2H (2.09 mm s^{-1}).

The reason for the extraordinary basicity of the ferrocenyl ketones however remains elusive. Some stabilisation is likely via the Cp rings but this would not account for the large effects observed. One of the few remaining possible explanations is that the basicity is governed by direct field effects of the Cp rings creating a favourable electric field gradient at the carbonyl oxygen. Such effects are, of course, not uncommon, and have been invoked to explain the greater difference between the two acid dissociation constants of protonated diacetylferrocene [6].

Experimental

Trifluoroacetic acid was redistilled from P_2O_5 prior to use. Analar 98.0% H_2SO_4 (SG 1.84 BDH) was used without further purification.

The ferrocenyl ketones were synthesised by a standard literature method [23]. NMR spectra were run on a Varian EM-360 instrument (probe head at 28.4°). Solutions of the ketones were made at 0.5 *M*. In the case of the sulphuric acid work, the acid media were made up by carefully adding the concentrated acid to ice-cooled D_2O in the appropriate weight proportions. The ferrocenyl ketones were then dissolved in the resultant cold acid mixture and the NMR spectrum run within 5 min of preparation using external TMS as reference.

The Mössbauer techniques have been reported in detail elsewhere [24]. Solutions of the ketones in 98% H_2SO_4 were frozen immediately after preparation to avoid sulphonation.

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