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PROTONATION OF ACYLFERROCENES WITH SbF_5—FSO_3H IN SO_2ClF SOLUTION

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Summary

Protonation of acylferrocenes in weak superacids shows stable oxygen and iron diprotonated species.

Olah and Mo [1] studied the protonation of a series of monoacylferrocenes in FSO_3H—SO_2ClF solution, and concluded that oxygen protonation predominates in this medium but that protonation at carbon gains in importance with increasing temperature. No indication of protonation at the iron atom was found. We considered it of interest to reinvestigate this problem by use of stronger superacids in order to measure the barrier to rotation around the Fc—CO bond and throw more light on the protonation sites. We found that formyl-, acetyl-, chloroacetyl- and benzoyl-ferrocene dissolved in $FSO_3H/SbF_5/SO_2ClF$ (molar ratio 8 : 1 : 20, acid A) to give stable diprotonated species, for which oxygen and iron protonation can be observed by NMR under slow exchange conditions. Stronger acids (higher SbF_5 concentration) give less stable solutions and in a weaker acid ($FSO_3H/SbF_5/SO_2ClF$, molar ratio 14 : 1 : 20, acid B) the proton on iron exchanges with the acid solvent. The molar ratio of base to acid was in all cases about 1 : 10.

In acid B at —80°C ferrocenaldehyde showed a spectrum similar to that reported by Olah and Mo [1], with signals from protons 2 and 5 at higher field than those from protons 3 and 4. In the stronger acid A (see Fig. 1), however, a crossover had occurred, and the 3 and 4 protons gave a singlet while the 2 and 5 protons gave a doublet at lower field (Table 1). The assignment is based on a

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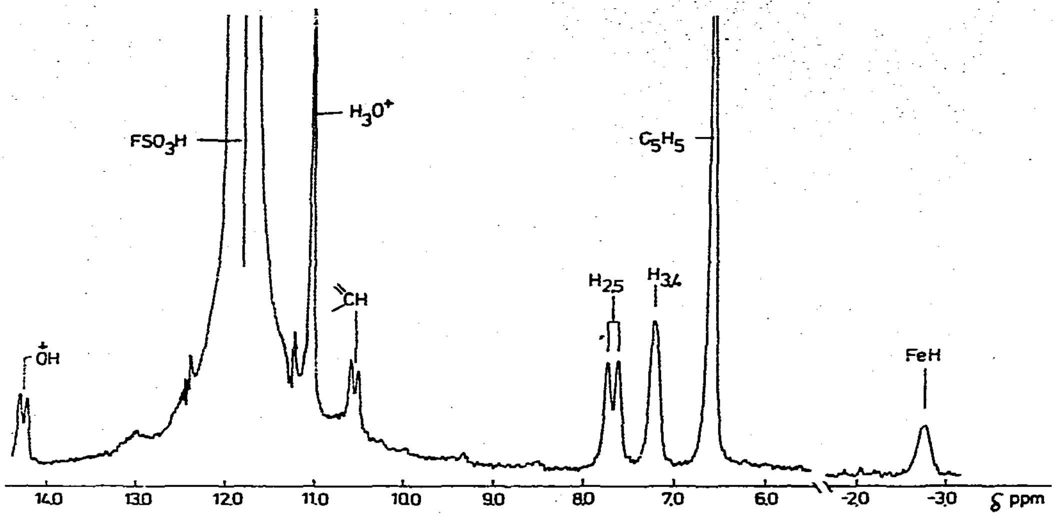
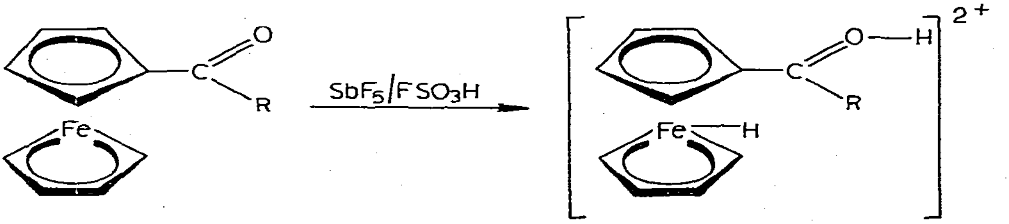


Fig. 1. 100 MHz ^{1}H NMR spectrum of formylferrocene in acid A.

comparison with the spectrum of the 2(5)-deuterio analog [2]. Inm contrast to the spectra in FSO_3H, the spectra in acid A show no fine structure, probably due to the viscosity of the solvent.

The spectrum in acid A displayed an *AB* quartet at low field due to the formyl (H_A) and OH (H_B) protons (δ_A 10.5 ppm, δ_B 14.2 ppm, J_{AB} = 8 Hz). This *J*(HCOH) value indicates *E* configuration for the protonated carbonyl group (for the *Z* form *J*(HCOH) would be ca. 20 Hz [3]). A broad singlet at δ —2.7 ppm ($\Delta w_{1/2}$ 14 Hz) was assigned to a proton attached to the iron atom [4].

When the temperature was raised, the spectrum was unchanged until at about —40°C decomposition set in and all the signals rapidly disappeared. In acid B no signals due to protonation on iron or oxygen were observed.



(I) (II)

Acetylferrocene showed the same spectrum in acid B as in FSO_3H. The strong charge delocalisation into the ferrocenyl ring is indicated by the $C{=}OH^+$ chemical shift, δ 11.2 ppm, in agreement with monoprotonation on oxygen. In acid A, however, the $C{=}OH^+$ proton is shifted downfield to δ 14.7 ppm and the Fe—H proton is detected at —2.7 ppm, consistent with stable diprotonation. The protons of the substituted ring appear in the same order in both acids.

With increasing temperature the signals due to the protons in the substituted ring showed exchange broadening, and coalescence was observed for the 3 and 4

TABLE 1

NMR DATA AND FREE ENERGY VALUES OF FORMYL-, ACETYL- AND CHLOROACETYL-FERROCENE

R	δ(2,5) [a] (ppm)	δ(3,4) (ppm)	δ(R) (ppm)	δ(OH) (ppm)	δ(FeH) (ppm)	$\Delta G_{I}^{\neq}$ (kcal mol^{-1}) [b]	$\Delta G_{II}^{\neq}$ (kcal mol^{-1}) [b]
H (—71°C)	7.6, 7.7	7.2	10.5	14.2	—2.7	8.8 [d]	>12.0
CH_3 (—91°C)	6.8, 7.2	7.6, 7.8	3.9	14.7	—2.2	8.5 [d]	10.0 (H_3,H_4)
CH_2Cl (—78°C)	7.0, 7.1	7.8, 7.7	6.0 [c]	14.6	—2.3	8.1	9.8

[a] In acid A, ppm downfield from external TMS. [b] At coalescence temperature. [c] In acid B, δ_A 5.65, δ_B 5.44, J_{AB} 16 Hz. [d] See ref. 8.

H signals at —76° C and for the 2 and 5 H signals at —62° C. The coalescence approximation applied to these data gives different free energy barriers (Table 1), which may reflect the increase in rate of exchange of the iron-bound proton with increasing temperature. Decomposition occurred above —30° C.

Chloroacetylferrocene behaved in general like the acetyl analog, though the 3H—4H and 2H—5H chemical shifts were the same. The chloromethylene protons gave an *AB* quartet in acid B, which coalesces at —75° C, which gives the same free energy of activation as the coalescence of the 2,5 and 3,4 proton pairs. Evidently the averaging process is the same for all protons, viz. the rotation of the protonated chloroacetyl group, which gives the molecule a time-averaged plane of symmetry. No fixed conformation of the chloromethyl group is required to explain the nonequivalence of its protons [5]. In acid A no resolved *AB* quartet was observed.

Benzoylferrocene also showed stable diprotonation (on the carbonyl oxygen and iron atoms) in acid A, whereas in acid B only monoprotonation can be detected in the NMR spectrum.

Protonation of aromatic aldehydes and ketones with "magic acid" in general leads to a doubling of the free energy barrier to rotation of the RCO ($RC\overset{+}{O}H$) group [6,7]. This is evidently not the case with acetyl- and chloroacetyl-ferrocene (Table 1), because of the protonation at iron. This decreases the electronic charge density in the cyclopentadienide ring and diminishes its interaction with the protonated acyl group. The higher barrier in the diprotonated ferrocenaldehyde is not yet completely understood, but it is hoped that a ^{13}C NMR investigation will shed light on this problem.

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