

## PROTONATION OF DIFERROCENYL KETONE\*

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### SUMMARY

Solutions of diferrocenylketone,  $(C_{10}H_9Fe)_2CO$ , have been studied by nuclear magnetic resonance, UV/visible absorption, and infrared spectroscopic methods. In chloroform solution the ketone itself has been characterised, but in chloroform to which small amounts of trifluoroacetic acid have been added there is evidence for formation of the monocarbonium ion  $(C_{10}H_9Fe)_2\overset{+}{C}OH$ . The characteristic PMR spectrum of this ion has been obtained from pure trifluoroacetic acid solution of the ketone. Further protonation of this monocarbonium ion may have resulted in the production of the dicarbonium ion  $(C_{10}H_9Fe)_2C^{2+}$ .

### INTRODUCTION

It is well-established<sup>1</sup> that an unusual degree of positive charge delocalisation is achieved in the  $\alpha$ -metallocenylcarbonium ions. A number of stable salts of such monocarbonium ions have been isolated<sup>1,2</sup>, and stable dicarbonium ions of the type  $Fc-\overset{+}{C}R-C_6H_4-\overset{+}{C}R-Fc$ <sup>3,4</sup>, with Fc being the ferrocenyl residue,  $C_{10}H_9Fe$ , and R being H or  $C_6H_5$ , and  $Fe[Cp\overset{+}{C}(CH_3)_2]_2$ <sup>5</sup>, with Cp being the cyclopentadienyl residue, also have been prepared and identified. However, no dicarbonium ion wherein both positive charges reside formally on the same carbon atom has been characterised. The work reported here was aimed at utilising the excellent charge-delocalising properties of the ferrocenyl moiety to this end.

### EXPERIMENTAL

Diferrocenyl ketone,  $(C_{10}H_9Fe)_2CO$ , was prepared from ferrocenemono-carboxylic acid<sup>6</sup> by conversion to the acid chloride, using oxalyl chloride, followed by a Friedel-Crafts condensation with ferrocene<sup>7</sup>. The final product was purified by chromatography on basic alumina and recrystallisation from benzene, giving a red coloured material with melting point 209–211° (Lit. value<sup>8</sup>, 211–212°).

Proton magnetic resonance spectra were obtained using a Varian A-60 spectrometer, equipped with a model V-6040 variable temperature controller. Ab-

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sorption spectra in the ultraviolet and visible regions were obtained using Perkin-Elmer model 137 UV and Cary 14 spectrophotometers, with 1 cm path length cells. Infrared spectra were run on the Perkin-Elmer model 237 instrument.

## RESULTS

In Fig. 1 are reproduced the essential features of the PMR spectra of solutions of diferrocenyl ketone,  $\text{Fc}_2\text{CO}$ , in deuteriochloroform (A) and trifluoroacetic acid (B) solvents. The former solution was an orange colour, while the latter was deep blue.

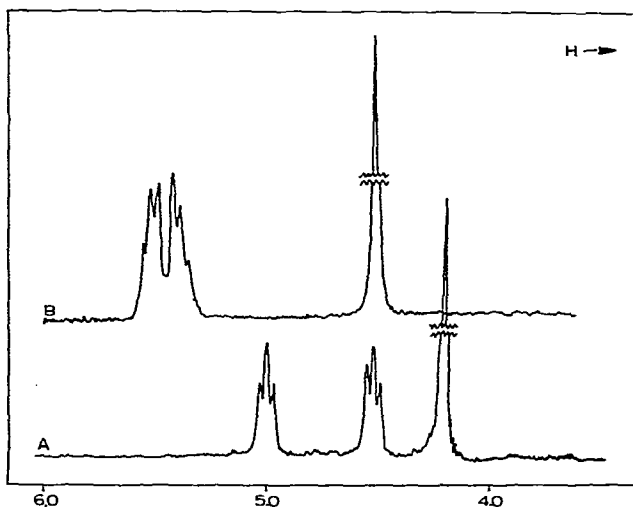


Fig. 1. Proton magnetic resonance spectra of solutions of diferrocenyl ketone,  $(\text{C}_{10}\text{H}_9\text{Fe})_2\text{CO}$ . A.  $\text{CDCl}_3$  solution; B.  $\text{CF}_3\text{CO}_2\text{H}$  solution. Chemical shifts in ppm relative to TMS.

Each solution gave sharp, well-defined PMR bands, consisting of an intense singlet (relative intensity 5) and a pair of triplets (each of relative intensity 2) at lower field, these triplets interacting due to similar chemical shift values in the case of the  $\text{CF}_3\text{-CO}_2\text{H}$  solution spectrum. The chemical shifts of the bands are given in Table 1, together with the spin-spin coupling constants obtained from the multiplet structures of the low-field bands.

Fig. 2 shows the effect on the PMR spectrum of  $\text{Fc}_2\text{CO}$  in  $\text{CDCl}_3$  solution (A) of addition of successive small amounts of  $\text{CF}_3\text{CO}_2\text{H}$  (B to G). The solution changed

TABLE I

PROTON CHEMICAL SHIFTS<sup>a</sup> AND COUPLING CONSTANTS FROM DIFERROCENYL KETONE,  $(\text{C}_{10}\text{H}_9\text{Fe})_2\text{CO}$ , IN DEUTEROCHLOROFORM AND TRIFLUOROACETIC ACID SOLUTIONS

Solvent	$\delta(\text{C}_5\text{H}_5)$ (ppm)	$\delta(\text{H}^{2,5})$ (ppm)	$\delta(\text{H}^{3,4})$ (ppm)	$J(\text{H}^{2,5}-\text{H}^{3,4})$ (cps)
$\text{CDCl}_3$	-4.20	-5.00	-4.52	2.0
$\text{CF}_3\text{CO}_2\text{H}$	-4.48	-5.36	-5.47	2.0

<sup>a</sup> Chemical shift values referred to a tetramethylsilane internal standard in each case.

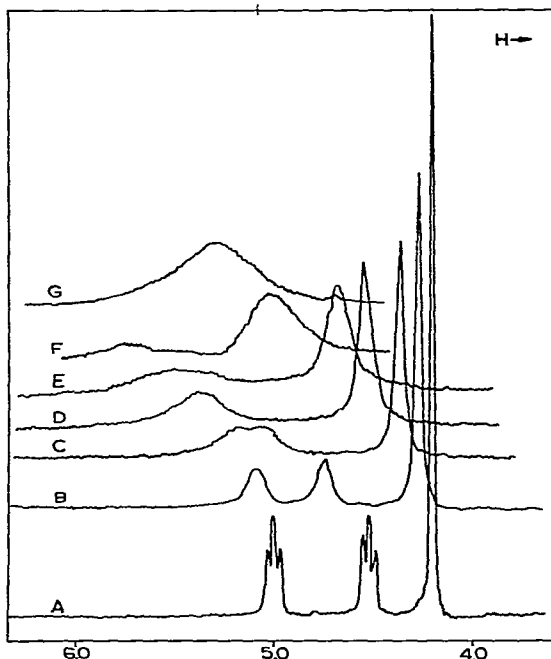


Fig. 2. Proton magnetic resonance spectra of solutions of diferrocenyl ketone in  $\text{CDCl}_3$  (A), and in  $\text{CDCl}_3$  with successively increasing amounts of  $\text{CF}_3\text{CO}_2\text{H}$  added (B to G).

from an orange colour through a deep red to a very deep blue as acid was added, and the PMR bands all shifted progressively to lower field. Together with the low-field shifts, all bands showed progressive broadening, and no fine-structure was determinable. At the highest acid concentration (approx. 2/1,  $\text{CF}_3\text{CO}_2\text{H}/\text{CDCl}_3$ ) the low-field bands had broadened to such an extent that they could no longer be distinguished from the background, and only the higher-field band was discernable, though this too was greatly broadened. Cooling the acidic solutions to  $-15^\circ$  (freezing point of  $\text{CF}_3\text{CO}_2\text{H}$  is  $-15.2^\circ$ ) did not produce significant sharpening of the bands.

Spectrum D of Fig. 2 is seen to correspond roughly to spectrum B of Fig. 1 (i.e. pure  $\text{CF}_3\text{CO}_2\text{H}$  solution of  $\text{Fc}_2\text{CO}$ ), though all the bands are much broadened in Fig. 2D. However, it was observed that on standing, bands in the spectra from pure  $\text{CF}_3\text{CO}_2\text{H}$  solutions also broadened, the rate of broadening varying from one solution to another, depending on concentration. Furthermore, addition of one drop of anhydrous sulphuric acid to such a  $\text{CF}_3\text{CO}_2\text{H}$  solution resulted in an immediate large increase in the band broadening, accompanied by down field shifts of the type shown in Fig. 2E, F and G.

Investigation of the UV/visible absorption spectra of  $1.05 \cdot 10^{-4} M$  solutions of  $\text{Fc}_2\text{CO}$  in  $\text{CHCl}_3$ , in  $\text{CF}_3\text{CO}_2\text{H}$ , and in mixtures of these two solvents, produced the family of curves shown in Fig. 3. The important result here is the successive formation of two isosbestic points, the first at 432 nm occurring at very low acid concentration, the second at 530 nm forming only at relatively high acid concentration. It was found that the transitions through intermediate spectral types were reversible, and a solution obtained by neutralisation of the acid in a strongly acidic  $\text{CF}_3\text{CO}_2\text{H}/$

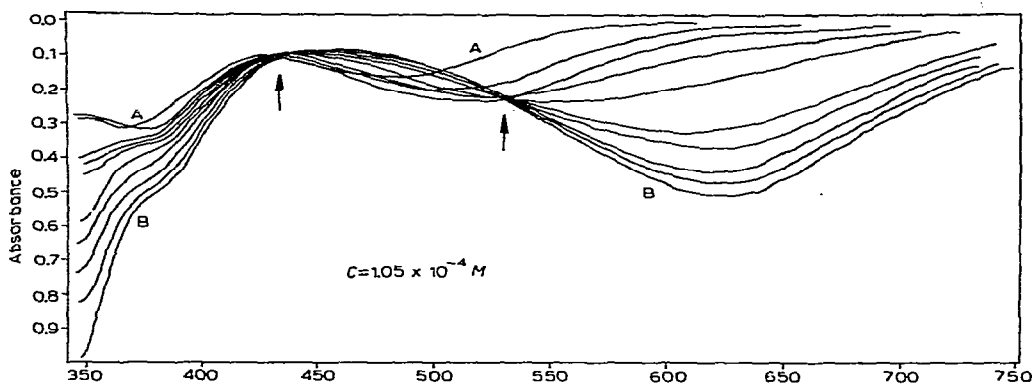


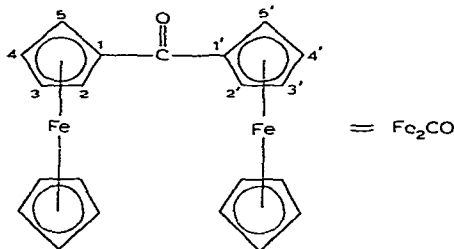
Fig. 3. Absorption spectra in the UV/visible region of solutions of diferrocenyl ketone in  $\text{CHCl}_3$  (A), and in  $\text{CHCl}_3/\text{CF}_3\text{CO}_2\text{H}$  (1 : 2) (B).

$\text{CHCl}_3$  solution with aqueous bicarbonate gave a spectrum identical with that given by a fresh  $\text{CHCl}_3$  solution. Similarly, a more concentrated  $\text{CHCl}_3$  solution (ca. 10%, as used for PMR work) after acidification with an equal volume of  $\text{CF}_3\text{CO}_2\text{H}$ , followed by neutralisation with aqueous bicarbonate, gave back the starting material, as shown by thin-layer chromatography.

The infrared spectrum of  $\text{Fc}_2\text{CO}$  in  $\text{CHCl}_3$  solution showed a strong ketonic carbonyl absorption at  $1630\text{ cm}^{-1}$ . This disappeared completely upon addition of  $\text{CF}_3\text{CO}_2\text{H}$  to the solution. However, very strong absorption of infrared radiation by the deep blue solutions prevented further use of the spectra for diagnostic purposes.

## DISCUSSION

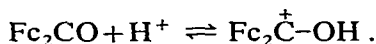
The PMR spectrum of diferrocenyl ketone in  $\text{CDCl}_3$  solution, reproduced in Figs. 1 and 2, is assigned in Table 1 by analogy with other monosubstituted ferrocene derivatives<sup>9</sup>. Electron withdrawing substituents cause lower-field chemical shifts of the  $\alpha$ -protons (H-2 and H-5) than of the  $\beta$ -protons (H-3 and H-4) in the substituted cyclopentadienyl rings<sup>9</sup>. Relative band intensities establish unambiguously that the



—4.20 ppm signal arises from the unsubstituted rings. The two triplets, nearly identical in appearance, centered at  $-5.00$  and  $-4.52$  ppm, approximate those expected for an  $\text{A}_2\text{M}_2$  system, thus indicating that protons H-2 and H-5 (and likewise H-3 and H-4) can be considered both chemically and magnetically equivalent. Recognising that the ketonic carbon is  $sp^2$  hybridised,  $\pi$ -electron interaction between the two ferrocenyl residues via the carbonyl group would be expected to impose co-planarity on the

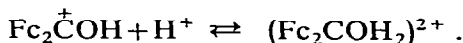
entire system of atoms 2, 3, 4, 5, C, O, 2', 3', 4', 5', distorted only by the fact of steric interaction between hydrogen atoms at positions 2 and 2' (or 2 and 5' if one ferrocenyl residue is rotated 180° with respect to the other). However, inspection of simple molecular models shows that this arrangement is unlikely since it should lead to inequivalence of H-2 and H-5, and probably also H-3 and H-4, as already established for some carbonium ion derivatives of the type  $\text{Fc}\overset{+}{\text{C}}\text{HPh}$ , where four separate signals are generated by the protons of the substituted cyclopentadienyl (Cp) ring<sup>10</sup>.

The appearance of an isosbestic point in the UV/visible absorption spectra at 432 nm, corresponding with the elimination of the ketonic carbonyl absorption from the infrared spectrum, suggests protonation of the diferrocenyl ketone in dilute  $\text{CF}_3\text{CO}_2\text{H}$  in chloroform to form a hydroxycarbonium ion, as follows:

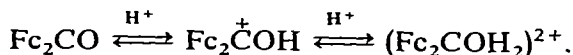


The proton exchange equilibrium implied in this reaction is presumed to be responsible for the line broadening and loss of fine structure in the PMR spectra of  $\text{CDCl}_3$  solutions of  $\text{Fc}_2\text{CO}$  to which  $\text{CF}_3\text{CO}_2\text{H}$  was added (Fig. 2). In the presence of excess acid complete conversion to the hydroxycarbonium ion evidently occurs, and the PMR spectrum is again sharp and distinct, as shown in Fig. 1. The assignment of bands given in Table 1 with H-2, H-5 protons absorbing at higher fields relative to the H-3, H-4 protons, is made by analogy with previous studies of ferrocenyl monocationium ions with deuterium or methyl group substitution for the  $\alpha$ -protons<sup>11</sup>. The double triplet structure of the low-field band is less symmetrical in appearance, this being due probably to overlap of the accidentally similar chemical shifts in the  $\text{CF}_3\text{CO}_2\text{H}$  solvent. This accidental near-degeneracy of the chemical shifts makes it difficult to decide on the magnetical equivalence of each of the two pairs of protons in the substituted ring. However, stepwise addition of acid to a  $\text{CDCl}_3$  solution of  $\text{Fc}_2\text{CO}$  did not result in a PMR spectrum of the form shown in Fig. 1B, even when the acid was present in large excess. Instead, the downfield shifts of all the proton signals were observed to progress beyond the values believed to characterise the monocationium ion  $\text{Fc}_2\overset{+}{\text{C}}\text{OH}$ , the broadening of the bands also increasing further as more acid was added.

The fact that the observed chemical shifts in an intermediate spectrum, Fig. 2D, correspond roughly with those of  $\text{Fc}_2\overset{+}{\text{C}}\text{OH}$  shown in Fig. 1B, suggests that the increasing down field shifts of the proton resonances are due to a further protonation of the hydroxycarbonium ion, as follows:



Again the proton exchange equilibrium between the mono- and di-protonated forms could account for the line broadening. The UV/visible absorption provides supporting evidence for this second protonation, in that the second isosbestic point, shown in Fig. 3 at 530 nm, formed only with those solutions containing acid concentrations well in excess of the  $\text{Fc}_2\text{CO}$  concentration. This suggests successive equilibria:



Moreover, the gradual loss of fine structure and increase in line widths observed in the spectrum from pure  $\text{CF}_3\text{CO}_2\text{H}$  solution of  $\text{Fc}_2\text{CO}$ , attributed to  $\text{Fc}_2\overset{+}{\text{C}}\text{OH}$ , can

be rationalised by slow formation of the diprotonated species in this medium.

It remains only to comment on the structure of the diprotonated species. Most interesting would be the form  $\text{Fc}_2\text{C}^{2+}$ , resulting from loss of water from  $(\text{Fc}_2\text{COH}_2)^{2+}$ , but our results do not allow us to distinguish between these two species, making further speculation unprofitable. The absence of doublet splitting of the signals from the unsubstituted cyclopentadienyl ring protons eliminates the possibility of metal protonation in these systems<sup>12</sup>. Future work should be aimed at isolating the diprotonated species, probably by use of more highly acidic media such as the  $\text{SO}_2/\text{SbF}_5/\text{HSO}_3\text{F}$  reagent<sup>13</sup>. It is clear that at most we have only a mixture of mono- and di-carbonium ions in trifluoroacetic acid.

#### ACKNOWLEDGEMENT

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