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Preliminary communication

PROTONATION OF HOMOTROPONEIRON TRICARBONYL AND CYCLOOCTATRIENONEIRON TRICARBONYL COMPLEXES

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Summary

2,3-Homotroponeiron tricarbonyl, 8-methyl- and 8,8-dimethyl-2,3-homotroponeiron tricarbonyl complexes have been shown to undergo *O*-protonation in trifluoroacetic (TFA) and 96% sulfuric acids. In the latter acid the *O*-protonated cations rearrange to give the thermodynamically more stable *C*-protonated isomers. Cyclooctatrienoneiron tricarbonyl undergoes protonation in H_2SO_4 to give the same cation as was obtained from the protonation of the homotroponeiron tricarbonyl complex in H_2SO_4. On the basis of reactions in D_2SO_4, it is suggested that the kinetically preferred site of protonation of the cyclooctatrienone complex is at C(2) one of the coordinated carbon atoms.

There has recently been considerable interest in the protonation of troponeiron tricarbonyl (I) [1,2,3]. While some details of these reactions remain unclear, the major sequence of events appears to be an initial, kinetically controlled proton transfer to the carbonyl oxygen of I, followed by an isomerization of the protonated species to the thermodynamically preferred, *C*-protonated cation (III) [2]. In contrast to this behaviour, cycloheptadienoneiron tricarbonyl, IV, is reported to undergo only *O*-protonation to give V [3].

In view of the above differences in behaviour and with the potential of "cyclopropyl walk" reactions in mind [4], we have examined the protonation of various 2,3-homotroponeiron tricarbonyl complexes.

The homotropone complexes VI, VII and VIII [5] each dissolved in trifluoroacetic acid (TFA) to give blood red solutions of the *O*-protonated cations IX to XI, respectively. The assignment of the structures of these cations was made on the basis of their ^1H NMR spectra (Table 1) which showed the resonances of the ring protons to be shifted downfield on protonation in comparison with their neutral precursors. The magnitude of the proton, proton coupling constants

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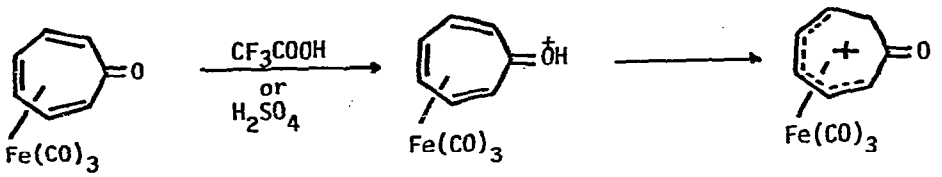
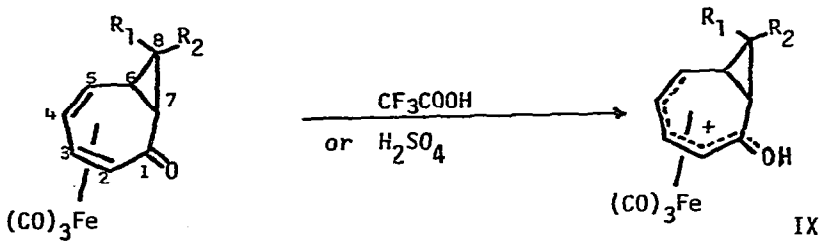


I II III

IV V

varied little between the original complexes and their *O*-protonated derivatives. The shifts observed on protonation are similar to these previously reported for the *O*-protonation of I and IV [2,3].



VI $R_1 = R_2 = H$

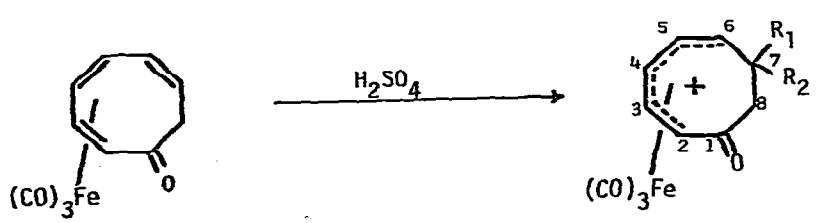
VII $R_1 = H$, $R_2 = CH_3$

VIII $R_1 = R_2 = CH_3$

IX $R_1 = R_2 = H$

X $R_1 = H$, $R_2 = CH_3$

XI $R_1 = R_2 = CH_3$



XV

XII $R_1 = R_2 = H$

XIII $R_1 = H$; $R_2 = CH_3$

XIV $R_1 = R_2 = CH_3$

TABLE 1

^{1}H NMR SPECTRA OF CATIONS[a]

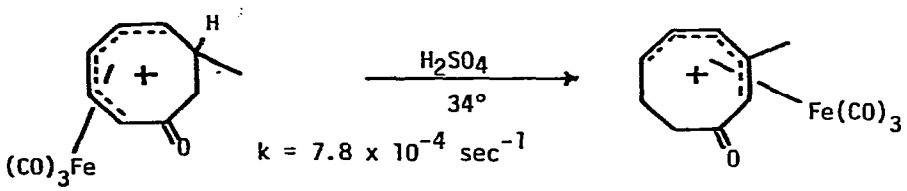
Cation	Solvent	Chemical shift (ppm)[b]								Coupling constant (Hz)					
		H(2)	(H(3)	H(4)	H(5)	H(6)	H(7)		H(8)	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6,7}$	J(Me,H)
IX	TFA	3.40 (d)	6.69 (t)	5.53 (dd)	3.80 (t)	2.84 (bt)	1.90 (m)		1.90 (m)	6	6	9	9	7.5	—
XII	H_2SO_4	4.03[d] (d)	6.87 (t)	7.87 (t)	6.20 (dd)	5.60 (bd)	3.43 (m)	3.43[d] (m)	2.28[d] (bd) 1.82[cd] (bd)	7.5	7.5	8	11	8	—
X	TFA	3.46 (d)	6.69 (m)	5.59 (dd)	3.97 (bt)	2.72 (dd)	1.79 (m)		2.27 (m) (0.86) (d)	7	6	8	8	—	6
XIII	H_2SO_4	3.96 (d)	6.92 (t)	7.86 (t)	6.23 (t)	5.56 (bt)	3.69 (m)	(1.72) (d)	2.16 (m) 2.16 (m)	7.5	7.5	8	10.5	—	6
XVI	H_2SO_4	3.09 (s)	(2.82) (s)	7.79 (d)	6.20 (bt)	5.68 (bd)	3.53 (m)		2.36 (m) 1.89 (m)	—	—	7.5	11	—	—
XI	TFA	3.56 (d)	6.85 (t)	5.86 (dd)	3.84 (t)	2.99 (t)	2.00 (d)		(1.22) (s) (1.06) (s)	7	7	9	9	9	—
XIV	H_2SO_4	4.07 (d)	6.89 (t)	7.83 (t)	6.07 (dd)	5.58 (d)	(1.66) (s)	(1.46) (s)	2.00 (m) 2.00[c] (m)	8	7.5	7.5	11	—	—

[a]Numbers in parentheses represent methyl group resonances. s, singlet; d, doublet; t, triplet; m, multiplet; b, broad. [b]Shifts referred to internal $(CH_3)_4N^+ BF_4^-$ taken as δ 3.10 ppm. [c]Signals absent in D_2SO_4. [d]Signals absent in generation of XII by solution of XV in D_2SO_4.

The TFA solutions of these cations were stable and no thermally induced isomerizations could be detected. For example, no change was seen in the ^1H NMR spectrum of XI when the NMR sample was heated to +60°C for 30 min. This thermal stability contrasts markedly with the ready isomerization of the *O*-protonated tropone complex, II, to III at 0°C [2] and also with the facile cyclopropyl walk type rearrangements of protonated 8,8-dimethyl-2,3-homotropone itself [4]. No deuterium incorporation could be detected (other than on oxygen) when these protonations of VI to VIII were carried out in deuterated TFA. The starting homotroponeiron complexes were recovered on neutralization of the TFA.

When 96% H_2SO_4 was used for the protonation of VI, VII and VIII further reactions occurred. Examination of the ^1H NMR spectra of these H_2SO_4 solutions at sub-ambient temperatures showed that in each case the initially formed cation was the *O*-protonated species. As the solutions were warmed, however, these cations isomerized to the more stable *C*-protonated ions XII, XIII and XIV, respectively. The structural assignments of cations XII, XIII and XIV were made on the basis of their ^1H NMR spectra (Table 1) and also by the independent generation of XII by the protonation of the cyclooctatrienone complex XV [6]. The half-life for the isomerization of IX to XII was 3 min at −10°C; for X to XIII was 4 min at +5°C; and for XI to XIV was 3 min at +34°C. Dissolution of VI, VII and VIII in D_2SO_4 led to the formation of XII, XIII and XIV with the incorporation of a single deuterium atom at C(8). Further deuterium exchange of these cations was very slow at 34°C.

Cation XIII rearranged at room temperature. This isomerization occurred cleanly to give a new cation which was assigned the structure XVI on the basis of its ^1H NMR spectrum (Table 1).



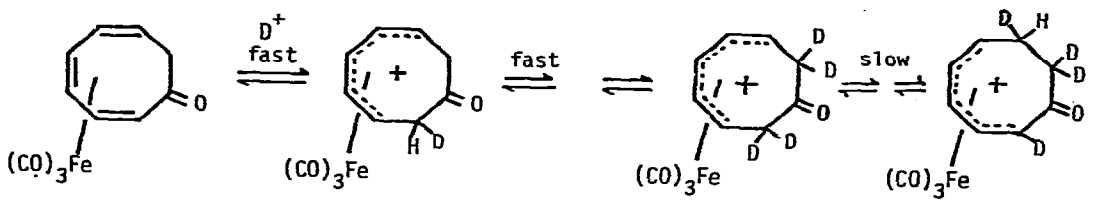
XIII XVI

Examination of the solution obtained on dissolving XV in D_2SO_4 by ^1H NMR showed that the formation of XII occurred with the incorporation of four deuterium atoms which were located at C(2), C(7) and two at C(8). Since the experiments with the homotropone complexes described above showed that deuterium exchange at C(2) and C(8) of XII to be very slow in D_2SO_4, then it must be concluded that rapid deuterium exchange occurs with XV at these sites before a deuteron is added at C(7) and XII produced.

One possible way* in which this deuterium exchange could occur is that in addition to a possible *O*-protonation of XV in H_2SO_4, a kinetically controlled,

*A referee has suggested that an alternative way to account for the deuterium incorporation results would be via an acid catalysed enolization of XV to give hydroxycyclooctatetraeneiron tricarbonyl which could undergo proton—deuterium exchange and rapid valence tautomerism. At this present stage we have no evidence to distinguish between the two possibilities.

reversible protonation also occurs at C(2) to give the symmetrical cation XVII. Eventual protonation at this uncoordinated C(7) position of XV would lead to the thermodynamically stable cation XII. There is some question in the protonation of troponeiron tricarbonyl whether the proton attachment occurs at the coordinated or uncoordinated double bond. If the mechanism suggested above is correct then it would mean that the rate of proton attack on XV is much faster at the coordinated rather than the free double bond.



XV XVII

The results obtained on the protonation of the homotropone complexes bear a marked similarity to those found for the tropone complex. However, *C*-protonation with the homotropones now requires a proton be joined to an sp^3 hybridized carbon and it would appear that a stronger acid (H_2SO_4) than TFA is required to induce protonation at this site.

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