Redox Behaviour and Mössbauer Spectra of Some Dinuclear Bridged Sulphido-derivatives of Iron

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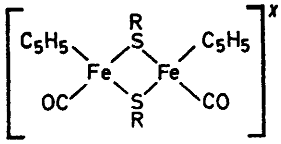
Summary The reversible oxidation of *cis*- and *trans*-$[Fe(\pi\text{-}C_5H_5)(CO)SR]_2$ to *cis*- and *trans*-$[Fe(\pi\text{-}C_5H_5)(CO)SR]_2^+$ and *cis*- and *trans*-$[Fe(\pi\text{-}C_5H_5)(CO)SR]_2^{2+}$ is reported and discussed.

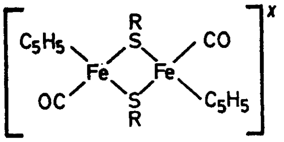
CONSIDERABLE attention has been focussed of late on bridged sulphido-derivatives of iron in view of the possible relevance of the chemistry of these species to that of the non-haeme iron protein systems termed ferredoxins. It has been established by a number of groups that $[Fe(\pi\text{-}C_5H_5)(CO)SMe]_2$ (I; R = Me) is readily oxidised electrochemically[1] and by reagents such as iodine[2] and silver salts[2-4] to paramagnetic $[Fe(\pi\text{-}C_5H_5)(CO)SMe]_2^+$ (II; R = Me). We have now observed that this oxidation is effected by oxygen in acidic media and in particular that passage of air through a suspension of (I; R = Me) in dilute hydrochloric or acetic acid containing excess of $NaBF_4$ gives the water-soluble derivative (II; R = Me),BF_4^- according to equation (1). Significantly this reaction is reversible and addition of OH^- to an aqueous solution of (II; R = Me),BF_4^- results in the separation of the neutral parent compound (I) from solution. The reduction is also effected by bases such as hydrazine, piperidine, and diethylamine in both aqueous

$$4[Fe(\pi\text{-}C_5H_5)(CO)SMe]_2 + O_2 + 4H^+ \rightarrow 4[Fe(\pi\text{-}C_5H_5)(CO)SMe]_2^+ + 2H_2O \qquad (1)$$

and non-aqueous, but not rigorously anhydrous, media. Water is essential for the reduction, establishing that the base functions as a proton acceptor and not as a reducing agent. Sodium amalgam, sodium borohydride, and a large excess of iodide ions are also effective.



cis-(I); $x = 0$
cis-(II); $x = +1$
cis-(III); $x = +2$



trans-(I); $x = 0$
trans-(II); $x = +1$
trans-(III); $x = +2$

The redox cycle (I) ⇌ (II) is stereoselective and, for instance, oxidation of the *cis*-isomer of (I; R = alkyl or aryl)† affords *cis*-(II) only. Similarly reduction of *trans*-(II) yields *trans*-(I).

Cyclic voltammograms of a number of compounds of types (I) and (II) exhibited, as well as the cycle (I) ⇌ (II) discussed above, a second cycle considerably more anodic in potential which we assign to equilibrium (2). The dication-

$$[\mathrm{Fe}(\pi\text{-}\mathrm{C_5H_5})(\mathrm{CO})\mathrm{SR}]_2{}^{+} - \mathrm{e} \rightleftharpoons [\mathrm{Fe}(\pi\text{-}\mathrm{C_5H_5})(\mathrm{CO})\mathrm{SR}]_2{}^{2+} \qquad (2)$$

ic species $[\mathrm{Fe}(\pi\text{-}\mathrm{C_5H_5})(\mathrm{CO})\mathrm{SR}]_2{}^{2+}$ (III) is readily obtained chemically by treatment of (I) with excess of bromine in solution and is isolated from solution by precipitation with large counteranions such as $\mathrm{PF_6}^-$. Significantly (III; R = Me),$(\mathrm{BF_4}^-)_2$ is also produced by passing air through an aqueous solution of (II), $\mathrm{BF_4}^-$ and excess of $\mathrm{NaBF_4}$ at pH $<2{\cdot}0$. The reduction of (III) to (II) is readily effected, not only by those reagents discussed above, but by weak reducing agents such as $\mathrm{BPh_4}^-$. The formation of (III) is also stereoselective and both *cis*- and *trans*-isomers of (III) have been observed.†

Mössbauer spectra were obtained at 77 K for the parent compounds (I; R = Me or Et) and for the derivatives (II; R = Et),$\mathrm{SbF_6}^-$ and (III; R = Me or $\mathrm{Pr^i}$),$(\mathrm{PF_6}^-)_2$. In each case only two sharp lines representing a quadrupole-split doublet were observed, consistent with equivalence of the two iron environments. The Mössbauer parameters are given in the Table. The removal of one electron from the neutral compound reduces the chemical isomer shift only slightly, whereas the removal of the second electron apparently has a greater effect. Nevertheless the trend indicates that oxidation is accompanied by an increase in the *s* electron density at the iron nuclei. The contribution from the metal *d* orbitals to the filled molecular orbital of highest energy in the neutral compound therefore predominates over any contribution from metal *s* orbitals.

Table

Compound[a]	Chemical isomer shift[b] δ/(mm s^{-1})	Quadrupole splitting Δ/(mm s^{-1})	Width at half-height Γ/(mm s^{-1})
(I; R = Me)	$0{\cdot}31 \pm 0{\cdot}01$	$1{\cdot}63 \pm 0{\cdot}01$	0·30, 0·30
(I; R = Et)	$0{\cdot}30 \pm 0{\cdot}01$	$1{\cdot}69 \pm 0{\cdot}01$	0·32, 0·33
(II; R = Et), $\mathrm{SbF_6}$	$0{\cdot}29 \pm 0{\cdot}01$	$1{\cdot}45 \pm 0{\cdot}01$	0·32, 0·31
(III; R = Me), $(\mathrm{OF_6})_2$	$0{\cdot}24 \pm 0{\cdot}01$	$1{\cdot}61 \pm 0{\cdot}01$	0·31, 0·30
(III; R = $\mathrm{Pr^i}$), $(\mathrm{PF_6})_2$	$0{\cdot}25 \pm 0{\cdot}01$	$1{\cdot}64 \pm 0{\cdot}01$	0·28, 0·28

[a] Primarily the *cis* isomer. [b] Relative to metallic iron at 295 K.

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† A wide range of compounds of the type *cis*- and *trans*-$[\mathrm{Fe}(\pi\text{-}\mathrm{C_5H_5})(\mathrm{CO})\mathrm{SR}]_2$(anion) and *cis*- and *trans*-$[\mathrm{Fe}(\pi\text{-}\mathrm{C_5H_5})(\mathrm{CO})\mathrm{SR}]_2(\text{anion})_2$ (R = alkyl or aryl) have been synthesised and fully characterised.

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