

Multiple Oxidation States in Iron Cluster Compounds

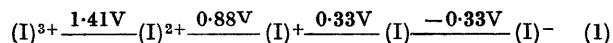
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Summary Electrochemical studies indicate that the cluster system $[(\pi\text{-C}_5\text{H}_5)\text{FeS}]_4$ remains intact in the oxidation states +3, +2, +1, 0, and -1 and $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$ in the oxidation states +2, +1, 0, and -1.

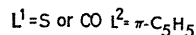
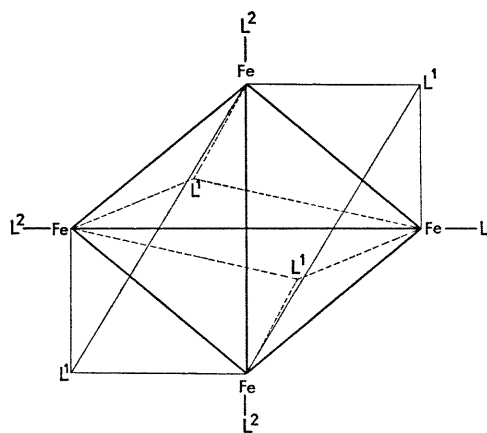
THE two cyclopentadienyl iron cluster compounds $[(\pi\text{C}_5\text{H}_5)\text{FeS}]_4$ (I)¹ and $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$ (II)² have similar structures with the four iron atoms arranged as a tetrahedron (Figure). We have studied the electrochemical properties of the two cluster compounds partly as an extension of our earlier work on the chemical and electro-chemical oxidation of compounds containing iron metal-metal bonds.³

Solutions of the monocation, $[(\pi\text{-C}_5\text{H}_5)\text{FeS}]_4^+$ or of the dication, $[(\pi\text{-C}_5\text{H}_5)\text{FeS}]_4^{2+}$, can be conveniently prepared by the suspension oxidation of (I) [at +0.60 or +1.20 V respectively *vs.* saturated sodium chloride calomel electrode (SSCE)] in hot MeCN at a platinum electrode using $\text{NH}_4\text{-PF}_6$ as supporting electrolyte. From these solutions the salts $[(\pi\text{-C}_5\text{H}_5)\text{FeS}]_4(\text{PF}_6)$ or $[(\pi\text{-C}_5\text{H}_5)\text{FeS}]_4(\text{PF}_6)_2$ have been isolated in 60–70% yields. The salts are stable to light and air. The monocation, $[(\pi\text{-C}_5\text{H}_5)\text{FeS}]_4^+$, is paramagnetic and gives a very broad n.m.r. signal centred at τ 4.23 (acetone τ 7.93) and an e.s.r. spectrum at room temperature in dichloromethane gives $g = 1.980$. The dication, $[(\pi\text{-C}_5\text{H}_5)\text{FeS}]_4^{2+}$, is diamagnetic and has a sharp proton resonance at τ 3.99. Cyclic voltammograms of $[(\pi\text{-C}_5\text{H}_5)\text{FeS}]_4^{2+}$ at a platinum bead electrode have four electrochemically reversible waves indicating that the cluster remains intact in five distinct oxidation states. $E_{1/2}$ values relating the various oxidation states [*vs.* SSCE in 0.1M-Bu₄NPF₆ (TBAH) acetonitrile solution, uncorrected for junction potentials] are given in equation (1). Attempts



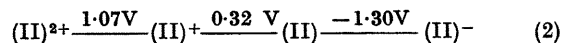
to prepare $[(\pi\text{-C}_5\text{H}_5)\text{FeS}]_4^-$ and $[(\pi\text{-C}_5\text{H}_5)\text{FeS}]_4^{3+}$ electrochemically have been unsuccessful. Oxidation of $[(\pi\text{-C}_5\text{H}_5)\text{FeS}]_4^{2+}$ to the trication results in catalytic oxidation of either trace amounts of water or solvent, passage of large amounts of current, and eventual decomposition to Fe^{3+} .

From cyclic voltammetric measurements we also find that tetrakis(π -cyclopentadienylironcarbonyl) (II) exists in the



FIGURE

three additional electrochemically reversible oxidation states: -1, +1, and +2. In 0.1M TBAH-acetonitrile solution, the $E_{1/2}$ values relating the various oxidation states (*vs.* SSCE at Pt electrode, uncorrected for junction potentials) are given in equation (2).



Controlled potential electrolysis of (II) at a platinum electrode at +0.70 V vs. SSCE in a 0.1 M-TBAH-dichloromethane solution gives the salt $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4(\text{PF}_6)$ in 85% yield. In contrast to the halide and polyhalide salts previously reported,^{1,4} this salt is soluble in polar organic solvents. It is paramagnetic, with $\nu(\text{CO}) = 1695\text{ cm}^{-1}$ (CH_3CN). Solutions of the air-sensitive, paramagnetic anion $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4^-$ [$\nu(\text{CO}) = 1576\text{ cm}^{-1}$ and $g = 2.013$ (CH_3CN)], have been prepared by the electrochemical reduction of the cation at platinum in acetonitrile. It

reacts rapidly with oxygen to give (II). Attempts to prepare the dication of (II), $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4^{2+}$, electrochemically in MeCN resulted in catalytic oxidation of trace amounts of water and ultimate decomposition to Fe^{2+} and $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{NCCH}_3)]^+$.

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