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Reactions of Ferrocene With Iodine

by

N. GÜNDÜZ, B.C. SMITH, PJ. TURNER and MARGUERITE A. WASSEF

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Reactions of Ferrocene With Iodine

N. GÜNDÜZ, B.C. SMITH, PJ. TURNER and
MARGUERITE A. WASSEF

Department of Chemistry, Birkbeck College (University of London), Malet Street, London WCIE 7HX, England

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ABSTRACT

Ferrocene reacts rapidly with iodine in 1, 2- dichloroethane to form an intermediate, cp_2FeI_4, which is converted slowly into ferricinium tri-iodide, cp_2FeI_3. Both products are isolated as violet-brown paramagnetic crystals.

INTRODUCTION

Ferrocene, cp_2Fe, is a potential π- electron - donor [1], which absorbs weakly in the ultraviolet and visible regions of the spectrum [2]: ν_{max} 30, 700 cm^{-1}, $\epsilon \sim 50$; ν_{max} 22, 700 cm^{-1}, $\epsilon \sim 100$. Iodine is a well-known electron - acceptor, which forms violet solutions in nondonor solvents [3]: ν_{max} 19, 200 cm^{-1}, ϵ 950. The positions and intensities of these bands are unchanged when dilute equimolar solutions of ferrocene and iodine in n-hexane are mixed together ($\sim 10^{-4}$ mole / litre) showing that interaction is negligible under these conditions.

When similar solutions of ferrrocene and iodine in 1, 2- dichloroethane are mixed together there is an immediate brown colouration. Strong absorption bands, characteristic of polyiodide anions [3], appear at 34.000 and 27,600 cm^{-1}. Their optical den sities increase over a period of several hours at room temperature. Plots of the reciprocal of concentration against time are linear, showing that the formation of polyiodide obeys a second order rate law. Extrapolation of the straight lines indicates that finite

quantities of polyiodide are present in all solutions at the time of mixing.

Equimolar solutions of ferrocene and iodine in 1,2 - dichloroethane (1.5×10^{-4} mole / litre) were investigated by Job's method of continuous variation [3]. Optical densities at 34.000 and 27,600 cm^{-1} were plotted against mole fraction of the components. The maxima at the time of mixing correspond to the composition cp_2 Fe, $2I_2$, whereas the maxima at equilibrium correspond to the composition cp_2 Fe, $1{,}5I_2$. This suggests that an intermediate, cp_2FeI_4, is formed rapidly on mixing, and is converted slowly into cp_2FeI_3.

A more concentrated solution of ferrocene (5.3×10^{-3} mole) and iodine (7.8×10^{-3} mole) in 1,2 - dichloroethane (200 ml) gave crystals of violet - brown cp_2Fe, $2I_2$, decomp. 182°, which were removed by filtration. (Found: C, 17.2; H, 1. 35; I, 73.5 % C_{10} H_{10} FeI_4 requires C, 17,3 ; H. 1.45; I, 73.20) Decomposition occurred on attempted sublimation under reduced pressure, giving iodine and violet-brown crystalline ferricinium tri-iodide [4], decomp. 192°. (Found: C, 21.3; H, 1.7; I, 67. 5. Calc. for $C_{10}H_{10}FeI_3$: C, 21.2; H, 1.8; I, 67. 2 %) Ferricinium tri-iodide was obtained also by slow crystallisation from the mother-liquor ($\sim$ 4 days). (Found: C, 21.3; H, 1.9; I. 66.8 %).

Several samples of cp_2FeI_4 and cp_2FeI_3, and products of intermediate compositions, were prepared by cyrystallisation from 1, 2- dichloroethane. Their magnetic susceptibilities, measured at room temperature by the Faraday method, are in the range $3.8 - 4.2 \times 10^6$ cgsu. The effective magnetic moment of iron, corrected for diamagnetic contributions, corresponds to that expected from one unpaired electron. It is clear that these crystalline samples all contain ferricinium cations.

Nesmeyanov and his co-workers [5] prepared cp_2FeI_{20}, which recrystallises from acetone to give cp_2FeI_6. Brand and Sneddon [6] prepared cp_2FeI_5, and suggested that such compounds should be regarded as ferricinium polyiodides. The compound cp_2FeI_4 has not been reported previously, but the crystal structure of

cp_2FeI_3 by Bernstein and Herbstein [4] confirmed the presence of ferricinium cations and tri-iodide anions.

It is concluded that rapid reaction between ferrocene and iodine in 1, 2- dichloroethane gives an intermediate of the type $cp_2FeI^+ I^{3-}$, which causes the initial brown colouration in solution. Electron-transfer on crystallisation produces paramagnetic ferricinium cations, cp_2Fe^+, together with I^{3-} and I^{5-} anions, or I_8^{2-} anions *cf.*, Cs_2I_8 [7]. A second order reaction in solution produces ferricinium tri-iodide. Higher polyiodides are obtained with an excess of iodine.

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ÖZET

Ferrosen 1,2 diklor etan içinde, iyotla hemen reaksiyona girerek Cp_2FeI_4 ara maddesini verir. Bu madde de yavaş yavaş ferrisiniyum triiyodür, Cp_2FeI_3 bileşiğine dönüşür. Her iki bileşik te viyole kahverengi paramagnetik kristaller halinde izole edildi.

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