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The Preparations and Properties of Ferricinium Polyiodides

By

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Solid Polyiodides of the composition, Cp_2FeI_3, Cp_2FeI_4 and Cp_2FeI_5 are obtained from the reactions of ferrocene and iodine in 1,2-dichloroethane. Some physical properties of these compounds are investigated.

INTRODUCTİON.

It is reported that ferrocene is a potential π - electron-donor.[1–3] Previous investigations[1] indicate that when equimolar solutions of ferrocene and iodine in 1,2-dichloroethane are mixed together, there is a direct change in colour; and two distinct new bands appear.

This work deals with the preparations of ferricinium polyiodides and the study of some of their properties.

EXPERİMENTAL.

Ultraviolet and visible spectra were recorded on a Veb Carl Zeiss Jena Specord. Infrared spectra were recorded on a Unicam SP200G. Spectrophotometer. Molecular weights[4] were measured using a vapour pressure osmometer Model 301A. Conductivities were measured using Beckman apparatus model RA-2A with balance indicator.

Starting materials: (a) 1,2-dichloroethane (BDH) spectrograde, (b) Ferrocene, m.p. 173 °C[5] (BDH) and (c) iodine, (Prolapo) were used after sublimation.

Preparations of the Polyiodides. The reactions between ferrocene and iodine solutions in the mole ratios ranging from 1:1 to 1:3 gave only one product; the ferricinium triiodide, decomp. 192°C The compounds, Cp_2FeI_4 and Cp_2FeI_5 were obtained by mixing stoichiometric quantities of ferrocene and iodine solutions.

Action of stannous chloride: The addition of stannous chloride to solutions of the ferricinium polyiodides, causes reduction of the cation, Cp_2Fe^+, to ferrocene, Cp_2Fe.

Results and Discussion

The absorption spectra of the polyiodide solutions show two maxima at 294 nm. and 270 nm. Fig. 1 and 2. The molar absorptivity values, ϵ, of the polyiodide solutions at these two bands are are given in the table.

Table 1.

Compound	ϵ(mole^{-1}mm.$^{-1}$) at λ_{max} 294	ϵ(mole^{-1}mm.$^{-1}$) at λ_{max}. 370	conc. (mg.L)
1-Cp_2FeI_3	93.23x 10^2	38 x 10^2	15–78
2–Cp_2FeI_4	50.5 x 10^3	24.4 x 10^3	6.5–16.2
3–Cp_2FeI_5	109.9 x 10^2	51.5 x 10^2	16–41

Neither ferrocene solution[6] nor iodine solution in 1,2-dichloroethane absorbs at these wavelengths.

It is notable that ϵ has very high values. Similar large magnitude of ϵ is reported.[8] Other polyiodides of the type Me_3PNI_3, Me_3PNI_5 and KI_3, show absorption bands nearly in the same region of the spectra. This indicates that ferricnium polyiodides dissociate in 1,2-dichloroethane to give I_3^- and Cp_2Fe^+. Evidence for the presence of Cp_2Fe^+ cation was found by the reucing action of stannous chloride on solutions of the ferricinium polyiodides.[11]

Both bands obey Beer's law in the concentration range recorded in Table 1.

The infrared spectra of ferricinium polyiodides are all notably similar to each other and to the spectrum of ferricinium tetrachlorogallate, Cp_2Fe, $GaCI_4$, which contains the ferricinium cation.[11]

Molecular weight determination of ferrocene solution in 1,2-dichloroethane shows that it is a monomer. Similar results are reported for ferrocene using other solvents.[12] The molecular weight determination of Cp_2FeI_3 indicates that there two ions in the solution corresponding to Cp_2Fe^+ and I_3^-. This in accordance with the inoization suggested by Gündüz et al[1].

Conductivity measurements of the polyiodide solutions in 1,2-dichloroethane in the concentration range equivalent to 0.3-2 / L, showed that all the polyiodide solutions are good conductors. Ferrocene solution proved to be non-electrolyte.

It is concluded that the polyiodides Cp_2FeI_3, Cp_2FeI_4 and Cp_2FeI_5 all dissociate in solutions to give ferricinium cation and the polyiodide anion. The compound Cp_2FeI_3 was found to be the most stable crystalline polyiodide.

It was of our interest to carry out similar reactions using bromine, but we found that the reaction between bromine and ferrocene was very vigorous and catch fire.

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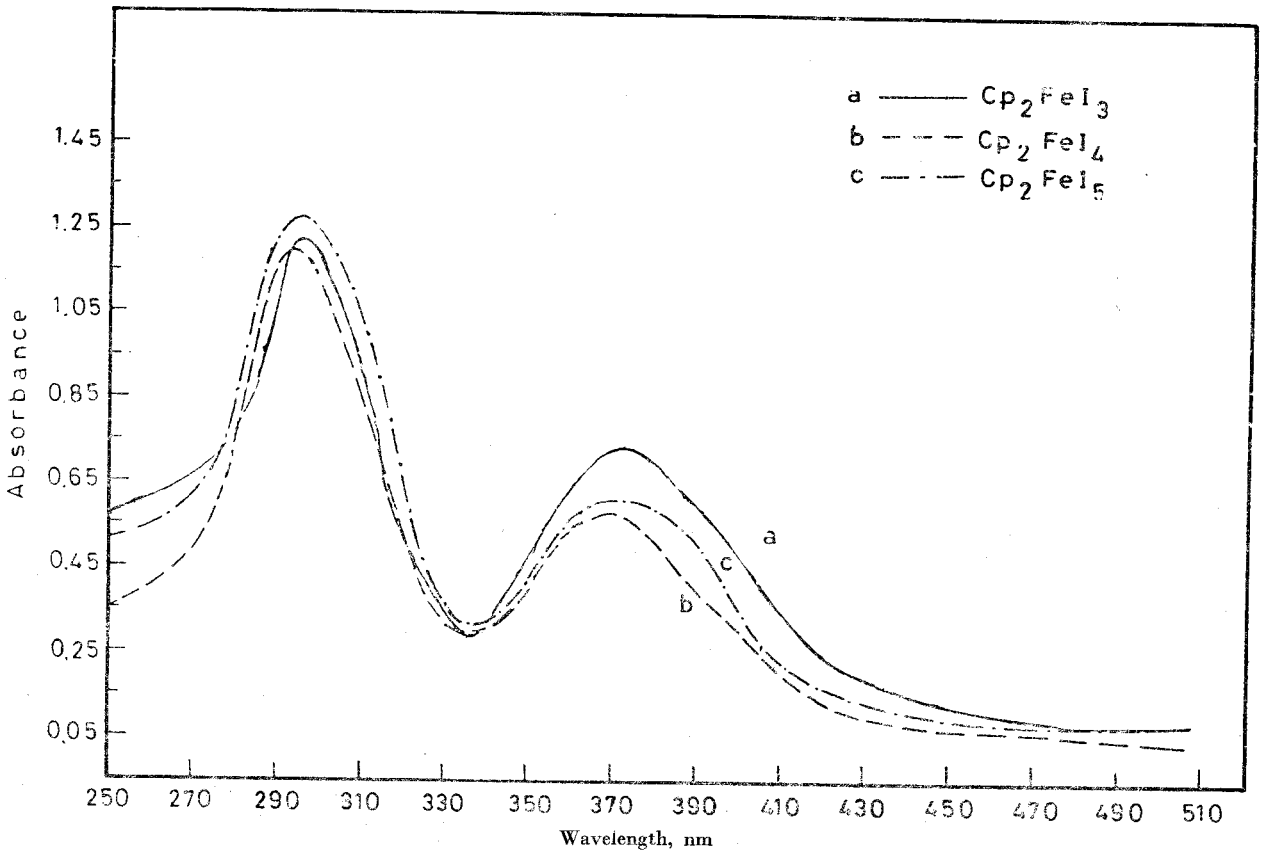

Fig. (1) The relation between the absorbance and wavelength for the ferricinium triodide, ferricinium tetraiodide and ferricinium pentaiodide.

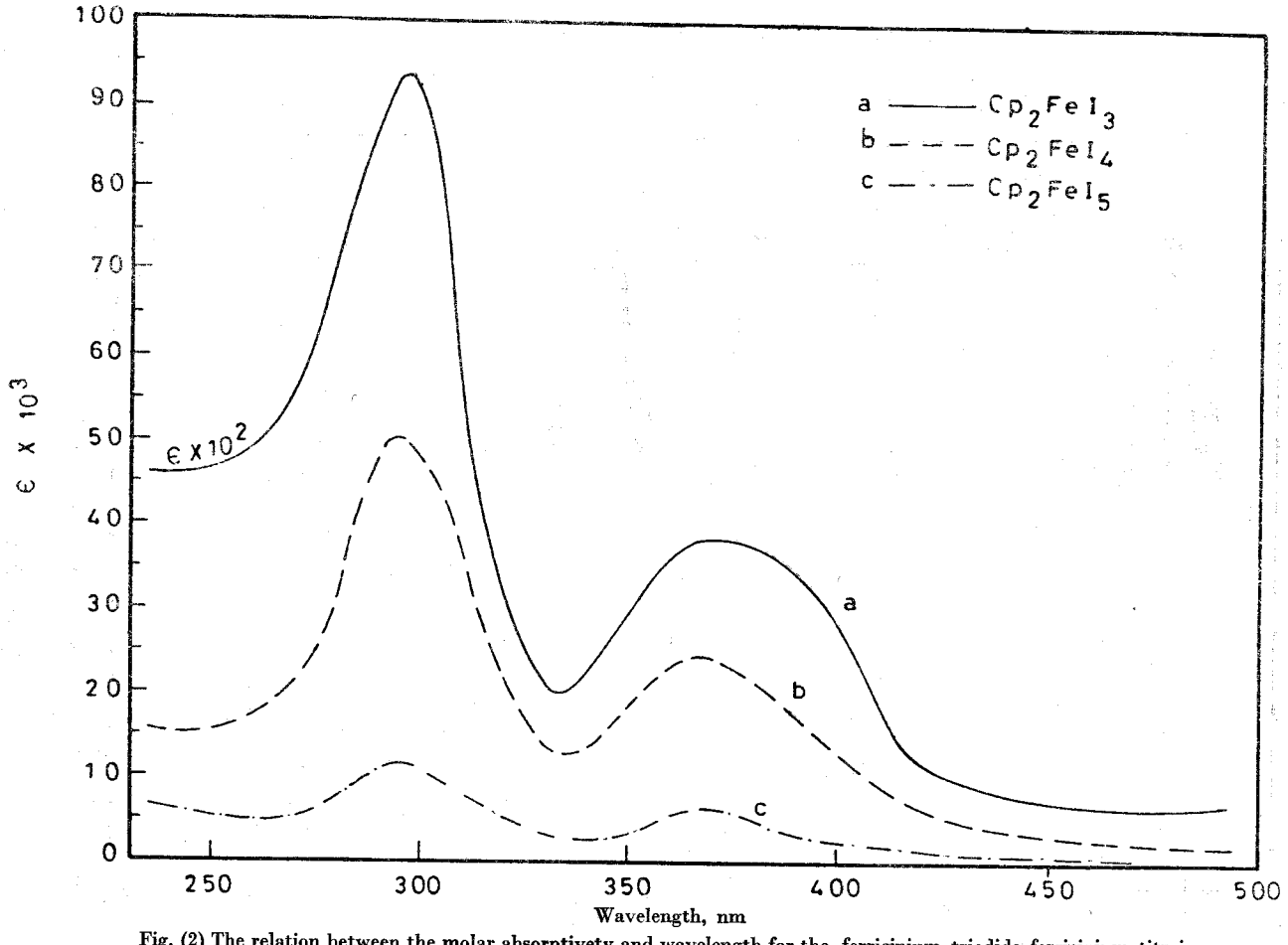

Fig. (2) The relation between the molar absorptivety and wavelength for the ferricinium triodide ferricinium titraiodide and ferricinium pentaiodide.

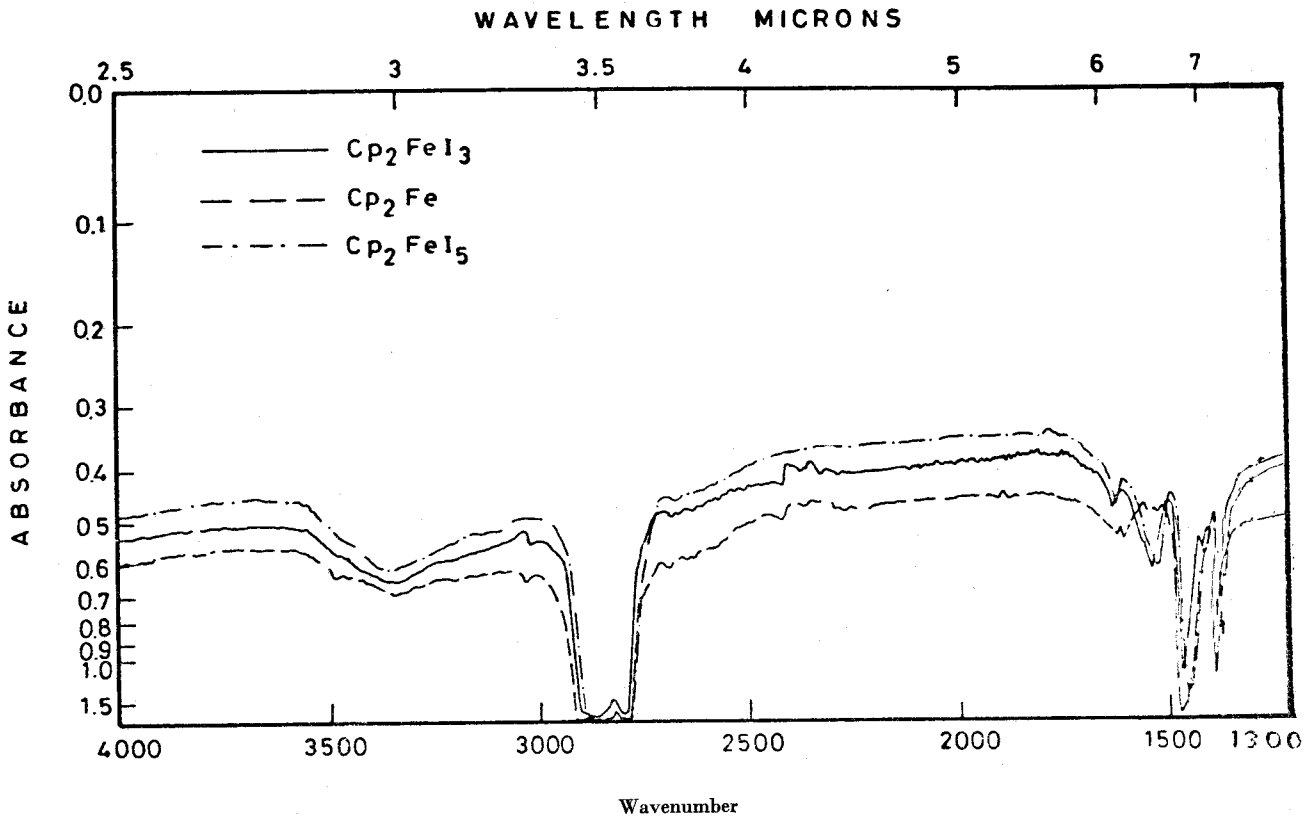

Fig. (3b) Infrared spectra of Ferrocene - Ferricinium trirodide and ferricinium pentaiodide.

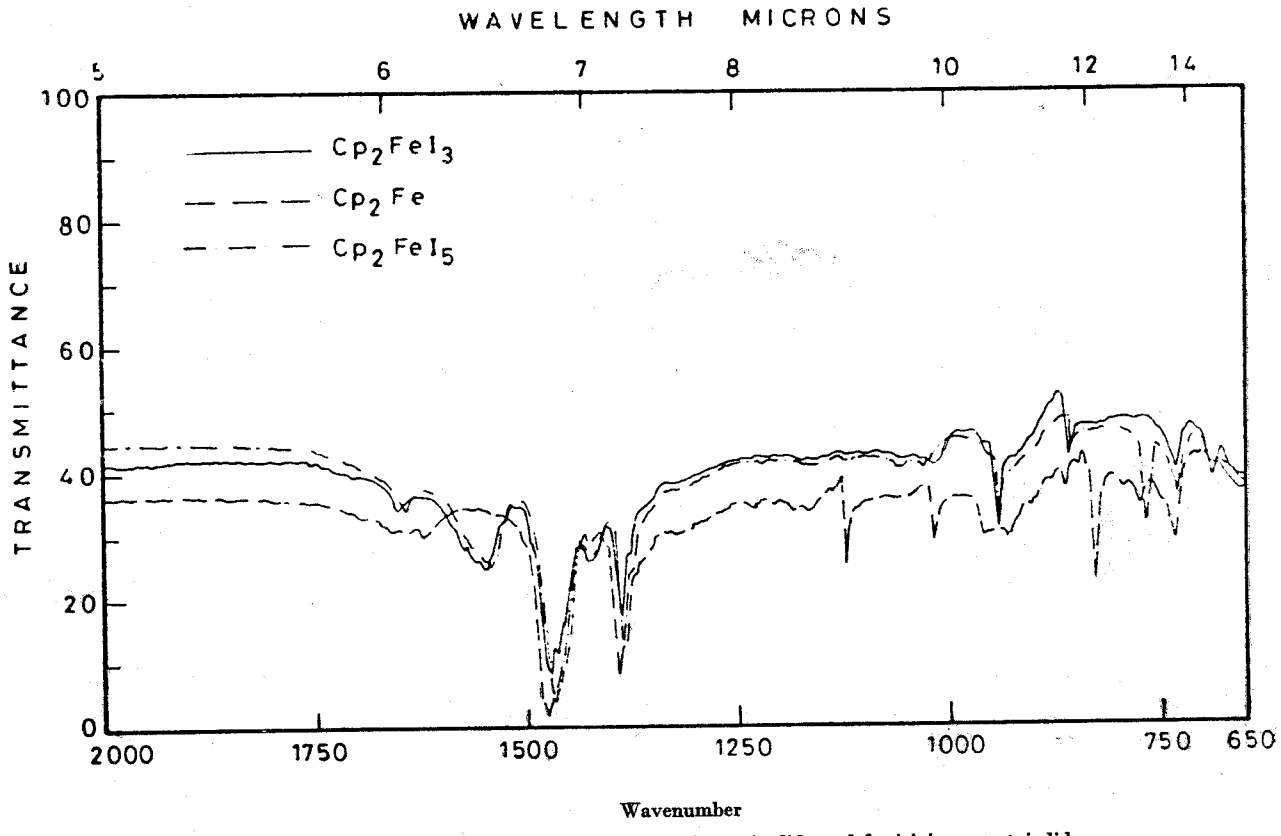

Fig. (3a) Intrared spectre of Ferrocene - Ferricinium trirodide and ferricinium pentaiodide.

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