

NOTE

Ferricinium salts

Oxidation of ferrocene to ferricinium ion has been achieved electrolytically and by a variety of inorganic and organic oxidants^{1,2}. Brand and Snedden³ observed the electron-transfer spectrum of ferrocene in halogenated alkane solutions and attributed this to a dissociative charge-transfer. Chlorination at 0° is reported⁴ to destroy ferrocene completely. However, in chlorination at -40° Nesmeyanov and his coworkers⁵ obtained ferricinium tetrachloroferrate. They⁵ proposed that ferrocene and chlorine react to give first ferricinium chloride and ferric chloride which then combine to form ferricinium tetrachloroferrate, $C_{10}H_{10}Fe^+FeCl_4^-$.

In this work it was found that hexachlorocyclopentadiene releases chlorine photolytically at a rate which allows oxidation of ferrocene and precipitation of ferricinium tetrachloroferrate crystals at room temperature. Formation of the ferricinium salt was spectrally observed (610-620 m μ peak) almost immediately when hexachlorocyclopentadiene solution of ferrocene was irradiated with a mercury lamp. The same blue ferricinium salt precipitated also in photolysis of a benzene solution of ferrocene which contained a small amount of hexachlorocyclopentadiene.

Ferric chloride exists in a benzene solution as a dimer, Fe_2Cl_6 . Addition of ferrocene to it precipitates ferricinium hexachlorodiferrate, $C_{10}H_{10}Fe^+Fe_2Cl_6^-$. Photolysis of a benzene solution of ferrocene and hexachlorocyclopentadiene, however, did not give the hexachlorodiferrate but the tetrachloroferrate. Therefore, the intermediate formation of ferric chloride, *i.e.* dimer, does not appear to take place in the photolytic ferricinium formation. More likely, chlorine, liberated by the photolytic cleavage of C-Cl in hexachlorocyclopentadiene, reacts first with ferrocene forming ferricinium chloride, $C_{10}H_{10}Fe^+Cl^-$. This and ferrocene may form a transient cationic complex, $(C_{10}H_{10}Fe \cdot C_{10}H_{10}Fe)^+Cl^-$. Further chlorination may decompose the complex with the resulting precipitation of the stable ferricinium tetrachloroferrate.

Ferricinium tetrachloroferrate was also formed when triphenylmethyl chloride and ferrocene were dissolved in benzene. Unlike ferrocene and hexachlorocyclopentadiene, the salt formation in this case took place also in the dark and was not accelerated by light.

When ferricinium, substituted ferricinium and biferricinium salts were formed by mixing solutions of ferric chloride and the respective ferrocene compounds, the composition of the salt varied for the different solvents used. This variation appears to depend on the degree of association of ferric chloride in a solvent. The change of ferrocenes to the corresponding ferricinium chloroferrates was indicated by a drastic decrease in the intensity of the infrared band in the 1100-1110 cm^{-1} region* and a replacement of a strong band at about 810-830 cm^{-1} by a band at 850-870 cm^{-1} **.

* Fritz⁶ assigns 1104 cm^{-1} band to be due to cyclopentadienyl C-H out-of-plane deformation. Lipincott and Nelson⁷ report the band is due to C-C vibration.

** Pavlik and Plechacek⁸ associate these changes with shifts in two cyclopentadienyl C-H out-of-plane bending frequencies.

When benzene or ether solutions of ferrocene and mercuric chloride were mixed, an insoluble red precipitate was formed. On standing the red solid turned into a water-soluble blue salt. This color change was accompanied by a replacement of the infrared bands (Nujol) at 1450, 1410, 1020, 990, 920 and 868 cm^{-1} with bands at 1430, 1010 and 860 cm^{-1} . The change, which could be accelerated by ultraviolet light, also resulted in the disappearance of the ESR signal (g -value 2.087, linewidth 691 gauss). This suggests that the red solid is a ferrocene-mercuric chloride charge transfer complex with an unpaired d -electron of the complexed ferrocene. On standing the complexed mercuric chloride is reduced and the complexed ferrocene is oxidized to ferricinium cation*.

The ESR spectra of ferricinium chloroferrates show lines with g -values of 2.046 and linewidths of 600 gauss which is compatible with the presence of Fe^{3+} in the anions. The ferricinium cation is orbitally degenerate and therefore does not show electron resonance⁹.

The ferricinium and substituted ferricinium chloroferrates, as well as the water-soluble blue ferricinium salt from ferrocene and mercuric chloride, gave no ferricinium NMR signal in deuterium oxide or deuterated acetone solutions. The absence of the signal is due to the line broadening¹⁰.

Experimental

The infrared spectra were determined with a Perkin-Elmer 137B spectrophotometer. The ultraviolet and visible spectra were obtained using a Beckman DK spectrophotometer. The NMR determinations were made on HA-60 Varian High Resolution Spectrometer. For the ESR determinations an EPR-Varian V-4500 Spectrometer was used.

Ferricinium tetrachloroferrate from photolysis of the hexachlorocyclopentadiene solution of ferrocene. A solution of ferrocene (3.0 g, 0.016 mole) in 50 ml of hexachlorocyclopentadiene was irradiated in a nitrogen atmosphere and at room temperature with a Hanovia high-pressure quartz mercury-vapor lamp (550 watts). After 2.5 h of photolysis, 2.1 g of blue crystalline ferricinium tetrachloroferrate was collected by filtration and repeated washing with benzene.

The infrared spectrum (Nujol, Fluorlube) has 3150, 1415, 1110 (w), 1010, 880 (w), 852 and 805 (w) cm^{-1} bands. The ultraviolet and visible spectra (in water) have λ maxima at 250 $\text{m}\mu$ ($\epsilon = 1.57 \times 10^6$) and 615 $\text{m}\mu$ ($\epsilon = 4 \times 10^4$). The NMR spectrum (in D_2O) showed no lines. (Found: C, 31.34; H, 2.82; Cl, 37.31; Fe, 29.39. $\text{C}_{10}\text{H}_{10}\text{Cl}_4\text{Fe}_2$ calcd.: C, 31.30; H, 2.61; Cl, 36.99; Fe, 29.10%.)

Ferricinium tetrachloroferrate from ferrocene and triphenylmethyl chloride. Ferrocene (5 g) and triphenylmethyl chloride (5 g) were dissolved in 250 ml of benzene and stored in the dark. After 20 h, 0.4 g of ferricinium tetrachloroferrate was collected by filtration and washing with benzene. The infrared, NMR and ESR spectral analyses results were found to be identical to those for the ferricinium tetrachloroferrate from the photolysis of hexachlorocyclopentadiene solution of ferrocene. (Found: C, 31.18; H, 2.66; Fe, 28.70. $\text{C}_{10}\text{H}_{10}\text{Cl}_4\text{Fe}_2$ calcd.: C, 31.30; H, 2.61; Fe, 29.10%.)

* The reaction is reminiscent of Eder's chemical photometer.

1,1'-Bis (triphenylsilyl) ferricinium tetrachloroferrate. 1,1'-Bis (triphenylsilyl)-ferrocene (0.5 g) was dissolved in 5 ml of hexachlorocyclopentadiene and 50 ml of benzene. After irradiating the solution with the mercury vapor lamp for one hour, 0.2 g of shiny green crystals of the tetrachloroferrate (decomp. between 210–235°) were collected. The strong 830 cm^{-1} band of the silyl ferrocene compound had disappeared and a new infrared absorption at $850\text{--}865\text{ cm}^{-1}$ was found. The ferricinium salt (in deuterated acetone) showed no NMR lines. (Found: C, 61.37; H, 4.21. $\text{C}_{46}\text{H}_{38}\text{Si}_2\text{Cl}_4\text{Fe}_2$ calcd.: C, 61.38, H, 4.22 %.) The ferricinium salt could be reduced to the starting ferrocene compound (m.p. 254–255°) by dissolving it in acetone and adding water.

Ferricinium salts from ferrocene and ferric chloride. By mixing ferrocene and ferric chloride solutions in benzene a blue-green salt with the composition corresponding to $(\text{C}_{10}\text{H}_{10}\text{Fe})^+(\text{Fe}_2\text{Cl}_6\cdot 3\text{H}_2\text{O})^-$ was precipitated. The infrared spectrum of this salt, after repeated washing with benzene, is identical with the spectrum for the tetrachloroferrate, except that the water of hydration bands are found at 3450, 1640 and 1620 cm^{-1} . (Found: C, 21.16; H, 2.99; Cl, 37.08; Fe, 29.40. $\text{C}_{10}\text{H}_{10}\text{Cl}_6\text{Fe}_3\text{O}_3$ calcd.: C, 21.26; H, 2.83; Cl, 37.74; Fe, 29.66 %.) Recrystallization from hot ethanol gave $\text{C}_{10}\text{H}_{10}\text{Fe}^+\text{FeCl}_4^-$.

1,3-(1,1'-Ferricinium)tetraphenyldisiloxane. The dark green salt formed in benzene solution from 1,3-(1,1'-ferrocenylene)tetraphenyldisiloxane and ferric chloride no longer has 820 cm^{-1} and 840 cm^{-1} bands in the infrared. A new ferricinium band has appeared at 855 cm^{-1} but the asymmetric Si–O–Si stretching vibration remains at 1110 cm^{-1} . The composition of the salt corresponds approximately to $(\text{C}_{34}\text{H}_{28}\text{FeSi}_2\text{O})^+(\text{Fe}_2\text{Cl}_6\cdot 2\text{H}_2\text{O})^-$. (Found: C, 41.93; H, 3.41; Si, 5.82; Cl, 21.46; Fe, 18.77 %.)

Biferricinium salts from biferrocenyl and ferric chloride. Mixing of ether solutions of biferrocenyl and ferric chloride gave a green precipitate. After a thorough and repeated washing with ether, the infrared spectrum (Nujol, Fluorlube) of the salt has 3100(w), 1420(w), 1100(vw), 1030(vw), 1005(w), and 855 (s) cm^{-1} bands. The spectrum has also bands at 3450, 1640 and 1610 cm^{-1} due to the water of hydration present. The composition of the salt corresponds approximately to $(\text{C}_{20}\text{H}_{18}\text{Fe}_2)^+(\text{Fe}_3\text{Cl}_{10}\cdot 5\text{H}_2\text{O})^-$. (Found: C, 22.80; H, 2.88; Cl, 36.4; Fe, 30.07 %.)

The same reactants in benzene solution gave a dark blue precipitate. After a thorough and repeated washing with benzene, the infrared spectrum (Nujol, Fluorlube) of the precipitated salt has weak bands at 3100, 1410, 1110, 1055, 1045, 1030 and 1000 cm^{-1} and medium strong bands at 830–850 and 815 cm^{-1} . Composition of this salt corresponds to $(\text{C}_{20}\text{H}_{18}\text{Fe}_2)^+(\text{Fe}_2\text{Cl}_6\cdot 4\text{H}_2\text{O})^-$. (Found: C, 30.53; H, 3.37; Cl, 27.2; Fe, 28.90. $\text{C}_{20}\text{H}_{26}\text{Cl}_6\text{Fe}_4\text{O}_4$ calcd.: C, 31.36; H, 3.40; Cl, 27.83; Fe, 29.05 %.)

Ferricinium salt from ferrocene and mercuric chloride. Mixing of ether or benzene solutions of ferrocene and mercuric chloride precipitated a fine red solid. After washing with the solvents, the infrared spectrum (Nujol, Fluorlube) of the red solid has bands at 3120 (w), 1450 (m), 1410 (m), 1060 (w), 1020 (w), 990 (w), 920 (w), and 868 (s) cm^{-1} . The ESR spectrum has a line with a g -value of 2.087 and a linewidth of 691 gauss. Addition of water to the solid regenerated ferrocene. On standing under nitrogen the red solid gradually changed to a water-soluble dark blue salt. After 48 h and later the infrared spectrum (Nujol, Fluorlube) of the product was found to have bands at 3120 (w), 1430 (m), 1105 (vw), 1060 (vw), 1010 (m) and 860 (s) cm^{-1} . The NMR (in D_2O) and ESR (solid) spectra of the blue solid did not show any lines. (Found: C, 6.98; H, 0.80; Cl, 12.0; Fe, 3.67; Hg, 69.6 %.)

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- 1 M. ROSENBLUM, *Chemistry of the Iron Group Metallocenes*, Part 1, Wiley, New York, 1965, p. 48.
- 2 A. N. NESMEYANOV, E. G. PEREVALOVA AND L. P. JURJEVA, *Chem. Ber.*, 93 (1960) 2729.
- 3 J. C. BRAND AND W. SNEDDEN, *Trans. Faraday Soc.*, 53 (1957) 894.
- 4 A. N. NESMEYANOV, L. P. YUR'eva, R. B. MATERIKOVA AND B. HETNARSKI, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 4 (1965) 731.
- 5 A. N. NESMEYANOV, E. G. PEREVALOVA, R. V. GOLOVNYA, T. V. NIKITINA AND N. A. SIMONKOVA, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1956) 739.
- 6 H. P. FRITZ, in F. G. A. STONE AND R. WEST (Eds.), *Advances in Organometallic Chemistry*, Vol. 1, Academic Press, New York, 1964, pp. 267, 280, 281.
- 7 E. R. LIPINCOTT AND R. D. NELSON, *Spectrochim. Acta*, 10 (1958) 307.
- 8 I. PAVLIK AND V. PLECHACEK, *Collection Czech. Chem. Commun.*, 31 (1966) 2083.
- 9 R. M. GOLDING AND L. E. ORGEL, *J. Chem. Soc.*, (1962) 363.
- 10 M. W. DIETRICH AND A. C. WAHL, *J. Chem. Phys.*, 38 (1963) 1591.

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