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The iodotetracarbonyliron anion

The direct replacement of carbonyl groups in metal carbonyl compounds by halide ions has previously been reported for the hexacarbonyls of chromium, molybdenum and tungsten[1], the carbonyls and halogenocarbonyls of manganese[2] and rhenium[3], and the halogenocarbonyls of rhodium[4]. We now wish to report the formation of the anionic iodotetracarbonyl of iron from the reaction of iodide ion with both iron pentacarbonyl and triiron dodecacarbonyl.

Triiron dodecacarbonyl reacts with tetraethylammonium iodide in diglyme at 60° without evolution of carbon monoxide to produce tetraethylammonium iodotetracarbonylferrate.

$$Fe_3(CO)_{12}+3\,(C_2H_5)_4N^+I^- \rightarrow 3\,(C_2H_5)_4N^+[Fe(CO)_4I]^- \qquad (1)$$

The yield is low, and the product is isolated as deep red crystals. It is very soluble in diglyme, dichloromethane, acetone and chloroform; not very soluble in benzene and water, and insoluble in light petroleum, diethyl ether and hexane. It is stable under nitrogen in darkness, but decomposes quite rapidly in the atmosphere and in solution.

The iodotetracarbonylferrate ion is also obtained from the reaction of iron pentacarbonyl with iodide ion in diglyme at 90°. Carbon monoxide is evolved during this reaction, which is considerably slower than (1) above.

$$Fe(CO)_5+(C_2H_5)_4N^+I^- \rightarrow (C_2H_5)_4N^+[Fe(CO)_4I]^- +CO \qquad (2)$$

The four idealised structures of $Fe(CO)_4I^-$, together with the expected infrared activity of their CO stretching modes are outlined in Table 1. The measured infrared spectrum could not be obtained in a high resolution solvent such as cyclohexane due to insolubility. However, both in nujol mull and chloroform solution the spectrum contained only three maxima in this region. This strongly suggests the C_{3v} structure with the iodine on the trigonal bipyramidal three-fold axis. Further, this is the structure most commonly found for $Fe(CO)_4L$ species[5]. The relative intensities of the three modes may also be rationalised for such a structure by considering the strongly allowed E mode to be the most intense band at 2003(s)cm^{-1}, the next intense band at 1975(m)cm^{-1} to be the A_1^a mode arising from the stretching of the unique carbonyl group; and the other A_1^b mode, arising from the only weakly allowed symmetrical stretching of the three equivalent carbonyls, to be assigned to the weak high energy band at 2062 (w) cm^{-1}.

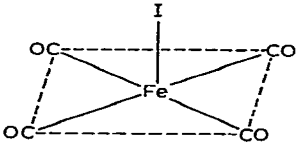
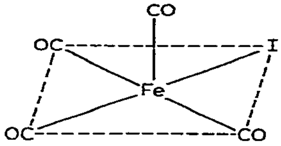
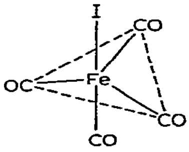
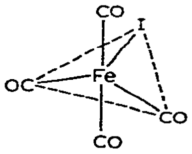
The salt $Na[Fe(CO)_4X]$ has been mentioned[6] as a product from the reaction between $Na_2Cr(CO)_5$ and $Fe(CO)_4I_2$. Though no characterisation is available it seems likely the anion of this salt is the same as that reported by us above.

Experimental

Tetraethylammonium iodotetracarbonylferrate. Triiron dodecacarbonyl (*ca.* 1.3 g) and tetraethylammonium iodide (*ca.* 0.9 g) were heated in diglyme (50 ml) at 60° under nitrogen for 2 h. Little or no carbon monoxide was evolved, but the solution turned an intense deep red colour. This was filtered while hot under nitrogen

TABLE 1

POSSIBLE STRUCTURES OF THE $Fe(CO)_4I^-$ ANION

	Symmetry class	*Infrared active CO stretch modes*
	C_{4v}	$2(A_1+E)$
	C_s	$4(3A'+A'')$
	C_{3v}	$3(2A_1+E)$
	C_{2v}	$4(2A_1+B_1+B_2)$

into air-free light petroleum (b.p. 40–60°) (50 ml) to give a dark red precipitate which was removed by centrifuging. Recrystallisation from diglyme/light petroleum gave

TABLE 2

INFRARED SPECTRA IN THE CO STRETCHING REGION OF THE IODOTETRACARBONYLFERRATE ION

ν(CO) (cm⁻¹) and suggested assignments based on a C_{3v} model			*Medium*
A_1^b	E	A_1^a	
2063 w	1990 s	1940 m	Nujol mull
2062 w	2003 s	1975 m	Chloroform

fine red crystals of tetraethylammonium iodotetracarbonylferrate. Yield about 10%. (Found: C, 33.5; H, 4.3; I, 30.8; N, 2.9. $C_{12}H_{20}FeINO_4$ calcd.: C, 33.9; H, 4.7; I, 29.9; N, 3.3%.)

In a similar experiment, replacing triiron dodecacarbonyl with iron pentacarbonyl, a temperature of 90° was required to cause the steady evolution of carbon monoxide. Work-up gave the same fine red crystalline species with identical infrared spectrum. The product may also be obtained from iron pentacarbonyl and tetraalkylammonium iodides in methanol at room temperature by ultra-violet irradiation.

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