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FERRICENIUM POLYIODIDES

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Summary

A study of the oxidation of ferrocene (Fc) by elementary iodine under conditions used previously by others has been made with the objective of establishing unambiguously the stoichiometric composition of the resultant ferricenium polyiodides and clarifying inconsistencies in the literature reports. It has been found that at initial I_2/Fc ratios of up to and including 1.5 the composition of the salt produced corresponds to FcI_3 (**1**) irrespective of the reaction medium employed. I_2/Fc ratios of 2–15 gave mixtures of higher-order polyiodides FcI_x $x = 4–10$, from which, by painstaking fractional crystallization from nitromethane the five crystallographically distinct compounds **2**–**6** separated, ranging in composition from about FcI_4 to $FcI_{7.5}$. The higher-order polyiodides, notably those with $x \geqslant 5$, are unstable; when exposed to the atmosphere, either in acetone solution or in the solid state, they lose molecular iodine, to give species of lower iodine content. Raman scattering data were useful in distinguishing the higher-order polyiodides **2**–**6** from the triiodide **1**.

Introduction

The oxidation of ferrocene (Fc) by elementary iodine represents one of the most convenient procedures for the preparation of ferricenium (Fc^+) salts, the halogen acting both as the oxidant and as the anion source. The reaction leads to ferricenium polyiodides of variable anion composition [1–11], and the formation of the thermodynamically most stable triiodide **1** is favored over that of higher-order iodides. Non-polar solvents, such as aliphatic or aromatic hydrocarbons, are satisfactory media, as are halocarbons and even the protic solvent ethanol. The reaction proceeds readily in the dark, and in the case of, for example, triiodide formation * in benzene,

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* Under conditions of photoassistance the mechanism of triiodide formation is believed [2,9] to involve primary photodissociation of I_2 and subsequent, extremely rapid redox reaction of (solvent-complexed) atomic iodine with ferrocene to give Fc^+ I^-, this being followed by anion complexation with I_2.

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in which the product exists as an ion pair (eq. 1) [2], the equilibrium constant has been determined (log $K = 2.24$) [2].

$$Fc + \tfrac{3}{2}I_2 \rightleftharpoons \underset{(\mathbf{1})}{Fc^+\ I_3^-} \qquad (1)$$

Although there have been many investigations of the ferrocene/iodine reaction the results are by no means consistent. Thus, Wassef and Abou el Fitouh [8], as well as Hendrickson and collaborators [5,7], working with 1,2-dichloroethane and hydrocarbon solvents, respectively, obtained the ferricenium triiodide (**1**) at I_2/Fc molar ratios of 1.0–3.0. Brand and Snedden [2], on the other hand, reported the formation of the pentaiodide, FcI_5, under very similar conditions, but at a I_2/Fc ratio as low as 1.5. At variance with both reports, a study by Nesmeyanov's group [1] indicated that the interaction of ferrocene and iodine in organic solvents gave a compound of the average composition FcI_{20} (m.p. 170–172°C, dec.) irrespective of whether an excess or a deficiency of the halogen was used. The initial product on recrystallization from acetone was converted into a compound described as a hexaiodide, FcI_6 (m.p. 125–130°C, dec.) [1]. A more recent study [4] employed the hexaiodide (presumably obtained by Nesmeyanov's procedure [1]), which was transformed into **1** by controlled, slow crystallization from acetone. The triiodide (for which no analytical or melting point data were given) was characterized by X-ray crystallographic analysis. In a later publication from Nesmeyanov's laboratory [3] two polyiodides of unspecified compositions were prepared from the two reactants in ethanol solution in I_2/Fc ratios of 10.0 and 0.5, respectively, and both products were converted into **1** by recrystallization from acetone. Similarly Prins et al. [6] obtained a polyiodide at a I_2/Fc ratio of 5.0 in carbon tetrachloride, and this compound, again, was transformed into **1** by several recrystallizations from acetone. Aly [10] obtained **1** by treatment of an aqueous ferricenium trichloroacetate solution with iodide anion. The compound isolated had a decomposition point of 140°C, whereas product **1** stemming from one of the aforementioned studies [3] decomposed at 169–171°C (i.e. at the same temperature as Nesmeyanov's icosaiodide [1]), and yet another triiodide [8] was found to decompose at 192°C. One of the triiodides reported was dark red [5], while another one was black [4].

Requiring authentic **1** for our studies of charged metallocenes as potential inhibitors of tumor growth [12], we set out to prepare the salt by some of the described methods. However, in keeping with the divergence of the observations by other authors, our results revealed that the stoichiometry of the ferrocene oxidation by iodine was less easily controlled than expected. This prompted a more detailed examination of the reaction conditions which give **1** and other ferricenium polyiodides.

Results and discussion

The approach involved the treatment of ferrocene with iodine in the solvents and molar ratios given in Table 1. The solvents employed were those used by previous workers. While most of the experiments tabulated were repeats of the work of other authors, several experiments were performed under different conditions. The preparative sequence was simple: solutions of the two reactants in the solvents indicated were combined at room temperature, the reaction was allowed to proceed to completion at 40–50°C, and the precipitated or crystallized ferricenium iodides were collected after allowing them to settle out at 20–25°C. The products were then cautiously washed (with only small volumes of solvent so as to prevent changes in composition through leaching-out of iodine) and were dried under mild standard conditions in vacuo.

Preliminary experiments established that crude polyiodides when recrystallized from acetone, a solvent observed to bring about elimination of I_2 from higher-order iodide salts, lost iodine successively on each recrystallization, ultimately being converted into the stable triiodide **1**, from which no further iodine elimination was observed *. This accords with earlier observations [1,3,4,6]. In contrast, there was no significant iodine elimination from higher-order polyiodides when the recrystallization was from acetonitrile or nitromethane under carefully controlled conditions. Accordingly, the crude products from all the experiments listed (fifth column, Table 1) were each recrystallized from acetonitrile under non-fractionating conditions so as to give a single crystalline crop. Carbon, hydrogen, iron and iodine analyses were obtained for each product batch. The compositions determined from the analytical results for both crude and recrystallized salts are listed in Table 1, together with yield data and melting or decomposition temperatures. Relevant results of other authors are indicated as footnotes.

Table 1 shows that up to and including an initial I_2/Fc ratio of 1.5, in keeping with the stoichiometry of eq. 1, the average product composition corresponds approximately to FcI_3 irrespective of the solvent used. This holds also for experiments employing a significant excess of ferrocene over the halogen, e.g. Bz-0.34, Et-0.34, and Et-0.5. The preferential formation of **1** under these conditions, which is in accord with some earlier observations [3,8] but in contrast to one report of pentaiodide formation [2], indicates the extraordinary stability of the triiodide as well as the instability of a diiodide apparently observed [11] in solution but never isolated. Ferricenium triiodide (**1**) as obtained in this work, crude or recrystallized, and unambiguously identified by its X-ray powder diffractogram (Table 3), melts rather sharply with decomposition at 182–187°C. The lower decomposition points observed by Aly [10] (140°C) and Nesmeyanov et al. [1] (169–171°C) for the supposed triiodide **1** were thus apparently recorded with higher-order iodides.

With I_2/Fc ratios higher than 1.5, the product salts FcI_x not surprisingly, always have iodine contents exceeding that of **1**; this is the case even in expt. Cy-2.5 ($x = 4$–5), performed under conditions reported [5] to give **1**. For most experiments, however, Table 1 shows x to average less than 7, and in our hands even use of the large excess of halogen employed in Et-15 raised the value of x at most to 10, disproving the ready formation of FcI_{20} claimed in the literature [1].

In an effort to gain further insight into the compositions of the higher-order polyiodides (FcI_x, $x > 3$), suitable combined, recrystallised product salts were subjected to laborious, anaerobic fractionating crystallization from nitromethane. The task, involving the collection and identification of more than 500 intermediary and terminal subfractions, proved exceedingly difficult in view of smooth cocrystallization of products over wide ranges of composition and the tendency of the higher-order iodides ($x \geq 5$) to lose iodine in the dissolved, and even in the solid,

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* The ability of acetone to bring about progressive loss of I_2 from the higher-order polyiodides is doubtless associated with its tendency [13] to complex with the halogen.

TABLE 1

FERRICENIUM IODIDES FROM IODINE AND FERROCENE [a]

Experiment Code	Solvent [b]	I_2/Fc [c]	Molarity of Fc	Ferricenium iodides (FcI_x)				
				Crude			Recrystallized	
				Yield (%)	Average x [d]	Representative m.p. (°C)	Average x [d]	Representative m.p. (°C)
Hx-1.5	Hx	1.5	0.02	75–86	3 [e]	185 dec. [e]	3	182–183 dec.
Hx-3		3.0	0.01	74–89	4–5	125 partial; 175–179 dec.	4–5	122 sint; 173–177 dec.
Hx-5		5.0	0.01	78–95	6–7	121–125; 179 dec.	6–7	125–129 partial; 185 dec.
Cy-2.5	Cy	2.5	0.04	88–94	4–5	124–128 sint.; 175–178 dec.	4–5 [f]	124–125 sint.; 168–172 dec.
Bz-0.34	Bz	0.34	0.15	75–81	3	183–184 dec.	3	183–184 dec.
Bz-1.5		1.5	0.03	84–92	3–3.5 [g]	179–180 dec.	3–3.5	174–179 dec.
Bz-3		3.0	0.02	68–78	4–5	171–173 dec.	4–5	170–174 dec.
Bz-5		5.0	0.02	71–81	4.5–5	126–127; 168 dec.	4.5–5	124–129; 179 dec.
DCE-1	DCE	1.0	0.15	75–78	3 [h]	184 dec.	3	183 dec.
DCE-1.5		1.5	0.14	72–75	3–3.5 [h]	181–182 dec.	3–3.5	174–178 dec.
DCE-2		2.0	0.10	83–88	4 [h]	181–182 dec.	4–5	179–181 dec.
DCE-3		3.0	0.05	87–92	4–5 [h]	125–127 sint.; 168–170 dec.	4–5	124–129 partial ;176–180 dec.
DCE-5		5.0	0.02	80–86	5–6	125–127; 180 dec.	5–6	112–120; 176 dec.
Et-0.34	EtOH	0.34	0.15	82–85	3	179–181 dec.	3	182–183 dec.
Et-0.5		0.5	0.04	89–95	3	182–183 dec.	3 [i]	183 dec.
Et-1		1.0	0.15	85–96	3	186 dec.	3	184 dec.
Et-1.5		1.5	0.08	87–91	3	185 dec.	3	183 dec.
Et-2		2.0	0.07	94–99	3.5–4	180–182 dec.	4	178–180 dec.
Et-3		3.0	0.05	95–99	4–5	172–174 dec.	4–5	176 dec.
Et-5		5.0	0.07	95–98	5–6	120–122; 170 dec.	5–6	125–128; 175 dec.
Et-10		10.0	0.07	97–99	7–8	115–119 dec.	7–7.5 [j]	115–120; 184 dec.
Et-15		15.0	0.07	87–93	8.5–10	112–13 dec.	7–8	110 partial; 120–122; 170 dec.

[a] Reactions performed for 30 min at 40–50°C, followed by 24 h at room temperature in the dark. [b] Hx = n-hexane; Cy = cyclohexane; Bz = benzene; DCE = 1,2-dichloroethane; EtOH = abs. ethanol. [c] Fc = ferrocene. [d] Range of av. compositions found in repeat experiments; see Experimental for microanalytical data. [e] Lit. [2] $x = 5$, m.p. 174°C dec. [f] Lit. [5] $x = 3$; no m.p. given. [g] Lit. [7] $x = 3$, no m.p. given. [h] Lit. [8] $x = 3$ for I_2/Fc ratios up to 3; m.p. 192°C dec. [i] Lit. [3] $x = 3$ (from acetone). [j] Lit. [3] $x = 3$ (from acetone), m.p. 169–171°C dec.

TABLE 2

SOME CHEMICAL AND PHYSICAL CHARACTERISTICS OF FERRICENIUM TRIIODIDE **1** AND POLYIODIDE TYPES [a] **2–6**

	Polyiodide type FcI_x					
	1	**2**	**3**	**4**	**5**	**6**
Approx. range of x	3	4.0–4.3	4.1–4.5	4.7–5.0	6.3–6.6	7.4–7.7
Most probable compn.	FcI_3	FcI_4	$FcI_{4.3}$	FcI_5	$FcI_{6.5}$	$FcI_{7.5}$
Crystal appearance [b]	A	B	B	C	D	E
Representative m.p. (°C)	183–184 dec.	178–180;181 dec.	179–181;182 dec.	124 sint.;174 dec.	126–129;180 dec.	117–119 dec.
IR (KBr) (cm^{-1}), ν_8, ν_{17} [c]	3095 wm	3095 wm	3095 wm	3095 wm	3095 wm	3094 wm
ν_{20}	1411 ms	1411 ms	1411 ms	1411 ms	1412 ms	1412 ms
(ν_{24}, ν_{30})	1260 vw,br	1258 w	1258 w	1260 w	1260 vw	1260 vw
ν_{10}	1111 m [d]	1111 w [d]	1111 w [d]	1111 w [d]	1111 w [d]	1111 w [d]
(ν_{25}, ν_{31})	1052 w	1051 w	1051 w	1051 w	1052 w,br	1052 w,br
ν_{18}	1007 m	1006 ms	1006 ms	1006 ms	1006 m	1006 m
	934 vw	931 w	931 w	931 w	932 vw	932 vw
(ν_{27}, ν_{33})	–	876 vw	876 vw	876 w	877 vw	877 vw
ν_{19}	848 s	847 s	848 s	848 s	848 s	848 s
(ν_2, ν_{14})	807 vw	808 vw,br	808 w,br	807 w,br	805 vw	805 vw
ν_{21}	501 vw					

[a] Obtained by fractionating crystallization from nitromethane. [b] A = black, shiny rhombic crystals; B = blackish needles with steely luster; C = crystals with metallic gloss; D = blackish crystals with silvery gloss; E = blackish glittering microcrystals. [c] Frequencies are averages derived from spectra taken on three different instruments. Frequency designation from E.R. Lippincott and R.D. Nelson, Spectrochim. Acta, 10(1958) 307; in parentheses, IR inactive or Raman active modes that have gained minor IR allowedness by symmetry distortion. [d] Very weak shoulder at 1099 cm^{-1}, probably due to ν_3.

TABLE 3

X-RAY POWDER DIFFRACTOGRAMS OF FERRICENIUM TRIIODIDE **1** AND POLYIODIDE TYPES **2–6** [a]

1		**2**		**3**		**4**		**5**		**6**	
2θ [b] (°)	*d*-spacing (pm)	2θ [b] (°)	*d*-spacing (pm)	2θ [b] (°)	*d*-spacing (pm)	2θ [b] (°)	*d*-spacing (pm)	2θ [b] (°)	*d*-spacing (pm)	2θ [b] (°)	*d*-spacing (pm)
										10.2(17)	867
				11.8(12.5)	750	11.8(17)	750				
		12.1(18)	731	12.1(9)	731						
13.0(10)	681										
								14.9(43)	594		
								17.7(100)	501		
		18.2(32)	487	18.2(13)	487						
								19.8(53)	448		
20.8(100)	427	20.9(100)	425	20.45(48)	434	20.6(100)	431	20.9(50)	425	20.3(100)	437
				20.9 (100)	425						
24.6(9)	362	24.4(16)	365	24.4(9)	365			24.1(31)	369		
								24.4(28)	365	25.8(5)	345
26.1(13)	341							26.2(16)	340		
28.7(20)	311							28.7(32)	311		
								29.4(26)	304		
								30.1(68)	297	30.4(8)	294
				31.6(5)	283	31.7(12)	282	31.4(17)	285		
32.4(10)	276	32.1(9)	279	32.1(8.5)	279			31.7(39)	282		
36.4(12)	247			36.15(18)	248	36.2(25)	248				
		37.0(15)	243	36.9(11)	244						
38.0(22)	237										

[a] Scanned over range $2\theta = 10–40°$; Cu-K_α radiation (λ 154.18 pm). Angles and intensities are averages derived from 10 different samples each of **1**, **3**, **4** and **5** (3 samples each of **2** and **6**). [b] Relative intensities in parentheses. Signals with $I_{rel} < 9\%$ of base peak (< 5% for **3** and **6**) were neglected.

state. The five X-ray diffractometrically distinct types of iodides ultimately identified are designated as **2**, **3**, **4**, **5**, and **6**, in increasing order of iodine content and decreasing order ($\mathbf{2} \simeq \mathbf{3} > \mathbf{4} > \mathbf{5} > \mathbf{6}$) of solubility. Characteristic features of the five types, including IR frequencies, are given in Table 2, and prominent *d*-spacings, taken from the X-ray diffractograms, are listed in Table 3. The range of elemental composition shown in Table 2 for each compound type is not to be regarded as the analytical error limits but rather as the variation of composition within each type. The data show that the individual types do not possess sharply defined stoichiometric compositions, although, with the exception of **3**, most of the samples in each group approach certain compositional stoichiometries rather closely. Thus, **2** substantially corresponds to the tetraiodide, FcI_4, and for the majority of samples of **4**, **5**, and **6** the average compositions approach FcI_5, $FcI_{6.5}$ and $FcI_{7.5}$, respectively. It appears that the crystal lattices of these types readily tolerate intrusion by members of the adjacent types, a clear manifestation of the ability of both I_3^- and I_2 units to combine to form a diversity of polyiodide anion structures [14]. Type **3** is quite exceptional in that it represents cocrystallizates of **2** and **4** in ratios ranging from about 2 to 4. The powder diagrams reveal that these are not simply mechanical mixtures of the two components but are indeed made up of true mixed crystals. Although most of the less prominent peaks of both **2** and **4** emerge at unchanged positions of 2θ, the most intense peak of **4**, at 20.6° (*d* 431 pm) in the pure compound type, is found shifted precisely to 20.45° (*d* 434 pm) in the diffractograms of all (68) samples of **3** investigated. While it proved difficult in our fractionations to isolate even milligram quantities of pure **2**, the mixed crystals of **3** separated most readily and turned out to be the most stable species of all higher-order polyiodides identified in this study. The lattice stabilization of **3** is also manifest in the absence of a melting (and decomposition) point depression relative to both **2** and **3** (Table 2).

The IR spectra of the ferricenium iodides **1**–**6** are all remarkably superimposable, which is what would be expected in view of the absence of anion bands in the conventional region of 4000–200 cm^{-1}. The spectrum of an iodide said to be FcI_5 was reported earlier [15], and the quoted frequencies are substantially in accord with our own data. The strong and sharp out-of-plane CH bending absorption (ν_{19}) at 849 cm^{-1}, characteristic of the ferricenium cation, is prominent in the spectra of all six types. The only noticeable difference is found at 1112 cm^{-1}, where **1** exhibits the antisym. ring-breathing absorption (ν_{10}) in appreciably higher intensity than observed with other ferricenium salts [16], while the remaining iodides **2**–**6** do not show this intensity enhancement. Of particular interest are the Raman spectra in the 400–100 cm^{-1} region. Only **1** exhibits the typical resonance-enhanced ferricenium band at 310 cm^{-1} (sym. ring-metal-ring stretch, ν_4) with high intensity; surprisingly, no resonance enhancement is shown by **2**–**6**, and the shift indeed is barely, if at all, detectable in these spectra *. The linear arrangement [4] of the three iodine atoms in

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* While the pronounced attenuation, or complete disappearance, of ν_4 might suggest that species **2**–**6** possess a bent cation structure involving Fe–I bonding as proposed, e.g., for the tetraiodide, $[(C_5H_5)_2FeI]^+ I_3^-$ [11], the remaining spectral features are invariably in agreement with axial cation symmetry as in other ferricenium salts, and in disagreement with the data reported [17] for the bent ruthenicenium structure of $[(C_5H_5)_2RuI]^+ I_3^-$. The central iron atom in **2**–**6** clearly lacks the bulk of the Ru atom required to accommodate the metal-bonded iodine ligand in a strain-free arrangement, and no other examples of ferricenium halides with formal Fe^{IV} centres are described in the literature.

the anion of **1** is manifested in the symmetric stretching band which appears as a resonance-enhanced shift at 112 cm^{-1} with a faint overtone signal at 225 cm^{-1}. This pattern is in accord with the Raman spectra of other undistorted linear triiodides [18]. In samples of **1** which had not been rigorously purified and so were slightly contaminated with higher-order iodides, the spectra additionally display a very weak shift at 167 cm^{-1} where the symmetric I–I stretching band of the $I{-}I \cdots I^- \cdots I{-}I$ arrangement in linear pentaiodides is generally observed [14]. The spectra of **2**–**6** are characterized by two major shifts near 170 and 118–110 cm^{-1}, which represent the respective symmetric stretching modes of weakly interacting I–I and $I{-}I^-{-}I$ units. The 170 cm^{-1} shift, of low intensity in **2**, increases in strength on going from **3** to **6**; in the spectra of both **5** and **6** it attains nearly the same height as the shift at 117 cm^{-1}. No other stretching bands (such as those of free I_2 or of unsymmetrically structured I_3 and bent polyiodide segments [14]) are apparent in the spectral range investigated. These observations suggest that the polyiodide anions of **2**–**6** are made up essentially of combinations of weakly coupled I_2 and (linear) I_3^- species, for example $(I_3^-)_2 \cdot I_2$ (in **2**) or $(I_3^-)_2 \cdot (I_2)_2$ (in **4**). The increase in intensity of the ν(I–I) band with increasing iodine content of the anion accords well with combinations of this kind.

Experimental

Instrumental work, analyses

Melting points (uncorr.) of up to 300°C were observed for samples in sealed capillaries; sintering (sint), partial melting (partial), and decomposition (dec.) points were recorded as required. X-Ray powder diffractograms, obtained with Cu-K_α irradiation (ν_0 154.18 pm), were scanned over the region 2θ 10–40°; powdered sample material was fixed to the sample holder with a thin film of silicon grease, towards which the iodides are inert. Laser-Raman spectra were scanned over the frequency range 400–100 cm^{-1} with powdered material contained in rotating Pyrex glass capillaries; the laser excitation wavelength was 514.5 nm. Iodine and iron analyses were performed in the analytical laboratory of this University; carbon and hydrogen analyses were performed by Robertson Laboratories, Inc., Florham Park, N.J., by Galbraith Laboratories, Inc., Knoxville, Tenn., and by the Microanalytical Laboratory, University of Mainz. All C, H, Fe, and I determinations were routinely performed in duplicate, and in critical cases up to 8 repeat determinations were made (error limits: C, ±0.3%; H, ±0.1%; Fe, ±0.3%; I, ±0.4%).

Solvents, reactants

All solvents were dried over 4A Molecular Sieves and freshly distilled. Ferrocene (Strem Chemicals) was recrystallized from hexane. Iodine was freshly sublimed.

Ferricenium iodides from ferrocene and iodine

A. In hexane. A molar iodine/ferrocene ratio of 1.5, as chosen by Brand and Snedden [2], was used in the experiment described here (Hx-1.5, Table 1). A solution of 762 mg (3.0 mmol) of iodine in hexane (60 ml) was slowly added to the vigorously shaken solution of 372 mg (2.0 mmol) of ferrocene in hexane (40 ml) at room temperature. Black ferricenium iodide immediately began to precipitate from the solution. The reaction was taken to completion by warming the mixture for 30 min at 40–50°C and leaving it to stand for 24 h in a stoppered flask at room temperature in the dark. The precipitated iodide was filtered off, washed with pentane (2 × 10 ml), and dried for 2 h at 40°C/0.5 torr. This gave 936 mg (82.5%) of black, microcrystalline triiodide **1**, m.p. 185°C dec (Lit. [2] 174°C dec.). Anal. Found: C, 20.95; H, 1.75; Fe, 9.02; I, 66.86. $C_{10}H_{10}FeI_3$ (**1**) (567) calcd.: C, 21.19; H, 1.78; Fe, 9.85; I, 67.17%. IR (KBr) (cm^{-1}): 3096 wm, 1413m, 1262 vw, br, 1112 wm, 1052w, 1008m, 849s, 809vw, 502vw. (Lit. [2]: 3093mw, 1411ms, 1256w, 1111wm, 1050w, 1007ms, 877w, 848s, 667w.) Product salts collected in repeat experiments (75–86%) had m.p. 182–188°C dec. (occasionally up to 190°C, dec.) and gave very similar analytical data. Similar results were obtained when the reaction time or the ferrocene molarity was halved or doubled.

The crude triiodide was dissolved in warm (50–60°C) acetonitrile (15 ml/g), and the solution was filtered warm and reduced to ca. 2/3 of its volume by rotatory evaporation at room temperature. The black, shiny crystals of **1** which separated after 24 h at −20°C (72% recovery) melted at 182–183°C with decomposition, and gave an IR spectrum (Table 2) practically identical to that of the crude triiodide. Anal. found: C, 20.99; H, 1.82; Fe, 9.66; I, 67.23%. Other recrystallization experiments gave very similar results (68–75% recovery), with (sharp) degradation points in the range 182–187°C.

A similar procedure but with the iodine quantity increased to 6.0 mmol and a total solvent volume of 200 ml (Hx-3, Table 1) gave crude polyiodide in 79% yield. The black microcrystals melted partially at 125°C and completely (with decomposition) at 175–179°C. IR (KBr) (cm^{-1}): 3096wm, 1412ms, 1340 vw, 1257w, 1111w, 1050vw, 1007ms, 930vw, 875vw, 849s, 808vw, 686vw, 502vw. Anal. found: C, 15.45; H, 1.25; Fe, 6.99; I, 75.63. $C_{10}H_{10}FeI_{4.5}$ (757) calcd.: C, 15.66; H, 1.33; Fe, 7.09; I, 75.43%. Similar results were obtained in repeat experiments, with yields in the range 74–89%, m.p. 122–130°C (partial), 169–177°C dec., and microanalyses corresponding to compositions of FcI_4–FcI_5. Careful recrystallization from acetonitrile as described for Hx-1.5 gave fine blackish, glittering needles, m.p. 173–177°C, dec. (mild sintering at 122°C), with 76% recovery. IR (KBr): as in crude product. Anal. found: C, 16.04; H, 1.27; Fe, 7.43; I, 75.77%.

Increasing the iodine quantity to 10 mmol in an experiment (Hx-5, Table 1) otherwise conducted as in Hx-3 gave crude blackish, microcrystalline material in 93% yield, m.p. 121–125°C, 179°C dec. The IR (KBr) spectrum was very similar to that of the product from Hx-3. Anal. found: C, 12.35; H, 1.03; Fe, 5.49; I, 80.44. $C_{10}H_{10}FeI_{6.5}$ (1011) calcd.: C, 11.88; H, 1.00; Fe, 5.52; I, 81.60%. Repeated experiments gave substantially the same results, with crude yields in the range 78–95%. The salt resulting from recrystallization as before (69% recovery) formed inhomogeneous needles with metallic luster, m.p. 125–129°C (partial), 185°C dec. IR (KBr): same as spectrum of crude salt. Anal. found: C, 12.01; H, 0.92; Fe, 5.41; I, 82.01%.

B. In cyclohexane. In the experiment described here (Cy-2.5, Table 1), the I_2/Fc molar ratio was 2.5 as in the work of Hendrickson et al. [5]. A solution of iodine (5.0 mmol) in cyclohexane (35 ml) was added to ferrocene (2.0 mmol) dissolved in the same solvent (15 ml). The mixture was treated as described under A for Hx-1.5. The black (Lit. [5] dark red) powdery product was collected in 92% yield, m.p. 175–178°C dec. (sintering at 124–128°C). Anal. found: C, 16.08; H, 1.30; Fe, 7.27; I, 74.92%. IR (KBr): as in spectrum of Hx-3. Very similar results were obtained in repeat experiments (88–94% yield). Recrystallization from acetonitrile as described under A gave blackish, glittering crystals, m.p. 168–172°C dec (sintering at 124–125°C), 71% recovery. IR (KBr): as in spectrum of crude material. Anal. found: C, 16.01; H, 1.45; Fe, 7.50; I, 75.15%.

C. In benzene. In the experiment listed as Bz-0.34 (Table 1), the solution of iodine (1.0 mmol) in benzene (10 ml) was added dropwise to the vigorously stirred solution of ferrocene (3.0 mmol) in benzene (10 ml). The mixture was warmed for 30 min at 40–50°C and was then treated as described under A for Hx-1.5. The black, powdery, crude triiodide (78.0%, based on iodine), m.p. 183–184°C dec., gave an IR spectrum identical to that of Hx-1.5. Anal. found; C, 21.22; H, 1.81; Fe, 9.42; I, 66.61%. A sample of the crude salt was recrystallized from acetonitrile in the ordinary manner to give pure **1**, m.p. 183–184°C dec.

In another experiment performed at the I_2/Fc molar ratio of 1.5 used by Morrison and Hendrickson [7], (Bz-1.5, Table 1), iodine (1.5 mmol) dissolved in benzene (15 ml), was added slowly to a solution of ferrocene (1.0 mmol) in the same solvent (18 ml). Work-up was as in the preceding experiment. The crude black, powdery product (85.2%), m.p. 179–180°C, dec., gave an IR spectrum essentially identical to that of Hx-1.5. Anal. found: C, 20.98; H, 1.66; Fe, 9.49; I. 68.07%. Conventional recrystallization from acetonitrile afforded (65% recovery) an inhomogeneous mixture of black, shiny crystals, m.p. 174–179°C dec. IR (KBr): almost identical to spectrum of Hx-1.5, but slightly reduced intensity of 1113 cm^{-1} band. Anal. found: C, 18.03; 1.61; Fe, 8.48; I, 70.42. $C_{10}H_{10}FeI_{3.5}$ (630) calcd.: C, 19.06; H, 1.60; Fe, 8.86; I, 70.48%. From a similar procedure (ferrocene molarity 0.02) but with the I_2/Fc ratio raised to 3.0 (Bz-3, Table 1), crude iodide (76.7%) precipitated out as a black powder, m.p. 171–173°C dec, IR (KBr): same as spectrum of Hx-3. Anal. found: C, 16.86; H, 1.48; Fe, 7.70; I, 74.07. $C_{10}H_{10}FeI_4$ (694) calcd.: C, 17.31; H, 1.45; Fe, 8.05; I, 73.18%. Repeated experiments afforded similar material (68–78%), melting with decomposition between 171 and 180°C and corresponding in composition to FcI_4–FcI_5. Recrystallization from acetonitrile gave a salt, m.p. 170–174°C dec, with IR (KBr) spectrum identical with that of the crude compound. Anal. found: C, 15.81; H, 1.30; Fe, 7.22; I, 74.01%. Raising the I_2/Fc ratio to 5.0 under otherwise unchanged conditions (Bz-5, Table 1) gave product salt (71–81%), typically melting at 126–127°C and decomposing at 168°C; the IR (KBr) spectrum was similar to that of the product from Bz-3. Anal. found: C, 15.06; H, 1.29; Fe, 6.89; I, 75.75%. A virtually unchanged salt was obtained after ordinary recrystallization.

D. In 1,2-dichloroethane. Under conditions loosely specified by Wassef and Abou El Fitouh [8], the solution of iodine (6.0 mmol) in 1,2-dichloroethane (20 ml) was added to a solution of ferrocene (4.0 mmol) in the same medium (9 ml). The usual work-up afforded a major batch of black, fine-crystalline iodide. Reduction of the volume of the filtrate gave a second, smaller portion of salt, bringing the total yield of combined crude material to 72.7%. The salt melted at 181–182°C with decomposition and gave IR and analytical data practically identical to those from Hx-1.5. This experiment is tabulated as DCE-1.5 (Table 1). Repeat runs gave products (72–75%) for which elemental analysis indicated compositions of FcI_3–$FcI_{3.5}$. Recrystallized samples melted sharply with decomposition in the range 174–178°C. Representative anal: found: C, 19.58; H, 1.63; Fe, 9.10; I, 68.31%. Reducing the initial amount of iodine to 4.0 mmol gave triiodide **1** (experiment tabulated as DCE-1, Table 1), whereas increase in the iodine concentration to 8 and 12 mmol (experiments DCE-2 and DCE-3 respectively), at ferrocene molarities of 0.10 and 0.05, resulted in product compositions ranging from FcI_4 to FcI_5. Use of a reactant ratio of 5.0, ferrocene molarity 0.02 (DCE-5), gave pentaiodide/hexaiodide mixtures (80–86%), m.p. 125–127°C, 180°C dec; the IR (KBr) spectrum was practically identical to that from product of Hx-3. Representative anal. found: C, 12.92; H, 1.10; Fe, 6.01; I, 80.02. $C_{10}H_{10}FeI_6$ (947) calcd.: C, 12.68; H, 1.06; Fe, 5.89; I, 80.36%. Recrystallization from acetonitrile in the conventional manner afforded material of similar composition, m.p. 112–120°C, 176°C dec.

E. In ethanol. Absolute ethanol, used by Nesmeyanov et al. [3], was employed in a series of experiments with molar reactant ratios ranging from 0.34 to 15 (Et-0.34 through Et-15, Table 1). The experiments were performed as described under A for Hx-1.5, but a small second portion was collected in each case from the concentrated (at room temperature) mother-liquor, and the data given in Table 1 refer to the combined material. Triiodide **1** was isolated in Et-0.34, Et-0.5, Et-1, and Et-1.5, m.p. (sharp) in the range 179–186°C (Lit. [3] 169–171°C dec after recrystallization from acetone). Higher-order polyiodides as tabulated (Table 1) were obtained from Et-2 through Et-15, all (crude and recrystallized) giving IR spectra essentially identical to that of Hx-3. The product from Et-10, a black microcrystalline solid with a strong iodine odor, had m.p. 115–119°C dec. (other samples degrading in the range 120–126°C). Anal. found: C, 10.31; H, 0.81; Fe, 4.98; I, 84.27%. $C_{10}H_{10}FeI_{7.5}$ (1138) calcd.: C, 10.56; H, 0.89; Fe, 4.91; I, 83.59%. Crude products from repeated experiments gave analytical results in agreement with compositions in the range FcI_7–FcI_8. Recrystallization of crude material from acetonitrile gave fine, black, shiny crystals, m.p. 115–120°C, 184°C dec. Anal. found: C, 10.85.; H, 0.85; Fe, 5.11; I, 82.39%. $C_{10}H_{10}FeI_7$ (1074) calcd.: C, 11.18; H, 0.94; Fe, 5.20; I, 82.68%. When the recrystallization of crude salt was from acetone, a product of average composition $FcI_{4.5}$, m.p. 178–180°C, was obtained (Lit. [3] FcI_3), and two more recrystallizations from the same solvent were required for complete conversion into the triiodide. The product of Et-15, a grayish black powdery solid with a strong iodine odor, melted at 112–113°C with decomposition (other samples, 125–130°C, dec.). Anal. found: C, 8.64; H, 0.96; Fe, 4.65; I, 85.96%. $C_{10}H_{10}FeI_{9.5}$ (1392) calcd.: C, 8.63; H, 0.72; Fe, 4.01; I, 86.63%. The recrystallized salt had m.p. 110°C (partial), 120–122°C; 170°C dec. Anal. found: C, 10.49; H, 0.89; Fe, 4.85; I, 82.93%.

Separation of iodide types 2–6 by fractionating crystallization

The combined recrystallized salts from experiments Hx-3, Bz-3, Bz-5, DCE-3 and Et-3, average composition $FcI_{(4.5 \pm 0.5)}$, were subjected to fractional crystallization from nitromethane. The procedure, following the conventional fractionating pattern, involved dissolving the combined material in warm (max. 50°C), deoxygenated nitromethane under Ar and allowing several fractions slowly to crystallize from the filtered and heat-insulated solution. Fractions of nearly identical composition and crystallographic behavior were then combined and re-recrystallized in the same fashion, and the process was continued until two major compound types, labeled **2** and **3** (Table 2), emerged as reproducibly defined species in addition to some **1**. Numerous repeat fractionation series, overall comprising more than 200 subfractions, were performed to check on reproducibility. All crystallizates were washed sparingly with cold nitromethane and dried for 1–2 h in an evacuated desiccator, with two argon flushings to assist solvent removal. The crystals were then stored under Ar in small, tightly sealed vials in the dark. Identification of the subfractions (all of them characterized by similar melting behavior, very similar macroscopic crystal appearance, and virtually identical IR spectra) rested on elemental analysis (2–5 CH, 2–3 I determinations) and X-ray powder diffractometry. Similar series of fractionating crystallization were performed on combined recrystallized salts from experiments Hx-5, DCE-5, Et-5, and Et-10, average composition $\mathrm{FcI}_{(6.5 \pm 1.5)}$, altogether involving some 180 subfractions isolated. The two iodide types in addition to **3**, ultimately collected, are labeled **4** and **5** (Table 2). Finally, combined recrystallized material from several repeat runs of Et-15 were fractionated as before; this gave type **6** in addition to type **5** and small quantities of **3** and **4**. Types **2**–**6** occurred within the approximate compositional ranges given in Table 2. The most probable compositions are also listed in the table for **1**–**6**, together with melting and decomposition data, as well as IR frequencies. Crystallographic data (*d*-spacings) are compiled in Table 3. Representative analytical data are given below. Anal. found for **1**: C, 21.23; H, 1.83; Fe, 9.61; I, 67.30. $C_{10}H_{10}FeI_3$ (567) calcd.: C, 21.19; H, 1.78; Fe, 9.85; I, 67.17%. Anal. found for **2**: C, 16.97; H, 1.44; Fe, 7.93; I, 73.96. $C_{10}H_{10}FeI_4$ (694) calcd.: C, 17.31; H, 1.45; Fe, 8.05; I, 73.18%. Anal. found for **3**: C, 16.20; H, 1.32; Fe, 7.71; I, 74.21. $C_{10}H_{10}FeI_{4.3}$ (732) calcd.: C, 16.41; H, 1.38; Fe, 7.63; I, 74.57%. Anal. found for **4**: C, 14.85; H, 1.28; Fe, 6.71; I, 77.10. $C_{10}H_{10}FeI_5$ (820) calcd.: C, 14.64; H, 1.23; Fe, 6.81; I, 77.33%. Anal. found for **5**: C, 11.85; H, 0.98; Fe, 5.39; I, 81.82. $C_{10}H_{10}FeI_{6.5}$ (1011) calcd.: C, 11.88; H, 1.00; Fe, 5.52; I, 81.60%. Anal. found for **6**: C, 10.41; H, 0.81; Fe, 4.86; I, 83.95. $C_{10}H_{10}FeI_{7.5}$ (1138) calcd.: C, 10.56; H, 0.89; Fe, 4.91; I, 83.65%. Both **5** and **6** were exceedingly unstable in the solid state, necessitating rapid manipulation during analysis, KBr pellet pressing, and X-ray powder pattern recording to prevent significant loss of iodine. Samples of **4**, although less susceptible to iodine elimination, were nonetheless handled with similar precaution. All types, including the well defined **1**, were practically insoluble in hydrocarbons but dissolved readily and without significant change in composition, in acetonitrile and nitromethane (some loss of iodine suffered by **6** and very small amount by **5**). Solubility was also observed in acetone, in which the higher-order iodides decomposed slowly, with loss of iodine and predominant formation of **1**.

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