895. *The Organic Chemistry of the Transition Metals. Part II.* A Spectroscopic Investigation of Polynuclear Iron Carbonyls and Derived Anions.*

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The oxidation products of alkaline solutions of iron hydro-carbonyl have been investigated spectroscopically, and successive formation of bi- and tri-nuclear species has been demonstrated. The interconversions, often complex, of these and the known polynuclear carbonyls have been studied, and earlier results are reviewed and re-interpreted.

During work on the preparation of complexes, $RC{:}CR^1,H_2Fe_2(CO)_8$,[1-3] from basic solutions of iron pentacarbonyl and acetylenes it became necessary to identify the species which were present before the acetylenic component was added. In the literature [4-6] there are contradictory accounts of the transformations which can take place in basic solutions of iron pentacarbonyl. It is clear that the initial products (eqn. 1) are salts of the hydride $H_2Fe(CO)_4$ which is a weak acid ($K_1 = 4 \times 10^{-5}$, $K_2 = 4 \times 10^{-14}$).[6] The solutions obtained possess strong reducing properties and have been shown [4] to hydroformylate and/or to isomerize certain olefins.

$$Fe(CO)_5 + 3HO^- \longrightarrow [HFe(CO)_4]^- + CO_3^{2-} + H_2O \quad \text{. . . . . (1)}$$

Krumholz and Stettiner [6] have reported that aqueous solutions of $KHFe(CO)_4$ are stable provided that oxidizing agents are rigorously excluded. Sternberg, Markby, and Wender,[4] on the other hand, suggest that (under their very slightly different conditions) the ion $[HFe(CO)_4]^-$ slowly dimerizes to $[H_2Fe_2(CO)_8]^{2-}$, which then gives $[Fe_2(CO)_8]^{2-}$ by spontaneous decomposition or oxidation. The observed absorption maxima at about 4750 and 5350 Å were assigned respectively to these two binuclear species, to which the hydrogen transfer and hydroformylation reactions were attributed. Sternberg and his co-workers did not study the effect of oxidizing agents on their solutions of $NaHFe(CO)_4$ although their scheme requires the oxidation to be preceded by the dimerization of $[HFe(CO)_4]^-$, which on the evidence cited is a slow process. The American workers [4] were able to isolate solid sodium and nickel tris-*o*-phenanthroline salts from their aged solutions, but their analytical data, although proving the presence of polynuclear carbonyl hydride anions of some type, did not distinguish between di- and tri-nuclear derivatives.

We have verified that two species—and apparently, only two—were spectroscopically detectable in aged solutions of the mononuclear hydro-carbonyl anion, with absorption maxima close to the reported wavelengths. In our experiments, however, rigorous exclusion of air and light prevented their formation. On illumination in the absence of air or when any of several oxidizing agents (including air) was added these maxima appeared successively. We therefore doubted the representation of " the 4800 Å species " as simply a dimer of the hydro-carbonyl anion; both species appeared to be oxidation products. Indeed, with active manganese dioxide [7] the reaction almost stopped at the 4800 Å stage, whilst more vigorous oxidation, *e.g.*, with excess of nitromethane, led through the 4800 Å and 5400 Å stages to ferric hydroxide and a colourless solution, methylamine being formed.

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* Part I, *J.*, 1959, 551.

[1] Reppe and Vetter, *Annalen*, 1953, **582**, 133.

[2] Sternberg, Friedel, Markby, and Wender, *J. Amer. Chem. Soc.*, 1956, **78**, 3621.

[3] Clarkson, Jones, Wailes, and Whiting, *J. Amer. Chem. Soc.*, 1956, **78**, 6206.

[4] Sternberg, Markby, and Wender, *J. Amer. Chem. Soc.*, 1956, **78**, 5704; 1957, **79**, 6116.

[5] Hieber and Brendel, *Z. anorg. Chem.*, 1957, **289**, 324.

[6] Krumholz and Stettiner, *J. Amer. Chem. Soc.*, 1949, **71**, 3035.

[7] Attenburrow, Cameron, Chapman, Evans, Hems, Jansen, and Walker, *J.*, 1952, 1104.

Any solution containing the 4800 Å species as the main spectroscopically evident constituent changed on weak acidification (*e.g.*, with acetic acid to pH 4—6) to one of the 5400 Å species, even in the absence of air.

Hieber and Brendel[5] have suggested that the effect of oxidizing agents (including manganese dioxide) on solutions of $[HFe(CO)_4]^-$ is the production of anions derived from $H_2Fe_2(CO)_8$. They also state that the anions from $H_2Fe_2(CO)_8$ and $H_2Fe_3(CO)_{11}$ might be generated in solutions of $KHFe(CO)_4$ by the spontaneous decomposition of the free hydride $H_2Fe(CO)_4$, produced in turn by hydrolysis. These workers reported that these solutions were red, but did not isolate crystalline salts, or study the solutions spectroscopically. They did, however, prepare solid salts of these hydrides from the polynuclear carbonyls $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$. For example, after successive treatment of $Fe_3(CO)_{12}$ with alkali and acetic acid they were able to precipitate the well-defined salt $Me_4N^+[HFe_3(CO)_{11}]^-$. We readily obtained this salt by the same method, and an analogous triethylammonium salt from iron pentacarbonyl and triethylamine under vigorous conditions.[9] In solution both salts showed an absorption maximum at 5400 Å (approx.) and the log $\varepsilon_{at.}$ *versus* wavelength curves were identical and almost parallel to those obtained by the oxidation of $KHFe(CO)_4$, *e.g.*, with iodine or nitromethane, or by heating iron pentacarbonyl with ethanolamine (Fig. 1), and little dependent on the solvent used. On treatment with mineral acids these trinuclear salts rapidly yielded iron dodecacarbonyl ($\lambda_{max.}$ 6050 Å).

FIG. 1.

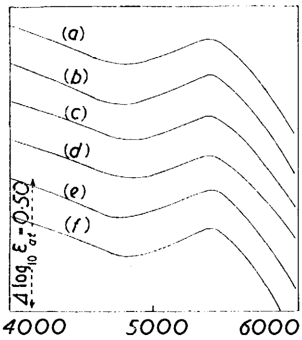

FIG. 2.

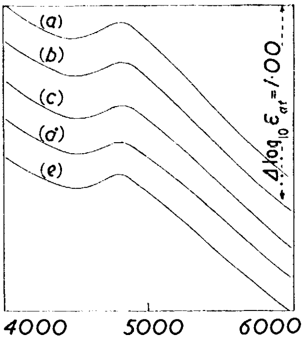

FIG. 1. Species of $\lambda_{max.}$ 5400: (*a*) $Me_4N^+[HFe_3(CO)_{11}]^-$, $\varepsilon_{at.}$ 1030 at maximum; (*b*) $Et_3NH^+[HFe_3(CO)_{11}]^-$, $\varepsilon_{at.}$ 1020; (*c*) treatment of $KHFe(CO)_4 + K_2CO_3$ with excess of $CH_3{\cdot}NO_2$, $\varepsilon_{at.}$ 420; (*d*) neutralisation of solution of $K_2Fe_2(CO)_8 + K_2CO_3$ to pH 7, $\varepsilon_{at.}$ 750; (*e*) heating $Fe(CO)_5$ with ethanolamine, $\varepsilon_{at.}$ 600; (*f*) treatment of $Fe_3(CO)_{12}$ with excess of K_2CO_3, $\varepsilon_{at.}$ 900.

FIG. 2. Species of $\lambda_{max.}$ 4800: (*a*) $Fe_2(CO)_9 + 4KOH$, $\varepsilon_{at.}$ 1040; (*b*) $Fe_2(CO)_9 + 3KOH$, $\varepsilon_{at.}$ 1020; (*c*) $KHFe(CO)_4 + K_2CO_3 +$ excess MnO_2, $\varepsilon_{at.}$ 520; (*d*) $KHFe(CO)_4 + K_2CO_3 + CH_3{\cdot}NO_2$ (0·18 mol.), $\varepsilon_{at.}$ 400; (*e*) $Fe_3(CO)_{12} + 5KOH$, $\varepsilon_{at.}$ 880.

Hieber and Brendel[5] were able to prepare solutions of salts of $H_2Fe_2(CO)_8$ from iron enneacarbonyl, $Fe_2(CO)_9$. Following their method, we were easily able to dissolve this very insoluble compound in four equivalents of methanolic potassium hydroxide; when a ball-mill was used it was possible to dissolve the carbonyl in only three equivalents,

$$Fe_2(CO)_9 + 3HO^- \longrightarrow [HFe_2(CO)_8]^- + CO_3^{2-} \text{ or } [Fe_2(CO)_8]^{2-} + HCO_3^- \quad . \quad . \quad . \quad (2)$$

giving a solution of pH 10. These solutions had absorption maxima at 4800 Å and behaved like those obtained by treatment of solutions of $KHFe(CO)_4$ with manganese dioxide; acidification to about pH 4 rapidly gave the 5400 Å species whereas mineral acid gave iron dodecacarbonyl. Again, the log $\varepsilon_{at.}$ *versus* wavelength curves were parallel for the solutions obtained in these different ways (Fig. 2).

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[8] Hieber, *Z. anorg. Chem.*, 1932, **204**, 165.

[9] BASF (M. Heintzeler), D.B.P. 928044, Kl. 12n (1955).

We therefore agree with Hieber and Brendel's hypothesis[5] that the oxidation of salts of $H_2Fe(CO)_4$ gives, successively, salts of $H_2Fe_2(CO)_8$ and of $H_2Fe_3(CO)_{11}$. This implies that in the experiments of Sternberg, Markby, and Wender[4] the 4750 Å maximum assigned to salts of $H_2[H_2Fe_2(CO)_8]$ really belongs to salts of $H_2Fe_2(CO)_8$, whilst the maximum at 5350 Å, assigned to the latter, must be attributed to salts of $H_2Fe_3(CO)_{11}$. If the dimer of $[HFe(CO)_4]^-$ exists at all, it must be non-absorbing and rapidly formed; however, the hydroformylation, reductive, and catalytic properties of these solutions can all be explained on the basis of the species derived from $H_2Fe(CO)_4$, $H_2Fe_2(CO)_8$, and $H_2Fe_3(CO)_{11}$ known to be present, and no reason remains for postulating that ion. The instability of the solutions of $NaHFe(CO)_4$ used by Sternberg, Markby, and Wender[4] may have been connected with the presence of an excess of iron pentacarbonyl when they were prepared.

However the species concerned was obtained, neither of the absorption curves reproduced (Figs. 1 and 2) underwent a rapid and reversible change on varying the pH value. This means either that these anions do not alter in absorption spectrum with degree of protonation—which is conceivable but would be surprising—or that only one degree of protonation is observed for the binuclear anion over a pH range of 10—14, and for the trinuclear anion over the range 5—14. Below pH about 10 and 5, respectively, irreversible reactions became too rapid for spectra to be obtained.

In one respect our results differ sharply from those of Hieber and Brendel.[5] When these authors treated iron dodecacarbonyl with methanolic potassium hydroxide (1—2N) they obtained solutions described as "tief rotbraun;" these were believed, not unnaturally, to contain the anion $[Fe_3(CO)_{11}]^{2-}$:

$$Fe_3(CO)_{12} + 4HO^- \longrightarrow [Fe_3(CO)_{11}]^{2-} + CO_3^{2-} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

and with nickel tris-*o*-phenanthroline dichloride and hexamminenickel dichloride precipitates giving good analyses for the expected neutral trinuclear salts were obtained. We, on the other hand, found that with potassium carbonate * solution the purple-red solution, $\lambda_{max.}$ 5400 Å, of the trinuclear anion was indeed formed (Fig. 1), but that with methanolic potassium hydroxide the deep brownish-red solution obtained had exactly the spectrum of the binuclear anion (Fig. 2). Some ferrous hydroxide and potassium methyl carbonate were obtained, as described by Hieber and Brendel[5] (although the latter report very little iron to be present in this). These results were observed repeatedly. The formation of the binuclear anion can be represented by reaction (4) or (5):

$$3Fe_3(CO)_{12} + 15HO^- \longrightarrow 4[Fe_2(CO)_8]^{2-} + 3CO_3^{2-} + H{\cdot}CO_2^- + Fe(OH)_2 + 6H_2O \quad . \; . \quad (4)$$

$$11Fe_3(CO)_{12} + 54HO^- \longrightarrow 15[Fe_2(CO)_8]^{2-} + 12CO_3 + 3Fe(OH)_2 + 24H_2O \quad . \; . \; . \quad (5)$$

These disproportions are no more complicated than that of reaction (6) advanced by

$$12[Fe_3(CO)_{11}]^{2-} + 30H^+ \longrightarrow 11Fe_3(CO)_{12} + 15H_2 + 3Fe^{2+} \quad . \; . \; . \; . \; . \; . \quad (6)$$

Hieber and Brendel[5] for the conversion of the trinuclear anion into $Fe_3(CO)_{12}$.

This method of preparing the binuclear anion is of some importance, as the best preparative route to the binuclear anion from iron pentacarbonyl known to us involves the salt[9] $Et_3NH^+[HFe_3(CO)_{11}]^-$, then $Fe_3(CO)_{12}$ and this reaction. Our conclusions conflict with those of Hieber and Brendel[5] only insofar as these authors reported isolation of two neutral *trinuclear* complex nickel salts after the action of alkali on $Fe_3(CO)_{12}$. The isolation of the tetramethylammonium hydrogen salt (see above), and of the other acid trinuclear salts, is of course expected as acidification with acetic acid intervenes.

Dr. W. Beck and Prof. W. Hieber suggested the spectroscopic examination of the complex formulated[10] as $Fe^{2+}en_3[Fe_2(CO)_8]^{2-}$ as an authentic example of the ion

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* *Added, June 7th.*—Repetition of this experiment with very careful exclusion of air has repeatedly led to a solution with $\lambda_{max.}$ 4800 Å, and we therefore conclude that this experiment involved accidental oxidation.

[10] Hieber, Sedlmeier, and Werner, *Chem. Ber.*, 1957, **96**, 284.

$[Fe_2(CO)_8]^{2-}$, because the $Fe^{2+}en_3$ ion, unlike the complex nickel cations used to precipitate this anion,[5] absorbs only weakly. Its preparation was repeated without difficulty, giving a highly crystalline orange-red product with the solubility properties described. This, however, had in either dimethylformamide or aqueous ethylenediamine, the only solvents found for it, absorption spectra without the maximum at 4800 Å characteristic of the alkali-metal salts of this anion; moreover, the molar absorption coefficient ($\varepsilon = 414$, $C_{14}H_{24}Fe_3N_3O_8$ being assumed) at this wavelength was much less than that of the binuclear anion, as prepared by the methods described above ($\varepsilon = 2080$ or more). We can only suggest that this compound either has a constitution of the type originally ascribed to it,[11] after all, or that it is actually the acid salt of the anion $[HFe(CO)_4]^-$, therefore having the formula $C_{14}H_{26}Fe_3N_3O_8$ and an analysis very close to that now accepted by Hieber, Sedlmeier, and Werner.[10] In the latter case the absorption spectrum—merely a smoothly rising curve down to 4000 Å, where $\varepsilon = 2000$—would have to be ascribed to species present other than $Fe^{2+}en_3$, as Ciampolini, Paoletti, and Sacconi have shown [12] that this cation shows no absorption with $\varepsilon > 10$ in the visible region.

Recently, Vlček [13] has reported polarographic evidence that the reaction of iron dodecacarbonyl with alcoholic alkali is more complex than was suggested by Hieber and Brendel,[5] a result obviously in harmony with our findings.

Anticipating a forthcoming paper on the preparation of the acetylene complexes, $RC⋮CR^1,H_2Fe_2(CO)_8$, we may say that solutions rich in the species with $\lambda_{max.}$ 4800 Å (however obtained), and ascribed by us to salts of $H_2Fe_2(CO)_8$, are by far the most efficient progenitors of these complexes. As the molecular formula of these, proposed on analytical grounds,[1,2] has been confirmed by chemical [3] and *X*-ray studies,[14] we may treat this evidence as additional support for that attribution.

EXPERIMENTAL

Ultraviolet spectra were measured on a Cary recording spectrophotometer, model 14 M-50. The atomic extinction coefficients ($\varepsilon_{at.}$) are calculated per g.-atom of iron added as the carbonyl to 1 l. of the solution (*i.e.*, l. g.-atom^{-1} cm.$^{-1}$).

Iron enneacarbonyl was prepared from iron pentacarbonyl by Speyer and Wolf's method: [15] the yields were improved when reaction mixtures were kept cool (*ca.* 5°) during the irradiation. Iron dodecacarbonyl was prepared by the methods of Hieber [8] and Heintzeler,[9] the latter being preferred; it had $\lambda_{max.}$ 6050 Å, $\varepsilon_{at.}$ 835, in ethanol.

The salt $Me_4N^+ [HFe_3(CO)_{11}]^-$ was prepared by Hieber and Brendel's method,[5] $\lambda_{max.}$ 5400 Å, $\varepsilon_{at.}$ 1030. It separated from acetone in plates 5 mm. across, and when dry was stable for several days in air at 20°. It dissolved in aqueous acetone, and from such solutions was readily extracted by ether. From the ethereal solution it was extracted by ethylene glycol, but not be water. These remarkable properties are presumably attributable to the exceptional size of the anion.

Triethylammonium Hydrogen Undecacarbonyltriferrate.—In the patent [9] describing this compound no details of temperature or reaction time are given; the following procedure was found convenient. Iron pentacarbonyl (40 g.), triethylamine (15 g.), and water (60 c.c.) were stirred at 80° under nitrogen for 10 hr. When the mixture was cooled the dark red, lower layer rapidly solidified and the supernatant liquid was poured off. After the solid product had been washed several times with water it was dried *in vacuo* at room temperature over silica gel to give, after crystallisation from aqueous methanol, dark red prisms (39 g., 95% based on the pentacarbonyl), $\lambda_{max.}$ 5400 Å, $\varepsilon_{at.}$ 1020.

Spectroscopic Investigation of the Reaction of Iron Carbonyls in Basic Media.—The solutions

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[11] Hieber and Sonnekalb, *Ber.*, 1928, **61**, 558.

[12] Unpublished work communicated by Dr. L. Venanzi.

[13] Vlcek, " International Conference on Co-ordination Chemistry," London, 1959 (Chem. Soc. Special Publication, No. 13).

[14] Hock and Mills, *Proc. Chem. Soc.*, 1958, 233.

[15] Speyer and Wolf, *Ber.*, 1927, **60**, 1424.

used in the following experiments were kept under an atmosphere of oxygen-free nitrogen. Immediately before their use as solvents, methanol and ethanol were distilled in a current of nitrogen, and distilled water was boiled for 4 hr. while a stream of nitrogen was passed through it.

Solutions containing the ion $[HFe(CO)_4]^-$ (0·5M) were prepared by dissolving iron pentacarbonyl (1·96 g.) in a solution of potassium hydroxide (1·68 g.) in a mixture of ethanol (18 c.c.) and water (3 c.c.). They were colourless and did not develop any colour during 96 hr. in the dark at room temperature.

Oxidation of Solutions containing the Ion $[HFe(CO)_4]^-$.—(i) *With manganese dioxide.* Activated manganese dioxide [7] (3·5 g.) was added portionwise during 15 min. to a stirred solution of $KHFe(CO)_4$ (0·4M, 25 c.c.). A broad maximum at 4800 Å rapidly developed and after 30 min. attained a constant intensity ($\varepsilon_{at.}$ 520). Further addition of manganese dioxide caused the slow development of an inflexion at 5400 Å. Addition of iodine (0·95 g., 0·5 equiv.) in ethanol caused the rapid disappearance of the maximum at 4800 Å and the formation of a maximum at 5400 Å ($\varepsilon_{at.}$ 354).

(ii) *With nitromethane.* Nitromethane (0·011 g.), dissolved in ethanol (3 c.c.), was added slowly to an ethanolic solution of $KHFe(CO)_4$ (0·1M, 10 c.c.). An absorption maximum at 4800 Å ($\varepsilon_{at.}$ 400) rapidly developed. Addition of more nitromethane resulted in the gradual development of a maximum at 5400 Å. The introduction of an excess of nitromethane (0·050 g.) at the start of the reaction resulted in the evolution of heat with vigorous effervescence and the rapid development of a maximum at 5400 Å ($\varepsilon_{at.}$ 420). This solution became colourless during 12 hr. with the formation of methylamine and ferric hydroxide.

(iii) *With iodine.* A solution of $KHFe(CO)_4$ (0·1M) was titrated with a solution of iodine in ethanol (0·1N). The titration was followed by measuring the intensity of the maximum at 5400 Å which formed immediately. An inflexion at 4800 Å was present in the early stages but later disappeared. When approximately 1·5 equiv. of iodine had been added the absorption at 5400 Å reached its maximum value ($\varepsilon_{at.}$ 450), then decreasing. The formation of the maximum at 5400 Å was shown not to be due to acidification alone, since a solution of the stoicheiometric composition $K_2Fe(CO)_4 + K_2CO_3$ behaved in exactly the same way.

Solutions containing the Ions $[HFe_2(CO)_8]^-$ *and/or* $[Fe_2(CO)_8]^{2-}$.—Owing to its very low solubility, iron enneacarbonyl could be made to react with 3 mol. of alcoholic potassium hydroxide only by grinding the mixture in a ball mill for 3 hr. The absorption maximum at 4800 Å ($\varepsilon_{at.}$ 1020) which developed (final pH 10) was replaced by a maximum at 5400 Å ($\varepsilon_{at.}$ 890) during 72 hr. at room temperature in the dark. The absorption band of the freshly prepared solution did not change significantly in position or intensity when the pH was adjusted within the range 10—14.

Solutions prepared by shaking iron enneacarbonyl (0·364 g.) for 20 min. with a solution of potassium hydroxide (0·224 g.) in methanol [5] were used in the following experiments (initially $\lambda_{max.}$ 4800 Å, $\varepsilon_{at.}$ 1040, unchanged after 72 hr. in the dark).

(i) *Neutralization.* Careful addition of oxygen-free hydrochloric acid (0·1N) to the solution to pH 7 resulted in irreversible development of a maximum at 5400 Å ($\varepsilon_{at.}$ 750) with the concomitant disappearance of that at 4800 Å.

(ii) *Oxidation.* Exposure of the solution to oxygen resulted in the immediate development of a maximum at 5400 Å. The addition of iodine (0·5 equiv.) had a similar effect.

Reactions of Iron Dodecacarbonyl.—(i) *With potassium hydroxide.* Following Hieber and Brendel's method,[5] iron dodecacarbonyl (1·0 g.) was dissolved in methanolic potassium hydroxide (2M, 10 c.c.). As soon as the intense dark green colour of the solution—stronger than that of the original carbonyl—had disappeared (*ca.* 3 min.) the solution, freed from a brown deposit by centrifuging, showed a broad maximum at 4800 Å ($\varepsilon_{at.}$ 880). The band at 4800 Å was still present after 12 hr. at room temperature but was shifted to 5400 Å either on the admission of oxygen to the solution or on its neutralization.

(ii) *With potassium carbonate.* Iron dodecacarbonyl, shaken with ethanol–water (95 : 5) in contact with solid potassium carbonate, dissolved slowly with the immediate development in the liquid phase of an absorption maximum at 5400 Å ($\varepsilon_{at.}$ 900 on complete dissolution after about 12 hours' shaking). When the solution was made strongly alkaline (KOH; 2N) no change in the intensity or position of the absorption maximum was observed.

Reaction of Iron Pentacarbonyl with Ethanolamine.—A solution of equimolecular proportions of iron pentacarbonyl and ethanolamine in aqueous ethanol was heated at 65°. An absorption maximum at 5400 Å developed rapidly, and maximal intensity ($\varepsilon_{at.}$ 600) at 5400 Å was attained after 10 hr., further heating resulting in a slow diminution (after 16 hr., $\varepsilon_{at.}$ 370).

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