Interaction of carbonylferrate- and hydridocarbonylferrate anions with Brønstad and Lewis acids

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Interaction of carbonylferrate anions $Fe_n(CO)^{2-}_{m-1}$ and hydridocarbonylferrate anions $HFe_n(CO)^{-}_{m-1}$ (where $n = 1$—4; $m = 5, 9, 12, 14$, respectively) with Brønstad and Lewis acids HX (X = AcO, CF_3CO_2, HSO_4) and RX (R = Alk, Ac, Bn, Bz; X = Cl, Br) is a radical-chain process, occuring *via* a one-electron redox-initiation stage, including preliminary activating complex formation. A common approach to the description of the processes of reduction and carbonylation of different organic compounds was suggested. It is based upon the exchange reactions and the interconversions within the coordination spheres of 17-electron coordinatively unsaturated iron carbonyl radical anions, $Fe_n(CO)^{\cdot -}_{m-1}$.

Key words: carbonylferrate anions, hydridocarbonylferrate anions; Brønstad acids, Lewis acids; iron carbonyl radical anions; radical-chain processes; Reppe synthesis.

Carbonylferrate anions (CFA) (**1**) are known to be sufficiently strong bases and to accept protons readily, turning into hydridocarbonylferrate anions (HCFA) (**2**), the further protonation of which gives rise to neutral forms (**3**) (Eq. 1).

$$\underset{\mathbf{1a-d}}{Fe_n(CO)^{2-}_{m-1}} \underset{-H^+}{\overset{H^+}{\rightleftharpoons}} \underset{\mathbf{2a-d}}{HFe_n(CO)^{-}_{m-1}} \underset{-H^+}{\overset{H^+}{\rightleftharpoons}} \underset{\mathbf{3}}{H_2Fe_n(CO)_{m-1}} \tag{1}$$

a: $n = 1, m = 5$ **c:** $n = 3, m = 12$
b: $n = 2, m = 9$ **d:** $n = 4, m = 14$

Protons add to iron atom in mononuclear complexes and to metal—metal bond in bi- and polynuclear complexes. The exception is provided by anions **2c** and **2d**, which add the second proton to the carbonyl moiety to give complexes $HFe_3(CO)_{10}(\mu_2\text{-}COH)$ (**3c**) and $HFe_4(CO)_{12}(\mu_3\text{-}COH)$ (**3d**).[1] The salts of anions **1** are stable under an inert atmosphere. Among HCFA salts, **2c** and **2a** are the most stable. All of the compounds **3** are unstable and decompose spontaneously, evolving hydrogen at room temperature.[1—3] Most stable compounds under these conditions ($Fe(CO)_5$ and the salts of the anion $HFe_3(CO)_{11}^{-}$) were also found[1,2,4,5] among decomposition products.

The same tendencies are observed in the reaction of CFA (HCFA) with Lewis acids. For instance, alkylation and acylation of anion **1a** result in the formation of compounds **4**, rather stable under an inert atmosphere (Eq. (2)).[6—8]

$$\underset{\mathbf{1a}}{Fe(CO)_4^{2-}} + RX \longrightarrow \underset{\mathbf{4}}{RFe(CO)_4^{-}} + X^- \tag{2}$$

R = Alk, Ar, Ac, Bn, ArCO; X = Cl, Br, Ts

$$\underset{\mathbf{4}}{RFe(CO)_4^{-}} + RX \longrightarrow \underset{\mathbf{5}}{R_2Fe(CO)_4} + X^- \tag{3}$$

Neutral complexes of the $R_2Fe(CO)_4$ type (**5**) (Eq. (3)) are generally unstable. They were synthesised only in the case of electron-acceptor substituents, for example R = C_2F_5, C_3F_7,[9] CH_2CO_2R',[10] and $COCO_2R'$ (R' = Alk)[11].

A binuclear complex, $R_2Fe_2(CO)_8$ (R = CO_2Bu^t), synthesised by an indirect method,[12] is known.

The interaction of carbonylferrate anions **1c** and **1d** with AcCl and MeOTfl results in acylation and alkylation of a carbonyl ligand respectively, giving rise to the complexes $[Fe_n(CO)_{m-2}(COR)]^-$, where R = Ac, Me; $n = 3$, $m = 12$; $n = 4$, $m = 14$.[1,13—15] As in the case of hydrogen analogs **3c** and **3d**, these complexes are characterized by carbonyl ligand transformations, which affect metal framework little. On the contrary, mono- and binuclear complexes **1** and **2**, as well as compounds **4**, appeared to be the most effective in the reactions involving metal coordination centers and having a redox character. Such reactions are realized in the course of preparative syntheses of aldehydes, ketones, carboxylic acids, their esters and amides,[16] α-diketones,[17] and reduction of α,β-unsaturated carbonyl compounds.[5,18] Thus, the principal interest of most workers was focused on

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the investigation on the interaction of Brønstad and Lewis acids with mono- and binuclear complexes **1a,b** and **2a,b**.

The next important fact is the following: the majority of catalytical carbonylation processes are catalyzed by either CFA (HCFA)— Brønstad (Lewis) acid system[19,20] or by iron carbonyl—Lewis base.[19–22]

We found that the reactions of iron carbonyls with different Lewis bases are radical-chain processes with a two-stage redox initiation.[23–25] For instance, in case a base is an anion L^- [L = OR, SR, NR_2 (R = H, Alk, Ar), H, Hal, CN, SCN, NO_2, and others] the reaction proceeds according to Eqs. (4) and (5).

$$Fe_n(CO)_m + L^- \rightleftharpoons [Fe_n(CO)_{m-1}C(O)L]^- \qquad (4)$$

$$[Fe_n(CO)_{m-1}C(O)L]^- + Fe_n(CO)_m \longrightarrow [Fe_n(CO)_{m-1}C(O)L]^{\cdot} + Fe_n(CO)_m^{\cdot-} \xrightarrow[-CO]{} Fe_n(CO)_{m-1}^{\cdot-} \qquad (5)$$

n = 1—3; m = 5, 9, 12

Radical and radical anion species, arising at the second stage, may be formally treated as Fe(1) and Fe(−1) derivatives. These species initiate the propagation of two transformation chains, due to substitution in the coordination sphere of radicals. The final diamagnetic products result either from the further disproportionation giving Fe^{2+} complexes and carbonylferrate anions of Fe(−2) or in electron-transfer reactions.[26–28]

When studying the reactions involving CFA (HCFA) and Brønstad (Lewis) acids, radical species were also found.[5,29] The radicals were supposed[30,31] to form by direct reduction of alkyl halide by CFA or HCFA, for example:

$$HFe(CO)_4^- + RX \longrightarrow HFe(CO)_4^{\cdot} + RX^{\cdot-} \longrightarrow Fe(CO)_4 + RH + X^- . \qquad (6)$$

There are two contradictions in this scheme. First, a 16-electron species, $Fe(CO)_4$, is supposed to arise, though the existence of such a species in solution has not been proved yet.[32] Second, the direct reduction of RX seems improbable for thermodynamic reasons and is possible only for aromatic iodides, characterized by less negative values of the reduction potential.[19,33] The purpose of this work is to clarify the role of radical transformations in different processes with participation of CFA (HCFA) on the one hand and Brønstad (Lewis) acids on the other.

Results and Discussion

ESR study of the reactions of CFA and HCFA with Brønstad acids. The interaction of $Na_2Fe(CO)_4 \cdot 1.5$(diox) (diox is dioxane), $Na_2[Fe_2(CO)_8]$, $(PPN)_2[Fe_2(CO)_8]$ (PPN^+ = $(PPh_3)_2N^+$), $(PPN)_2[Fe_3(CO)_{11}]$, $(PPN)_2[Fe_4(CO)_{13}]$, $KHFe(CO)_4$, $(PPN)[HFe(CO)_4]$, $(PPN)[HFe_3(CO)_{11}]$, and $(Et_3NH)[HFe_3(CO)_{11}]$ with acetic, trifluoroacetic, and sulfuric acids was studied.

In the reaction of all of the above-listed CFA and HCFA with Brønstad acids, intensive signals from iron carbonyl radical anions (ICRA) were observed: $Fe_2(CO)_8^{\cdot-}$ (**6b**) (g = 2.0385), $Fe_3(CO)_{11}^{\cdot-}$ (**6c**) (g = 2.0498), $Fe_4(CO)_{13}^{\cdot-}$ (**6d**) (g = 2.0135), and $Fe_3(CO)_{12}^{\cdot-}$ (**7**) (g = 2.0013). The g factor values are given for the temperature of −80 °C and agree with the published values.[23–25,34] At the same time, according to the gas chromatography data the elimination of hydrogen takes place.

The sequence of ICRA formation in the reactions of mono- and binuclear CFA and HCFA is the following: **6b** appears first, and **6c**, **6d** and **7** next. With $Fe_2(CO)_8^{2-}$ salts the signals with g = 2.0328 (weak signal on the shoulder of the intense **6b**) and g = 2.0180 are observed as well.

In the reactions of trinuclear anions $Fe_3(CO)_{11}^{2-}$ and $HFe_3(CO)_{11}^-$ radical anion **6c** is formed first, and **7**, **6b**, and **6d** next. In addition, low intensity signals with g = 2.0180 and 2.0205 are observed.

It is significant that the signals corresponding to $HFe_n(CO)_{m-1}^{\cdot}$ (n = 1—3; m = 5, 9, 12), known from the works of Krusic,[3] are absent in the ESR spectra. By analogy with the CFA protonation one would expect these radicals to form from ICRA in acidic medium according to Eq. (7).

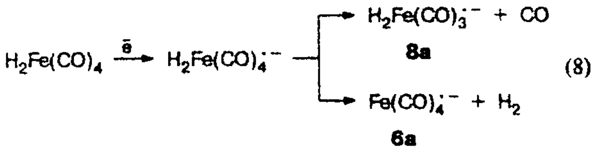
$$Fe_n(CO)_{m-1}^{\cdot-} + H^+ \longrightarrow HFe_n(CO)_{m-1}^{\cdot} \qquad (7)$$

ESR study of the reactions of $HFe_3(CO)_{11}^-$ and $HFe(CO)_4^-$ with ferricenium hexafluorophosphate. One-electron oxidation of the salts $(PPN)[HFe_3(CO)_{11}]$ and $(Et_3NH)[HFe_3(CO)_{11}]$ by ferricenium hexafluorophosphate ($FcPF_6$) gives the radical $HFe_3(CO)_{11}^{\cdot}$ (g = 2.0645, a_H = 18.95 G at −60 °C, published data[3]). It is rather stable at lower temperatures, but at temperatures higher than −30 °C passes slowly into $Fe_3(CO)_{11}^{\cdot-}$. At the later stages other ICRA (**7** and **6b**) emerge in the spectra.

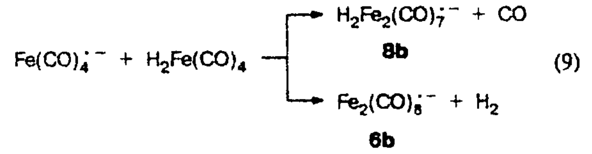
On the contrary, it is impossible to observe the formation of the radical $HFe(CO)_4^{\cdot}$ even at the temperature of −120 °C in the reaction of $KHFe(CO)_4$ and $(PPN)[HFe(CO)_4]$ with $FcPF_6$. The intensive generation of $Fe_2(CO)_8^{\cdot-}$, and then $Fe_3(CO)_{11}^{\cdot-}$ and $Fe_3(CO)_{12}^{\cdot-}$, accompanied by hydrogen elimination GC registeration takes place from the initial stages of the process. In addition to the ICRA signals, rather intense signals with temperature-dependent width and g factor were found in the ESR spectra at −80 °C. At such a temperature the parameters of these signals are the following: g = 2.0561 ($\Delta H_{0.5}$ = 18.8 G), g = 2.0206 ($\Delta H_{0.5}$ = 8.4 G), and g = 2.0052 ($\Delta H_{0.5}$ = 3.6 G). They are likely to belong to exchange systems [$Fc^{\cdot+}$ $M^{\cdot-}$] ($M^{\cdot-}$ is ICRA **6b**, **6c**, and 7).

ESR study of the reduction of $H_2Fe(CO)_4$ by sodium mirror. The compound $H_2Fe(CO)_4$, prepared by protonation of complex **1a**, decomposes slowly in MeTHF solution at temperatures higher than −30 °C. As this takes place the signals from ICRA **6b**, **6c**, **6d** and 7 as well as the triplet with g = 2.0489 and a_H = 24.2 G (−40 °C) are observed in the ESR spectrum. At room temperature only the signal corresponding to radical anion 7 remains in the spectrum for some time.

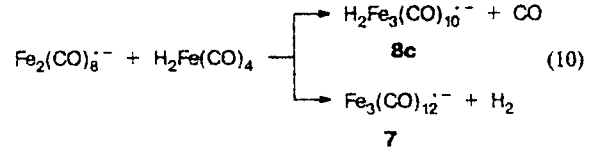
To elucidate the mechanism of the radical species formation in the course of $H_2Fe(CO)_4$ decomposition its reduction by the sodium mirror was carried out. At −110 °C the triplet with broadened lines in the g region of 2.0529 with a_H = 22.2 G appears. At −80 °C it disappears and the triplet with g = 2.0435 and a_H = 22.4 G (g = 2.0421 at −40 °C) and the signals corresponding to radical anions **6b**, **6c**, and 7 arise. Later the intensities of the ICRA signals decrease, and one more triplet with g = 2.0489 and a_H = 24.2 G arises (Fig. 1). It is likely that there is an analogy between the reduction of $H_2Fe(CO)_4$ and the corresponding reaction of $Fe(CO)_5$, followed by the subsequent formation of clusters of different nuclearity.[24] Thus the triplet structure signals can be supposed to correspond to mono-, bi-, and trinuclear radical anions: $H_2Fe(CO)_3^{\cdot-}$ (**8a**) (g = 2.0529), $H_2Fe_2(CO)_7^{\cdot-}$ (**8b**) (g = 2.0421), and $H_2Fe_3(CO)_{10}^{\cdot-}$ (**8c**) (g = 2.0489). It is interesting to note that the g factor values of isoelectronic ICRA are about the same: $Fe(CO)_4^{\cdot-}$ (**6a**) (g = 2.0486),[3,25] $Fe_2(CO)_8^{\cdot-}$ (**6b**) (g = 2.0385), $Fe_3(CO)_{11}^{\cdot-}$ (**6c**) (g = 2.0498). The formation of these radicals in the course of $H_2Fe(CO)_4$ reduction can be represented by Eqs. (8)—(11).



$$H_2Fe(CO)_4 \xrightarrow{\bar{e}} H_2Fe(CO)_4^{\cdot-} \begin{cases} \to \underset{\textbf{8a}}{H_2Fe(CO)_3^{\cdot-}} + CO \\ \to \underset{\textbf{6a}}{Fe(CO)_4^{\cdot-}} + H_2 \end{cases} \qquad (8)$$



$$Fe(CO)_4^{\cdot-} + H_2Fe(CO)_4 \begin{cases} \to \underset{\textbf{8b}}{H_2Fe_2(CO)_7^{\cdot-}} + CO \\ \to \underset{\textbf{6b}}{Fe_2(CO)_8^{\cdot-}} + H_2 \end{cases} \qquad (9)$$



$$Fe_2(CO)_8^{\cdot-} + H_2Fe(CO)_4 \begin{cases} \to \underset{\textbf{8c}}{H_2Fe_3(CO)_{10}^{\cdot-}} + CO \\ \to \underset{\textbf{7}}{Fe_3(CO)_{12}^{\cdot-}} + H_2 \end{cases} \qquad (10)$$

$$Fe_3(CO)_{12}^{\cdot-} \rightleftharpoons \underset{\textbf{6c}}{Fe_3(CO)_{11}^{\cdot-}} + CO \qquad (11)$$

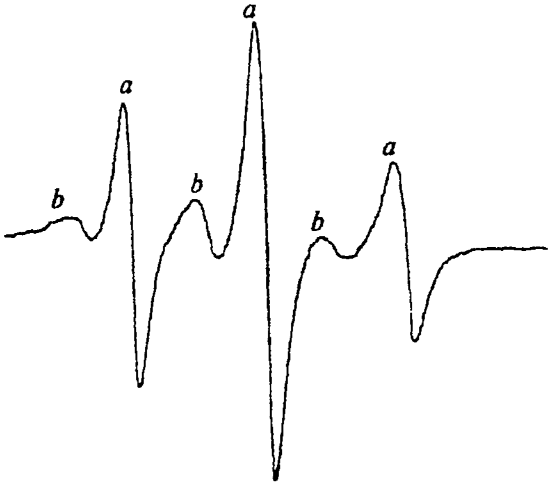


Fig. 1. The ESR spectrum, observed in the reduction of $H_2Fe(CO)_4$ by sodium mirror in MeTHF at −40 °C 7 min after the beginning of the reaction. Radical anions: $H_2Fe_2(CO)_7^{\cdot-}$ (g = 2.0421, a_H = 22.4 G) (*a*) and $H_2Fe_3(CO)_{10}^{\cdot-}$ (g = 2.0489, a_H = 24.2 G) (*b*).

ESR study of the reactions of CFA and HCFA with organohalogen compounds. When allowed to react with alkyl halides RX (R = Me, Et, Bu^n; X = Cl, Br, I), BnCl, and with acyl halides (R = Ac, Bz; X = Cl, Br) the salts $Na_2Fe(CO)_4 \cdot 1.5(diox)$, $Na_2[Fe_2(CO)_8]$, $(PPN)_2[Fe_2(CO)_8]$, $KHFe(CO)_4$, and $(PPN)[HFe(CO)_4]$ are most reactive. The intense growth of signals from ICRA **6b**, **6c**, 7, and **6d** (−60 °C, THF) is observed in the ESR spectra. When using the salts $(PPN)_2[Fe_3(CO)_{11}]$, $(PPN)_2[Fe_4(CO)_{13}]$, $(PPN)[HFe_3(CO)_{11}]$, and $(Et_3NH)[HFe_3(CO)_{11}]$ the ICRA signals of low intensity are present in the ESR spectra only in the case of the reactions with more active carboxylic acid halides.

Along with the ICRA signals the signal from the above mentioned radical (g = 2.0180) can be seen in the ESR spectra of such systems. This species arises in other reactions, accompanied by interconversions of ICRA as well.

In the reactions of the most active mononuclear anions $Fe(CO)_4^{2-}$ and $HFe(CO)_4^-$ with acid chlorides RCl (R = Ac, Bz) the acyl-containing iron carbonyl radicals arise in addition to ICRA. For instance, in the ESR spectrum of reaction mixture of $HFe(CO)_4^-$ with RCl at −60 °C the doublet with g = 2.0370, a_H = 26.0 G (R = Bz) (**9b**) or g = 2.0377, a_H = 22.1 G (R = Ac) (**9a**) appears at the first stages of the reaction. The structure $R(H)Fe(CO)_3^{\cdot-}$ can be assigned to these radicals, different from the known[3] species $HFe_n(CO)_{m-1}^{\cdot}$. In the reaction of benzoyl chloride the singlet with g = 2.0413 is also observed (Fig. 2).

The ESR spectrum of the reaction of $Na_2Fe(CO)_4 \cdot 1.5(diox)$ with benzoyl chloride (−90 °C, MeTHF) is the following: at the initial stages the inten-

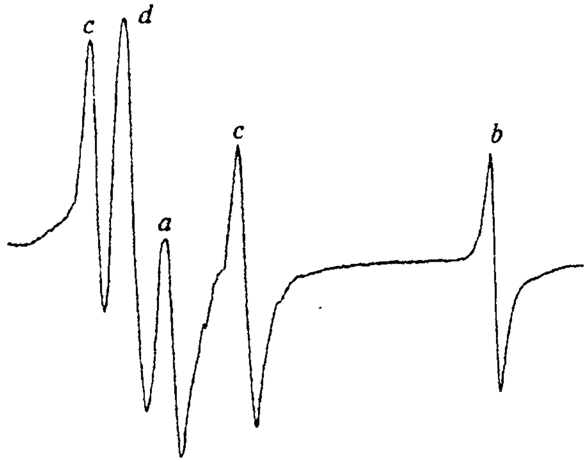


Fig. 2. The ESR spectrum, observed in the reaction of (PPN)[HFe(CO)$_4$] with BzCl in THF at −60 °C 4 min after the beginning of the reaction. ICRA: $Fe_2(CO)_8^{\cdot -}$ (*a*), $Fe_3(CO)_{12}^{\cdot -}$ (*b*). Benzoyl-containing iron carbonyl radicals, $Bz(H)Fe(CO)_3^{\cdot -}$: g = 2.0370, a_H = 26.0 G (*c*) and g = 2.0413 (*d*).

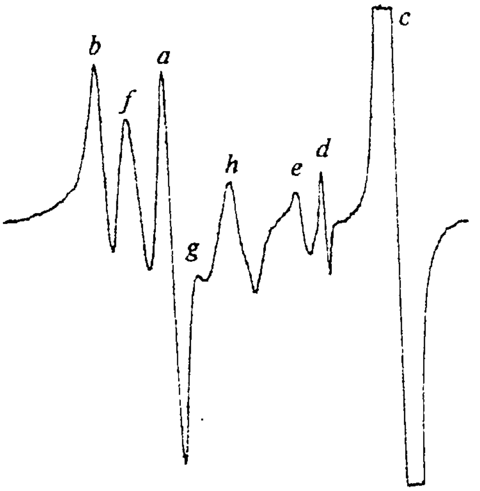
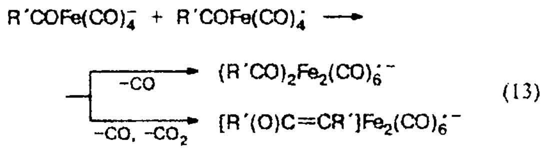


Fig. 3. The ESR spectrum, observed in the reaction of $Na_2Fe(CO)_4 \cdot 1.5(diox)$ with AcCl in THF at −60 °C 8 min after the beginning of the reaction. ICRA: $Fe_2(CO)_8^{\cdot -}$ (*a*), $Fe_3(CO)_{11}^{\cdot -}$ (*b*), $Fe_3(CO)_{12}^{\cdot -}$ (*c*), $Fe_4(CO)_{13}^{\cdot -}$ (*d*), g = 2.0180 (*e*). Acetyl-containing iron carbonyl radicals, $AcFe(CO)_4^{\cdot}$: g = 2.0436 (*f*), 2.0342 (*g*), and 2.0273 (*h*).

sity of the signal with g = 2.0489 ($\Delta H_{0.5}$ = 6.1 G) increases, then reaches the maximum, and falls. At the later stages the signal corresponding to radical anion **6b** appears in the same region. According to the published data the initial signal corresponds to $PhCOFe(CO)_4^{\cdot}$ (**10b**) (g = 2.0491).[35]

At the first stages of the same reaction with acetyl chloride the acetyl-containing radicals with g = 2.0436 (**10a**), g = 2.0342, and g = 2.0273 arise together with ICRA **6b** and **6c** (Fig. 3). However, unlike the previons case, the favourable arrangement of signals (between signals from **6b** and **6c**) in the ESR spectrum makes it possible to make more reliable assignment. The acetyl structure of these radicals can be proved by their preparation using model reaction of the oxidation of complex (PPN)[MeCOFe(CO)$_4$] by ferricenium hexafluorophosphate in THF at −80 °C. The formation of $(R'CO)_2Fe_2(CO)_6$ is related to a one-electron oxidation of $R'COFe(CO)_4^-$ to give the corresponding radicals which are dimerized.[29] Thus acetyl-containing radicals may be supposed to serve as intermediates in the process of binuclear complex formation (Eqs. (12) and (13)).

$$R'COFe(CO)_4^- \xrightarrow{\bar{e}} R'COFe(CO)_4^{\cdot} \qquad (12)$$



$$R'COFe(CO)_4^- + R'COFe(CO)_4^{\cdot} \longrightarrow \begin{cases} \xrightarrow[-CO]{} (R'CO)_2Fe_2(CO)_6^{\cdot -} \\ \xrightarrow[-CO,\ -CO_2]{} [R'(O)C{=}CR']Fe_2(CO)_6^{\cdot -} \end{cases} \qquad (13)$$

During the further one-electron reduction binuclear radical anions give known diamagnetic products.[29]

Hence, the reactions of CFA and HCFA with Brønstad and Lewis acids are redox processes, in which one-electron oxidation of CFA and HCFA resulting in the ICRA formation takes place. However, the acids mentioned above cannot serve as oxidizing agents for thermodynamic reasons. We described a similar situation earlier for the system iron carbonyl—Lewis base, where the one-electron reduction of iron carbonyl to give ICRA occurs as well, but Lewis base is not a reducing agent.[23–25] This problem can be solved using the concept, suggested earlier, of the one-electron redox process with initial activating complex-formation.[36] In a rather general form, as applied to iron carbonyl systems, where the interaction of a donor with an acceptor occurs, this concept can be formulated as follows:

Type I	Type II
$D^- + C \not\longrightarrow D^{\cdot} + C^{\cdot -}$	$B^- + A^+ \not\longrightarrow B^{\cdot} + A^{\cdot}$
$D^- + C \longrightarrow DC^-$	$B^- + A^+ \longrightarrow BA$
$DC^- + C \longrightarrow DC^{\cdot} + C^{\cdot -}$	$B^- + BA \longrightarrow B^{\cdot} + BA^{\cdot -}$

If donor D^- (or B^-) cannot reduce acceptor C (or A^+) directly, but the formation of a complex DC^- (or BA) takes place, it is this complex participation that makes the one-electron transfer possible.

The reaction of iron carbonyls (arbitrarily C) with Lewis bases (D^-) belongs to type I (see Eqs. (4) and (5)).[23–25] For the reactions of CFA and HCFA (B^-) with acids (A^+) the second scheme (type II) is applicable. In the context of this scheme one of the well-known processes — either the protonation of CFA and HCFA (see reaction (1)) or the oxidative addition of alkyl and acyl halides (see Eqs. (2) and (3)) — play the role of the activating complex-formation stage, for example

$$HFe(CO)_4^- + RX \longrightarrow R(H)Fe(CO)_4 + X^- . \qquad (14)$$

The one-electron transfer itself occurs at the next stage. The resulting complex is reduced by the initial $HFe(CO)_4^-$ according to Eq. (15).

$$R(H)Fe(CO)_4 + HFe(CO)_4^- \longrightarrow R(H)Fe(CO)_4^{\cdot -} + HFe(CO)_4^{\cdot} \qquad (15)$$

With R = H at this stage it is possible to isolate both components of the one-electron transfer reaction in a pure state.

ESR study of the reaction of $H_2Fe(CO)_4$ with (PPN)[$HFe(CO)_4$]. No signals were detected in the ESR spectrum of the solution of $H_2Fe(CO)_4$ in MeTHF at temperatures below −60 °C. The same is observed for the complex (PPN)[$HFe(CO)_4$], dissolved in MeTHF over a wide range of temperatures (up to room temperature). At the same time the interaction of $H_2Fe(CO)_4$ with (PPN)[$HFe(CO)_4$] in MeTHF solution leads to ICRA even at −100 °C. At the initial stages of the process the intense growth of the ICRA **6b** signals is seen in the ESR spectra. Then the signals corresponding to radical anions **6c**, **6d**, and **7** appear. The triplet of cluster **8c**, to which the structure $H_2Fe_3(CO)_{10}^{\cdot -}$ can be assigned, arises as well.

The studies on $HFe(CO)_4^-$ oxidation and $H_2Fe(CO)_4$ reduction (see above) showed that the 17-electron radical $HFe(CO)_4^{\cdot}$ and the 19-electron radical anion $H_2Fe(CO)_4^{\cdot -}$, arising initially at the one-electron transfer stage (see Eq. (15), R = H) are unstable under the conditions of this reaction and are transformed rapidly into $Fe_2(CO)_8^{\cdot -}$, the former according to Eq. (16), and the latter by Eqs. (8) and (9).

$$HFe(CO)_4^{\cdot} + HFe(CO)_4^- \longrightarrow H_2 + Fe_2(CO)_8^{\cdot -} \qquad (16)$$

The radical anions of greater nuclearity **6c**, **6d**, and **7**, as well as **8c**, originate in reactions (10) and (11).

The 19-electron radical anion $R(H)Fe(CO)_4^{\cdot -}$ (R = MeCO and PhCO), forming by Eq. (15), is also transformed into the more stable 17-electron state as a result of elimination of aldehyde molecule or CO (Eqs. (17) and (18)).

$$R(H)Fe(CO)_4^{\cdot -} \longrightarrow RH + Fe(CO)_4^{\cdot -} \qquad (17)$$

$$R(H)Fe(CO)_4^{\cdot -} \longrightarrow CO + \underset{\textbf{9a,b}}{R(H)Fe(CO)_3^{\cdot -}} \qquad (18)$$

In the last case radical species **9a** and **9b**, detectable in the reactions of acyl halides RX (R = MeCO, PhCO) with $HFe(CO)_4^-$, arise.

The highly active radical anion $Fe(CO)_4^{\cdot -}$ interacts with $H_2Fe(CO)_4$ by Eq. (9) or can be protonated in acidic medium, giving rise to the radical $HFe(CO)_4^{\cdot}$. The same conversions occur in the reactions of $Fe(CO)_4^{\cdot -}$ with RX.

$$Fe(CO)_4^{\cdot -} + RX \longrightarrow RFe(CO)_4^{\cdot} + X^- \qquad (19)$$

$$RFe(CO)_4^{\cdot} + HFe(CO)_4^- \longrightarrow RH + Fe_2(CO)_8^{\cdot -} \qquad (20)$$

Further ICRA conversions, followed by an increase in their nuclearity, proceed *via* a radical-chain mechanism according to analogous Eqs. (21) and (22).

$$Fe_2(CO)_8^{\cdot -} + RX \longrightarrow RFe_2(CO)_8^{\cdot} + X^- \qquad (21)$$

$$RFe_2(CO)_8^{\cdot} + HFe(CO)_4^- \longrightarrow RH + Fe_3(CO)_{12}^{\cdot -} \qquad (22)$$

The reactions of $Fe(CO)_4^{2-}$ with RX (R = alkyl and acyl) can be presented in a similar way. The one-electron transfer (Eq. (23)) operates with participation of the complexes produced in reactions (2) and (3).

$$R_2Fe(CO)_4 + RFe(CO)_4^- \longrightarrow R_2Fe(CO)_4^{\cdot -} + RFe(CO)_4^{\cdot} \qquad (23)$$

$$R_2Fe(CO)_4^{\cdot -} \longrightarrow R_2 + Fe(CO)_4^{\cdot -} \qquad (24)$$

$$RFe(CO)_4^{\cdot} + RFe(CO)_4^- \longrightarrow R_2 + Fe_2(CO)_8^{\cdot -} \qquad (25)$$

$$Fe(CO)_4^{\cdot -} + R_2Fe(CO)_4 \longrightarrow R_2 + Fe_2(CO)_8^{\cdot -} \qquad (26)$$

For acyl derivatives the formation of binuclear radical anion complexes (see Eq. (13)) is possible.

At the final stages of the interaction of CFA and HCFA with Brønstad and Lewis acids the reduction of ICRA **6c** and **6d** in the exchange reactions of the type (27) and (28) to give corresponding CFA **1c** and **1d** takes place, if the redox-potentials of these anions make such processes thermodynamically favourable.[37,38]

$$Fe_n(CO)_{m-1}^{\cdot -} + Fe_{n'}(CO)_{m'-1}^{2-} \longrightarrow Fe_n(CO)_{m-1}^{2-} + Fe_{n'}(CO)_{m'-1}^{\cdot -} \qquad (27)$$

$$Fe_n(CO)_{m-1}^{\cdot -} + HFe(CO)_4^- \longrightarrow Fe_n(CO)_{m-1}^{2-} + HFe(CO)_4^{\cdot} \qquad (28)$$

n = 3, 4; m = 12, 14
n' = 1, 2; m' = 5, 9

Then either the protonation of complexes **1c** and **1d** in acidic media or the addition of Lewis acid to carbonyl group of these compounds giving rise to products **5c** and **5d**[13—15] is possible.

Hence, the investigation on the interaction of CFA and HCFA with Brønstad and Lewis acids by means of ESR spectroscopy showed that it is a radical-chain process with the redox-initiation stage, including the preliminary activating complex formation. The key unit of the process is constituted by the chain propagation reactions, consisting in Brønstad or Lewis acid addition to ICRA.

On the one hand, ICRA are rather stable species and their concentrations can reach sufficiently high values in the process of the reaction, and on the other they are coordinatevely unsaturated and electron-deficient systems, thus having a labile coordination sphere, in which rapid ligand and electron exchange can take place. Such activity of ICRA was found by us first in the reaction of reductive carbonylation of nitro compounds,[23] and later was confirmed in some studies.[39,40]

The suggested scheme of radical-chain process used for the description of the interaction of CFA and HCFA with acids is of a common character, and it can be applied to all known reactions of such a type. Some of them are given below.

Reaction of $H_2Fe(CO)_4$ decomposition. At the first stage the deprotonation of a sufficiently strong acid $H_2Fe(CO)_4$, *e.g.*, upon interaction with a solvent or with glass walls of a vessel, proceeds in polar solvents when the temperature rise up to the room value. Then the stages (15) (R = H), (8)—(11), and (16) take place. The arising radical anion **6c** turns into complex **1c** according to the reaction (28). Then owing to its strong basicity anion **1c** deprotonates initial $H_2Fe(CO)_4$, and the process is repeated in the regimen of catalytic decomposition. Thus the instability of $H_2Fe(CO)_4$ is of a purely kinetic origin. This is true for similar compounds **5a**, the decomposition of which is also defined by the chain process with the key stages (23)—(26).

Synthesis of α-diketones. The preparative synthesis of α-diketones[17] in aprotic medium is based upon a one-electron oxidation of $RCOFe(CO)_4^-$. The formation of α-diketones proceeds by reaction (25).

Reduction of unsaturated compounds. A wide range of different compounds with double bond — olefins,[41] 1,3-dienes,[42] α,β-unsaturated carbonyl compounds,[5,18] enamines,[43] different nitrogen-containing heterocycles and anthracene[44] are reduced under the action of HCFA in proton-donating media. At first stage an alkyl-containing complex is formed according to Eq. (29).

$$R'CH{=}CHR'' + H^+ + HFe(CO)_4^- \longrightarrow$$

$$\longrightarrow (R'CH_2{-}CHR'')HFe(CO)_4. \quad (29)$$

Further the process proceeds in accordance with equations (15)—(17) (R = $R'CH_2{-}CHR''{-}$), giving rise to $R'CH_2{-}CH_2R''$. Apart from $HFe(CO)_4^-$, anion $HFe_2(CO)_8^-$ can be used[5] in the reduction reactions. Therefore, in order to describe the process with the help of similar schemes, it is necessary to change $Fe(CO)_4$ moiety for $Fe_2(CO)_8$. It should be noted that ICRA **6b**, **6c**, and **7** were detected in the reduction reaction, but their formation was explained[5] by side processes. The main trend of the reaction was interpreted in terms of the commonly accepted concept of the process proceeding through the 16-electron species.

Reppe synthesis. The mechanisms of radical-chain ICRA conversions in the iron carbonyl—Lewis base and CFA (HCFA)—acid systems must play an important role in catalytical carbonylation processes, such as Reppe synthesis.

The key stage of this reaction is the olefin addition to coordinatevely unsaturated 17-electron species ICRA in a proton-donating medium, giving rise to an alkyl-containing iron carbonyl radical (Eq. (30)).

$$R'CH{=}CHR'' + H^+ + Fe_n(CO)_{m-1}^{\cdot -} \longrightarrow$$

$$\longrightarrow R'CH_2{-}CHR''{-}Fe_n(CO)_{m-1}^{\cdot} \quad (30)$$

$n = 2, 3$; $m = 9, 12$

The next stage is addition of CO resulting in a 19-electron species formation and its transfer into a 17-electron species through carbonylation of the Fe—Alk bond.

$$\underset{(17\bar{e})}{R'CH_2CHR''Fe_n(CO)_{m-1}^{\cdot}} \xrightarrow{CO} \underset{(19\bar{e})}{R'CH_2CHR''Fe_n(CO)_m^{\cdot}} \longrightarrow$$

$$\longrightarrow \underset{(17\bar{e})}{R'CH_2CHR''C(O)Fe_n(CO)_{m-1}^{\cdot}} \quad (31)$$

Then by analogy with reactions (20)—(22) the interaction of the resulting radical with $HFe(CO)_4^-$ proceeds, giving rise to aldehyde and the ICRA of higher nuclearity. In the presence of CO ICRA **6b**, **6c**, **6d**, and **7** undergo interconversions[24] affording regeneration of radical anions **6b** and **6c** and consequently the catalytical character of the process.

The results of our study testify that the redox processes proceeding in the systems with participation of CFA (HCFA)—acids are radical-chain in character. This together with the earlier obtained data about the reactivity of the systems iron carbonyl—Lewis base allows us to make the following conclusion: the majority of redox reactions in the chemistry of iron carbonyls are radical-chain processes with one-electron redox initiation, the key role in which is played by exchange of ligands in coordination sphere of 17-electron coordinatevely unsaturated species. Therefore, the main transformations in complexes are realized not in accord with the Tolmen role ($18\bar{e} \rightarrow 16\bar{e} \rightarrow 18\bar{e}$) through the 16-electron intermediates, but by the scheme $17\bar{e} \rightarrow 19\bar{e} \rightarrow 17\bar{e}$. These species actually exist in solutions and can be easily detected by the ESR method.

Experimental

ESR spectra were recorded on an ERS-221 (ZWG DDR) instrument in the X-range with high frequency modulation of 100 kHz. GC analysis was carried out on a LKhM-8MD instrument (detector — katharometer, 4 m column, filled with molecular NaX sieves, gas carrier — helium, internal standard — argon).

The salts of carbonylferrate and hydridocarbonylferrate anions were prepared by the known procedures: $Na_2Fe(CO)_4 \cdot 1.5(diox)$,[45] $KHFe(CO)_4$,[46] $(PPN)[HFe(CO)_4]$,[47] $(PPN)_2[Fe_2(CO)_8]$,[48] $Na_2[Fe_2(CO)_8]$,[49] $(PPN)_2[Fe_3(CO)_{11}]$,[50] $(PPN)[HFe_3(CO)_{11}]$,[51] $(Et_3NH)[HFe_3(CO)_{11}]$,[52] and $(PPN)_2[Fe_4(CO)_{13}]$.[53] The complex $H_2Fe(CO)_4$ was prepared by the earlier described procedure[54] and was stored in sealed tubes and placed in liquid nitrogen. The acids AcOH, CF_3COOH, H_2SO_4, and organohalogen compounds (chemically pure grade) were distilled under an argon atmosphere before usage. THF and MeTHF were kept over sodium benzophenon ketyl. Samples were prepared according to the known procedures.[23,24] The reactions were carried out in a tube placed into the resonator of an ESR spectrometer using equimolar ratios of reagents (0.01—0.1 mol L^{-1}) within the temperature range from −100 to +20 °C.

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