

ELECTROCHEMICAL INVESTIGATION OF σ -BONDS IN π -COMPLEXES OF SOME TRANSITION METALS

III. THE OXIDATION-REDUCTION REACTIONS OF π -ALLYLIRONTRICARBONYL HALIDES

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SUMMARY

The polarographic and chemical reductions of π - $C_3H_5Fe(CO)_3X$ ($X=Cl, Br, I, NO_3$) have been studied. Both reductions have been shown to proceed in two stages: first, the cleavage of the $Fe-X$ σ -bond takes place giving the radical, $[\pi-C_3H_5Fe(CO)_3]^{\cdot}$, which further reduces into the 18-electron anion $[\pi-C_3H_5Fe(CO)_3]^{-}$. Some physicochemical and chemical properties of this anion have been investigated. It was shown that either the initial halides, or the anions generated, are able to react with solvents through the replacement of the π -allyl ligand.

Oxidation-reduction reactions are the most characteristic reactions for π -complexes of transition metals containing σ -bonds^{1,2}. These reactions usually entail a cleavage of the σ -bond with the rate depending on: the nature of the metal atom, the electronegativity of the σ -bonded groups, the nature of the stabilizing ligands, and other factors³.

In earlier papers^{4,5} we have studied the polarographic reduction at the dropping mercury electrode of π -cyclopentadienyliron dicarbonyl compounds containing different types of σ -bonds: Fe -metal, Fe -halogen, Fe -carbon. We have shown, that in all these cases, the homolytic activation of the reducing σ -bond takes place in the transition state on the surface of an electrode. The cleavage of this bond for the same radical, $C_5H_5Fe(CO)_2^{\cdot}$, proceeds at a rate depending upon the stability of the anion generated when the σ -bonded group attracts an electron. In order to ascertain how far this dependency could be applied to π -complexes of transition metals and to estimate the effect of ligands, bonded with an iron atom, on the nature of the σ -bond reduction, we have studied the reduction of π -allyliron tricarbonyl halides which have structures most similar to those of some iron complexes previously described.

The oxidation-reduction reactions of π -allyliron tricarbonyl compounds were reported in the paper of Murdoch and Lucken⁶. They found that π - $C_3H_5Fe(CO)_3$ halides could be transformed into the radical $[C_3H_5Fe(CO)_3]^{\cdot}$ when they interact with both Al_2O_3 and sodium salts of such anions as $[C_5H_5Fe(CO)_2]^{-}$ and $[(CO)_5Mn]^{-}$.

In the present paper we are concerned with the oxidation-reduction properties

of π -allylirontricarboxyl halides.

RESULTS AND DISCUSSION

Polarographic measurements in different solvents have indicated that all the compounds could be reduced on the dropping mercury electrode and may produce two waves of approximately the same height in the polarograms (Table 1). Some stages of this process have been studied in detail.

TABLE 1

POLAROGRAPHIC REDUCTION CHARACTERISTICS OF THE COMPOUNDS π - $C_3H_5Fe(CO)_3X$
(0.1 N(C_2H_5)₄NCIO₄, $c \cdot 1 \cdot 10^{-3}$ M SCE 25°)

Compound	CH ₃ CN			DMF			
	$-E_1$ (V)	i_d (mA)	b (mV)	Freshly prepared solution		After 30–60 min	
				$-E_1$ (V)	i_d (mA)	$-E_1$ (V)	i_d (mA)
I $C_3H_5Fe(CO)_3Cl$	0.44	2.50	110	0.42	1.00	0.14 ^a	1.00
	0.72	2.70	78	0.66	1.80	1.45	0.90
II $C_3H_5Fe(CO)_3Br$	0.39	2.20	110	0.34	1.10	0.23 ^a	1.10
	0.72	2.20	80	0.66	1.10	0.45	0.90
III $C_3H_5Fe(CO)_3I$	0.37	2.40	113	0.32	1.30	0.27 ^a	1.40
	0.72	2.60	80	0.66	1.30	1.44	1.00
IV $C_3H_5Fe(CO)_3NO_3$	0.48	1.70					
	0.72	2.70	80				
V $1-C_6H_5-C_3H_4Fe(CO)_3Cl$	0.43	1.90	110				
	0.69	2.0	80				
VI $2-C_6H_5-C_3H_4Fe(CO)_3Cl$	0.35	1.90	110				
	0.64	2.00	80				
VII $C_3H_5Fe(CO)_2P(C_6H_5)_3I$	0.47	1.70	80	0.45	1.09		
	1.16	2.0	75	1.12	1.30		
VIII $FeCl_2$				0.14 ^a	1.64		
				1.44	1.24		

^a The potentials of anodic waves.

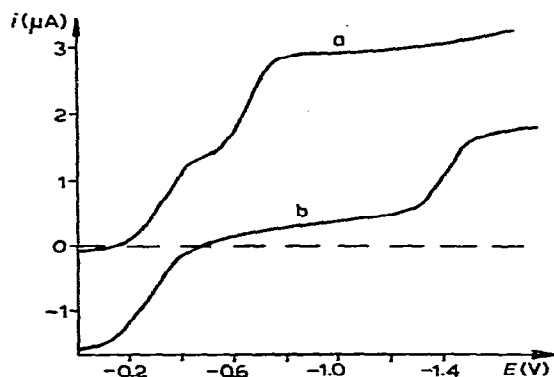
1. The stability of π - $C_3H_5Fe(CO)_3X$ (I–VII) in solution

First, it is of importance to note that compounds I–VII are unstable in some solvents. UV and nuclear γ -resonance spectra, and polarography have shown that all the compounds investigated are stable for a long time in CH₃CN in the atmosphere of argon. This was not the case when dimethylformamide (DMF) was used as solvent. The polarograms (Table 1), UV and nuclear γ -resonance spectra (Table 2) of freshly prepared solutions in DMF are practically identical with those measured in CH₃CN. However, even after 30 min sharp changes in spectra could be observed. In the UV spectrum, the absorption maxima of the initial compounds (310–320 m μ and 400–420 m μ , compound III) completely disappear. In the nuclear γ -resonance spectra some new signals were discovered characteristic of inorganic iron complexes (cf. 6 and 7 in Table 2). The reaction path may be followed also from a polarogram (Fig. 1),

TABLE 2

THE PARAMETERS OF THE NUCLEAR γ -RESONANCE SPECTRA
(80°K)

Compounds	Solvent	δ (mm·sec ⁻¹) ^a	ΔE (mm·sec ⁻¹)
(1) C ₃ H ₅ Fe(CO) ₃ Cl	CH ₃ CN	0.37	1.46
(2) C ₃ H ₅ Fe(CO) ₃ I	THF; benzene	0.42	1.24
(3) [C ₃ H ₅ Fe(CO) ₃] ₂	benzene	0.57	1.00
(4) C ₃ H ₅ Fe(CO) ₃ Na	THF	0.53	1.83 ^b
(5) C ₃ H ₅ Fe(CO) ₃ Cl	DMF	0.37	1.44
(6) C ₃ H ₅ Fe(CO) ₃ Cl	DMF after 30 min	1.80	2.05 ^c
(7) FeCl ₂	DMF	1.65	1.98

^a With respect to sodium nitroprusside. ^b In this spectrum we have also found a singlet with δ 0.30 mm·sec⁻¹.^c The spectrum is a complicated one. Besides the doublet indicated, a doublet of the initial compound was observed as well as a doublet of a zero-valent iron compound occurring in small concentration.Fig. 1. Polarogram of π -C₃H₅Fe(CO)₃Cl. (a), in DMF (0.1 N (C₂H₅)₄NClO₄); (b), in DMF (0.1 N (C₂H₅)₄-NClO₄) after 30 min.

the waves of initial compounds gradually disappear and the general pattern is reminiscent of that for FeCl₂ under analogous conditions (*cf.* I and VIII in Table 1). The rate of reaction with DMF is highest for I and lowest for VII. The data obtained indicate that π -allylirontricarbonyl halides do react with DMF, with substitution of the π -allyl ligand and formation of the complexes of bivalent iron halides with DMF*.

Acetonitrile was used as the main solvent in polarographic measurements. The UV-spectra of compounds I–III in CH₃CN, as well as in non-polar solvents such as cyclohexane, were practically the same in the region 220–600 m μ , which indicates the absence of any specific solvation (complex generation) by solvent. On the other hand, the absence of anodic waves of halide anions and the change in the first wave potential with change in X exclude any significant dissociation in solution of CH₃CN along the Fe–X σ -bond in I–VII. These experiments indicated that the polar-

* When the electrolysis of II was carried out under the conditions of Murdoch and Lucken⁶ (DMF, 0.1 N (C₂H₅)₄NBr) in the resonator of the ESR apparatus, we observed, as did these authors, a signal in the spectrum. However, since the initial compound decomposed in reaction with DMF, the signal appearing belonged to the Fe³⁺–DMF complexes and not to radical IX.

ographic solution contains some weakly solvated molecules of I–VII having polarized covalent Fe–X σ -bonds.

2. The first reduction stage of halides I–VII

The existence in the polarogram of two diffusive waves of the same height indicates a two-stage reduction process for the compounds investigated.

According to microcoulometric measurements⁷, the first stage of the electrochemical reduction of I–VII is a one-electron process. During the electrolysis where the potential was measured for the case of the limiting first wave current in the resonator of the ESR apparatus, a signal was observed analogous to that of Murdoch and Lucken⁶ for radical IX, which they obtained by chemical reduction of I–III. Thus, at the first stages of both chemical and electrochemical reductions of I–VII, cleavage of the Fe–X σ -bond occurs and the radical, $[\text{C}_3\text{H}_5\text{Fe}(\text{CO})_3]^\bullet$ (IX), is generated:



(X = Cl(I), Br(II), I(III), NO₃(IV); L = CO

X = I(VII); L = P(C₆H₅)₃)

The reversible chemical process of oxidation of radical IX into I–III⁶ becomes irreversible in the electrochemical process under the above conditions: the values of $b = 2.3 RT/\alpha F n$, obtained from the dependency of $\log [i/(i_d - i)]$ on E , exceed the theoretical value calculated for a reversible one-electron process. The potential of the anodic wave of oxidation of radical IX (-0.18 V vs. saturated calomel electrode, SCE) is not the same as that of the cathodic wave (Fig. 2).

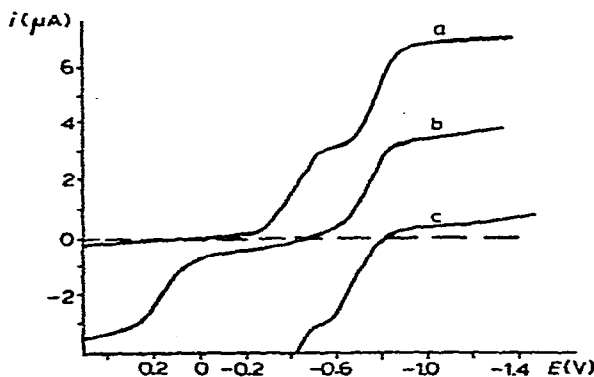


Fig. 2. Polarograms of $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{I}$. (a), $[\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3]^\bullet$; (b), $[\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3]^\bullet \text{Na}^+$; (c), (CH_3CN , 0.1 N $(\text{C}_2\text{H}_5)_4\text{NClO}_4$).

For preparation of solutions of radical IX in the reduction of halides I–III, dibenzenechromium may be used as a convenient reducing reagent for chemical modelling of the first stage. When solutions of III and dibenzenechromium are mixed, the oxidation–reduction process takes place and dibenzenechromium iodide precipitates. A pink colour, characteristic of the dimer $[\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3]_2$ (X) appears⁶.

The observed increase in rates of reduction of the Fe-X σ -bond (I > Br > Cl) is exactly opposite to the increase electronegativity of the halides, being the deciding factor in the polarity of this bond. The fact that the polarity of the Fe-X bond increases from I to Cl, is obvious from a comparison of the quadrupole splittings, ΔE , in the nuclear γ -resonance spectra; this value gives some information on the change in asymmetry of the p,d -electrons in the vicinity of the nucleus of the iron atom (Table 2, comp. 1 and 2). The rate of reduction of this bond follows the increase in basicity of halide anions (I⁻ > Br⁻ > Cl⁻)⁸ which are generated in the course of the electrochemical reaction (eqn. (1)) as in the case of the reduction process of the carbon-halide bond⁹. The same dependency for change in $E_{\frac{1}{2}}$ (I > Br > Cl) was observed for some other complexes of the transition metals^{4,10}, and, is probably a common characteristic, at least in protic solvents. We believe this could be associated with the fact that in the transition state, where the reaction proceeds on the surface of electrode, homolytic activation of the transition metal-halide σ -bond takes place. The rate of cleavage of this bond depends upon the stability of the halide anion produced, for the same radical (eqn. (1)).

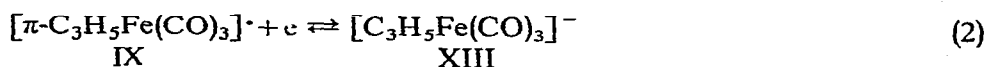
In a previous paper¹¹, compound IV was suggested as having an ionic structure, $[\pi-C_3H_5Fe(CO)_3]^+NO_3^-$. In this case, the reduction of the cation should proceed at more positive potentials than $E_{\frac{1}{2}(0)}$ of the Fe-X bond. However, as can be seen from the data obtained, $E_{\frac{1}{2}(0)}$ of compound IV is more negative than $E_{\frac{1}{2}(0)}$ of compounds I-III which is inconsistent with the above ionic structure. These data suggest that compound IV contains a covalent bond, Fe-O, and has an ester structure, $\pi-C_3H_5Fe(CO)_3ONO_2$.

A comparison of $E_{\frac{1}{2}}$ of the first wave for halides I-VII and for the previously reported π -cyclopentadienylirontricarbonyl halides ($\pi-C_5H_5Fe(CO)_2X$) (XI) indicates that the nature of the organometallic radical essentially effects the rate of reduction of the Fe-X σ -bond. Compounds I-VII could be reduced at more positive potentials and, moreover, the $\Delta E_{\frac{1}{2}}$ -value, going from chloride I to iodide III, is considerably smaller (0.07 V) than that for compounds XI (0.31 V). On the other hand, while the parameters of ΔE in the nuclear γ -resonance spectra are practically the same for all halides XI¹², the values of ΔE decrease from chloride Ia to iodide III.

The radicals IX and $[\pi-C_5H_5Fe(CO)_2]^\cdot$ (XII), produced at the first stage of reduction of compounds I-VII and XI, differ also in their stability. While radical XII is unstable and instantaneously reacts with the material of the electrode giving $[\pi-C_5H_5Fe(CO)_2]_2Hg$, radical IX is stable and it is due to this radical that halides I-VII are reduced at the second stage.

3. The second stage in reduction of compounds I-VII

Microcoulometric investigations have shown that only one electron is added at this stage. Since the π -bonds of the iron atom with the allyl ligand, as well as donor-acceptor bonds with carbonyl groups, are unaffected in the reduction¹³, the addition of an electron to radical IX should result in the unreported 18-electron anion, $[\pi-C_3H_5Fe(CO)_3]^-$:



Chemical reduction of halides I–VII into anion XIII requires stronger reducing agents than those used in our study for the reduction of halides I–VII into radical IX (Part 2). We have shown that sodium amalgam or the naphthalene–sodium system may reduce III into the sodium salt of anion XIII; also, the dimer X was found to be an intermediate product in these reactions. The formation of anion XIII in these reactions has been proved by measurement of the IR-spectra frequencies, by polarography and by nuclear γ -resonance spectra (*cf.* Part 4).

Process (2) is a reversible one from both chemical and electrochemical points of view. The electrochemical reversibility follows from the equality of the $E_{1/2}$ -potentials of the cathode wave in the reduction of IX into XIII and of the anodic wave in the oxidation of XIII into IX (Fig. 2), as well as from the approximation of value b (Table 1) to its theoretical value (60 mV) for a reversible one-electron process. We have also carried out the chemical oxidation of anion XIII. The reaction of I_2 with the sodium salt of anion XIII led to the initial iodide, III. The process proceeds through formation of a dimer as an intermediate which, in accordance with the data of Murdoch and Lucken⁶, converts quantitatively into III.

The reduction of III into anion XIII results in partial decomposition of the molecule, some iron-containing compounds of indefinite structure being produced. In the oxidation of the anion with iodide we have isolated 75% of initial iodide, although the conversion of the anion into the radical is reversible and the latter converts quantitatively into halides⁶. In the nuclear γ -resonance spectra measured in solutions obtained after the reduction of III, we have also observed (along with a doublet for anion XIII) a singlet of about the same intensity. On the other hand, in a polarographic study of this solution, not only the anodic wave of anion XIII, but also the cathodic wave at a potential of 1.8–1.9 V have been observed.

4. Physical and chemical properties of anion, $[\pi-C_3H_5Fe(CO)_3]^-$

(a) *IR-spectra.* The THF solution of the sodium salt of anion XIII, obtained by the reduction of III with sodium amalgam, exhibits bands in the carbonyl area at 1855 and 1910 cm^{-1} in the IR-spectra. A decrease in CO-stretching frequencies with respect to the initial compounds (2000 and 2055 cm^{-1}) occurs owing to the appearance of a negative charge on the metal atom. Analogous shifts of CO-stretching frequencies were also observed for a number of other carbonyl compounds in the investigation of charged anion particles^{13,14}. In the present case, the data support the generation of the anion, $[\pi-C_3H_5Fe(CO)_3]^-$ in the reaction of III with sodium amalgam.

(b) *Nuclear γ -resonance spectra.* The nuclear γ -resonance spectra of frozen THF solutions of the sodium salt of anion XIII contain a doublet with $\delta=0.53$ and $\Delta E=1.83$. A comparison of the data in Table 2 shows that, as in some other cases^{*15}, the oxidation–reduction transition (in the present case it is a conversion of IX into XIII) causes no essential deviations in chemical shifts. In the oxidation of the anion (for example, by air oxygen) a gradual decrease in intensity of the above doublet occurs and the spectrum of decomposition products is analogous to that of type $RFe(CO)_4$.

(c) *Reactions of anion XIII.* Anions of metal carbonyls are known to be com-

* The parameters, δ and ΔE , for $[C_5H_5Fe(CO)_2]_2$ and $[C_5H_5Fe(CO)_2]^-$ are practically the same: $\delta=1.49$, $\Delta E=1.96$. This subject will be discussed in detail in a later communication.

pounds of very high reactivity, participating in a number of reactions with various reagents; sometimes they produce a variety of compounds containing metal-carbonyl groups^{1,13}. The reaction of anion XIII with $(C_6H_5)_3SnCl$ (XIV) which we have tried for the preparation of a bimetallic derivative under the same conditions as for $\pi-C_5H_5Fe(CO)_2Sn(C_6H_5)_3$ ¹⁶, has, however, followed an alternative route, to give the one-electron reduction product of XIV—hexaphenyldistannane. The reaction of electron transfer is associated with the fact that anion XIII can be readily oxidized into radical IX. An analogous reaction was observed also for some other anions of metal carbonyls¹⁷⁻¹⁹.

In the paper of Nesmeyanov and Kritskaya²⁰, allyl chloride was shown to react with a solution of the sodium salt of anion XIII where the $\pi-C_3H_5Fe(CO)_3$ - $\sigma-C_3H_5$ produced quickly loses one carbonyl group, owing to its instability, giving $(\pi-C_3H_5)_2Fe(CO)_2$. The isolation of this compound is a further proof that anion XIII exists in the solution after reduction of III with Na/Hg. The nature of the products formed in the reactions of XIII with various reagents will depend, therefore, upon the oxidation rate of anion XIII into radical IX. On the other hand, it also depends upon the instability of the compounds produced which contain a σ -bond with the iron atom.

(5) *The effect of substituents in the π -allyl group on both the above stages observed in the reduction of halides I.*

We have studied the reduction of 1-phenyl- and 2-phenylsubstituted π -allylirontricarbonyl chlorides. The substituted compounds give two polarographic waves with characteristics approximating those of the unsubstituted chloride I. A substituent in the π -allyl group affects the value of $E_{\frac{1}{2}}$ at the first and second stages of the reduction process which is in good agreement with the reduction mechanism suggested. The introduction of the phenyl group in both cases facilitates the process of reduction. The effect of the phenyl group, as an electron-attracting substituent, is characteristic of the oxidation-reduction reactions of transition metal- π -complexes where the reaction centre (metal atom) and the substituent are in different planes. On the other hand, in the oxidation-reduction reactions of the π -complexes of some transition metals where the substituent (an aromatic system) and a metal atom lie in the same plane (*e.g.*, in some substituted palladium acetylacetonates²¹) the phenyl group behaves as electron-releasing substituent prohibiting the reduction process with respect to the unsubstituted compound. It should be noted that in the compounds investigated, the electron-attracting effect of a phenyl substituent in position 2 is about twice as great as that in position 1 and the value of $E_{\frac{1}{2}}$ (0.09 V) is twice that for a substituent in ferrocene (0.04 V)²² or in dibenzenechromium (0.05 V)²³.

EXPERIMENTAL

1. *The effect of reducing agents on $\pi-C_3H_5Fe(CO)_3I$ (III)*

All experiments were carried out under an atmosphere of pure dry argon.

(1) *Reduction of (III) with dibenzenechromium (XV).* 0.1 g (0.0003 M) of III in 10 ml of benzene was added dropwise to a solution of 0.07 g (0.0003 M) of XV in 15 ml of benzene, distilled under an argon atmosphere. An orange precipitate was formed immediately, and the solution became pink in colour. The polarogram of this solution

was identical with that for a solution of the dimer, $[\text{C}_3\text{H}_5\text{Fe}(\text{CO})_3]_2(\text{X})$, obtained by reaction of III with Al_2O_3 , in accordance with the method of Murdoch and Lucken^{6,24}. The pink colour disappeared on dilution with the supporting solution (CH_3CN , 1 N $(\text{C}_2\text{H}_5)_4\text{NClO}_4$), and the mixture became green owing to the dissociation of this dimer into a monomer⁶. The solid was filtered off and identified polarographically as dibenzenechromium iodide (yield 100%).

(2) *Reduction with sodium amalgam.* To a stirred sodium amalgam (from 0.12 g (0.005 M) of Na and 1 ml of Hg) was added dropwise a solution of 0.6 g (0.002 M) of III in 10 ml of THF. The solution became bright pink, characteristic of dimer X*. After several minutes, the colour disappeared, and in 10–15 min the solution became yellow-brown. The mercury was filtered off and several drops of filtrate were placed into the polarographic cell for measuring the polarogram (CH_3CN , 0.1 N $(\text{C}_2\text{H}_5)_4\text{NClO}_4$). Another portion (1 ml) was used for recording the IR-spectra.

(b) *Reaction with $(\text{C}_6\text{H}_5)_3\text{SnCl}$ (XIV).* To the remaining part of the salt solution was added, 0.5 g (0.0013 M) of XIV, and after 30 min stirring the solvent was evaporated. The residue was extracted with methylene chloride. After evaporation of methylene chloride and recrystallization of the residue from benzene, white crystals of hexaphenyldistannane were obtained (87%) m.p. 230–231° (lit.²⁵ m.p. 229–231°). The solid, remaining after treatment with methylene chloride, was a mixture of inorganic iron salts, insoluble in standard non-polar organic solvents.

(3) *Reduction with naphthalene-sodium.* 0.3 g (0.001 M) of III was added to the emerald-green solution of naphthalene-sodium (from 0.1 g (0.004 M) of Na and 0.52 g (0.004 M) of naphthalene) in 10 ml of absolute THF, distilled under an argon atmosphere. The mixture immediately became bright pink and slight heating of the flask was observed. After 15–20 min the colour became yellow-brown as in the case of sodium amalgam reduction. The solution was filtered and a small portion placed in the polarographic cell for measuring the polarogram; another portion was used for filling the cell of the nuclear γ -resonance spectrometer.

(4) *Reaction of $\text{C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{Na}$ (XIII) with I_2 .* To a THF solution of 0.127 g (0.001 M) of I_2 was added a solution of XIII (from equimolar amount of III**) (cf. 2). The solvent was evaporated, and the residue extracted with pentane. After evaporation of the solvent, 0.5 g of III (75% of the initial III) was obtained. The product was identified by polarographic comparison with a known specimen.

II. Polarographic measurements

The polarograms were recorded with a PE-312 electronic polarograph. The measurements were carried out using the dropping mercury electrode, provided with a forced dropping system^{26,27} ($m = 1.53 \text{ mg} \cdot \text{sec}^{-1}$, $t = 0.25 \text{ sec}$), in the cell containing two external saturated aqueous calomel electrodes (reference electrode and working anode) thermostatted at $25 \pm 0.1^\circ$. The values of $E_{1/2}$, listed in the Tables, were corrected for IR-drop.

The ESR electrolysis control of a $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3\text{I}$ ($c = 5 \cdot 10^{-3} \text{ M}$) solution in CH_3CN measured with supporting 0.5 N $(\text{C}_2\text{H}_5)_4\text{NClO}_4$ solution at a

* If several millilitres of THF were added to the amalgam, then, after the addition of a few drops of iodide III solution, the mixture became green, which indicates that the radical, $[\text{C}_3\text{H}_5\text{Fe}(\text{CO})_3]^\cdot$, is generated in dilute solutions⁶. On further addition of iodide III solution, this green colour changes to bright pink.

** The absence of the initial III was verified by polarography.

potential of -1.0 V, was carried out in a cell mounted in the resonator of the ESR apparatus.

All the compounds investigated in the present paper were prepared and purified by the methods described in the literature¹¹. The solvents, CH_3CN and DMF, were purified by standard methods used in electrochemical studies²⁸. Owing to the significant instability of the compounds investigated to oxygen, the solvents were either repeatedly distilled in an argon atmosphere or deoxygenated by prolonged passing of argon before preparation of polarographic solutions. All solvents were prepared directly before measurements.

III. IR-spectra

These were recorded using a UR-10 apparatus. The solution investigated was placed into a hermetically sealed cell (NaCl, the thickness of the layer was 0.35 mm). Thorough insulation of the solution from air oxygen ensured complete reproducibility of results.

IV. Nuclear γ -resonance spectra

These were measured with a device of electrodynamic type, using ^{57}Co in chromium, as a source of γ -quants.

For preparation of specimens, 2 ml of the solution investigated were quickly transferred under an argon atmosphere into a cell mounted in a special cryostat filled with liquid nitrogen. After 1–2 min the specimen solidified, and then it was cooled to 80°K . Data on nuclear γ -resonance spectra are presented in Table 2.

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