

## Electrochemistry of $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{X}$ -Series. I. Detailed Mechanism of Reduction of $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2$ and $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2\text{Hg}$

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Detailed electrochemical and spectroscopic study of the mechanisms of electrode reactions of  $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2$ ,  $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2\text{Hg}$  and  $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)^+$  at dropping mercury electrode has shown that the electrode reactions proper are coupled with chemical reactions between reactants and primary products of electrode reactions. The most abundant intermediate has been shown to be  $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_3\text{Hg}^-$ , which was characterized both at the electrode surface as well as in solutions after electrolysis. Even though some features of the polarographic behaviour of several compounds of the series  $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{X}$  were described [1–5], a more detailed investigation has shown the mechanism of electrode processes of the above compounds to be more complicated than described in the literature. Furthermore, the aim of our work was to follow the dependence of the electrode behaviour upon the type of X to establish the structural factors governing the course of the electrochemical processes, especially the stability of reduction products. The following groups of X were followed:

- 1, X = Cl, Br, I, H
- 2, X =  $\text{GeCl}_3$ ,  $\text{SnCl}_3$
- 3, X =  $\text{Si}(\text{C}_6\text{H}_5)_3$ ,  $\text{Ge}(\text{C}_6\text{H}_5)_3$ ,  $\text{Sn}(\text{C}_6\text{H}_5)_3$
- 4, X = CN

In this paper the reinvestigation and new study of  $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2$ ,  $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2\text{Hg}$  and  $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)^+$  is described as these compounds are essential intermediates or products of the electrode processes of most of the above mentioned compounds.

### Experimental

#### Chemicals

Tetrahydrofuran (THF), Merck, was used as solvent. Before use the solvent was purified using the 'ketyl method' [6]. Commercial THF was first treated with sodium hydroxide for several days and then refluxed with metallic sodium or potassium in

presence of benzophenone. After appearance of stable deep-blue colour of the solution, the solvent was freshly distilled for each experimental run. Tetrabutylammoniumperchlorate, dried *in vacuo* over  $\text{P}_2\text{O}_5$  at  $80^\circ\text{C}$  was used as supporting electrolyte (0.1 M in all experiments).  $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2$  was an  $\alpha$ -Inorganics product,  $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2\text{Hg}$  was prepared by the reduction with sodium amalgam followed by the reaction with  $\text{Hg}(\text{CN})_2$  [7].

#### Electrochemical Measurements

H-type cell (Fig. 1) was used throughout the work. The cell makes it possible to carry out polarographic

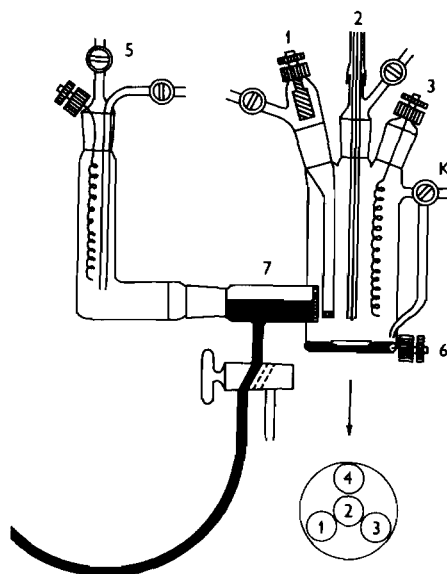


Fig. 1. Electrolysis H-cell: 1, reference electrode; 2, dropping mercury electrode; 3, auxiliary electrode for polarographic measurements; 4, inlet for the solution or connection to spectrophotometric cell; 5, auxiliary electrode for large-scale electrolysis; 6, working electrode for large-scale electrolysis; 7, connecting bridge with mercury valve;  $K_1$ , inlet of inert gas into or over the solution used also for evacuation of the electrolytic compartment.

studies as well as large scale electrolysis under polarographic control. The area of working electrode was 12 cm<sup>2</sup>. As reference electrode, an aqueous saturated calomel electrode was used. The aqueous and non-aqueous parts were separated by a bridge containing 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> in THF. For the electrolytic experiments, platinum wire in aqueous 0.1 M NaClO<sub>4</sub> was placed into the side arm 5. The solution, after electrolysis, can be transferred, using side arm 4, into a spectrophotometric cell under complete exclusion of air and moisture.

All operations were carried out in completely dry inert atmosphere. The method 'vacuum-inert gas' was used. Argon was purified from traces of oxygen with the use of BTS-catalyst and dried with P<sub>2</sub>O<sub>5</sub> and molecular sieve Calsit 5.

#### Instrumentation

Polarographic LP60 (Laboratorní přístroje, Prague) with recorder EZ4 or a Metrohm polarograph with the IR-Compensator were used. Coulometric measurements were done using Amel Integrator 558. UV-Vis. spectra were measured on Unicam SP800 spectrometer; for infrared spectra Perkin-Elmer M257 spectrometer was applied.

#### Results and Discussion

[Fe(CO)<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)]<sub>2</sub> is reduced in THF solution at the dropping mercury electrode in one two-electron wave with E<sub>1/2</sub> = -1.48 V. The process is electrochemically irreversible (the slope of the plot log i/(i<sub>d</sub>-i) vs E is 69 mV) and diffusion controlled. The use of Kalousek-commutator shows also the chemical irreversibility of the process (see Fig. 2): The product of the reduction gives an anodic wave at -1.18 V. Coulometric measurements show the consumption of two electrons (n = 2.02) per one molecule of

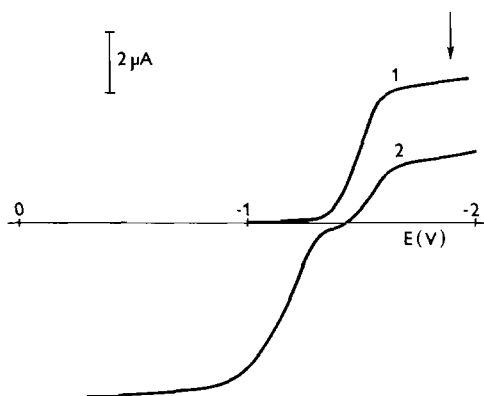
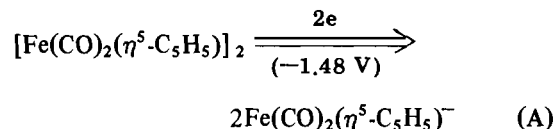


Fig. 2. Polarographic curves of [Fe(CO)<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)]<sub>2</sub>; 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>, THF, concentration of the complex = 1.1 × 10<sup>-3</sup> M. Curve 1: polarographic curve; curve 2: commutate wave with generation potential -1.9 V.

[Fe(CO)(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)]<sub>2</sub>. During the electrolysis a new oxidation wave at about -1.2 V is formed, the limiting current of which is exactly equal to the decrease of the original reduction wave. After exhaustive electrolysis the IR-spectra of the resulting solution show that the only product of the reduction is the anion Fe(CO)(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sup>-</sup> (ν<sub>CO</sub> = 1865 and 1785 cm<sup>-1</sup>).

The reduction process can thus be described by scheme A:



i.e. the electrode process results in the reduction of the metal-metal bond.

An anodic wave, identical with that described by Fergusson and Meyer [8], was also observed in THF solution (see Fig. 3). This wave has not been studied in more detail.

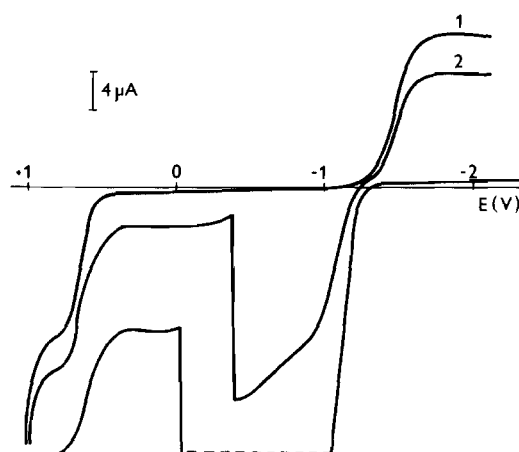


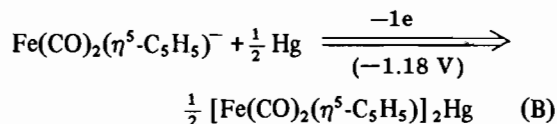
Fig. 3. Exhaustive electrolysis of [Fe(CO)<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)]<sub>2</sub>; 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>, THF, concentration of the complex = 3.4 × 10<sup>-3</sup> M. Coulometric and potentiostatic control, electrolysis potential -1.8 V. Curve 1: original solution; curve 2: n = 0.52 electron; curve 3: n = 2 electron.

#### Fe(CO)<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sup>-</sup>

This, prepared by chemical reduction of the dimer by sodium amalgam or by exhaustive electrolysis, gives one anodic wave, obscured by a large maximum which prevents the determination of the half-wave potential and morphology of the wave. This sort of maximum, characteristic for many oxidation processes in THF, cannot be suppressed by surface active compounds nor by changing the parameters of the dropping mercury electrode. However, as the study of [Fe(CO)<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)]<sub>2</sub> has shown the anion Fe(CO)<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sup>-</sup> to be the only reduction product, the value of the half-wave potential deter-

mined from the commutated wave, *i.e.*  $-1.18$  V, can be taken as characteristic for the anodic process of  $Fe(CO)_2(\eta^5-C_5H_5)^-$  in  $0.1$  M  $Bu_4NClO_4$  in THF (*vide infra*).

The electrode reaction is a one-electron (*vide ante*) diffusion controlled process. The *exhaustive* electrolysis [ $n = 1$  per one particle of  $Fe(CO)_2(\eta^5-C_5H_5)^-$ ] yields  $[Fe(CO)_2(\eta^5-C_5H_5)]_2Hg$  as the only product as was determined by IR and UV-Vis. spectroscopy. However, at values  $n < 1$  the composition of the products is more complicated (*vide infra*). The process at potentials of the *limiting current* can be described by scheme B:

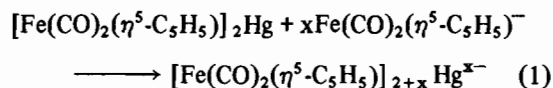


When the electrolysis of  $[Fe(CO)_2(\eta^5-C_5H_5)]_2$  is carried out in presence of lithium ions in most cases the anodic wave at  $-1.18$  V is not observed. Instead of this wave an anodic wave at  $+0.28$  V is formed and the colour of the resulting solution turns yellow showing a band at  $335$  nm. These results show that under these conditions  $Fe(CO)_2(\eta^5-C_5H_5)H$  is formed by the reaction of the primary anion with  $Li^+$  ions which, in presence of traces of water, function as relatively strong proton-donors [12] converting the anion  $Fe(CO)_2(\eta^5-C_5H_5)^-$  into the corresponding hydride by the mechanism described previously [13].

#### $[Fe(CO)_2(\eta^5-C_5H_5)]_2Hg$

This compound gives a rather complicated polarographic picture: Two reduction waves are observed at close potentials ( ${}_1E_{1/2} = 1.2$  V,  ${}_2E_{1/2} = 1.6$  V), the first wave is in most cases partly deformed by a maximum which makes it impossible to analyze it in more detail. The overall limiting current is diffusion controlled and corresponds to the exchange of two electrons per one particle of the depolarizer. The Kalousek-commutator experiments with production potential in the region of the overall limiting current show that the final product of the reduction gives a wave at  $-1.18$  V, *i.e.*  $Fe(CO)_2(\eta^5-C_5H_5)^-$  is formed. This has been confirmed by the exhaustive electrolysis ( $n = 2.06$  electrons) and IR-spectrophotometric identification of the product.

However, the first stages of the electrolysis show a much more complicated picture. Even after the passage of a small fraction of charge through the solution, the original bright yellow colour ( $\lambda = 388$  nm) changes into deep red ( $\lambda = 496$  nm). As the product of reduction of  $[Fe(CO)_2(\eta^5-C_5H_5)]_2Hg$  has been shown to be  $Fe(CO)_2(\eta^5-C_5H_5)^-$  it can be assumed that this deep red colour is due to the interaction of the product of the electrode reaction with the original depolarizer,



To determine the composition of the product of reaction (1) Jobb-analysis has been performed by mixing solutions of  $[Fe(CO)_2(\eta^5-C_5H_5)]_2Hg$  and  $Fe(CO)_2(\eta^5-C_5H_5)^-$  in various portions and following the change of absorbancy at  $496$  nm. Results are shown in Fig. 4. The maximum absorbancy is reached

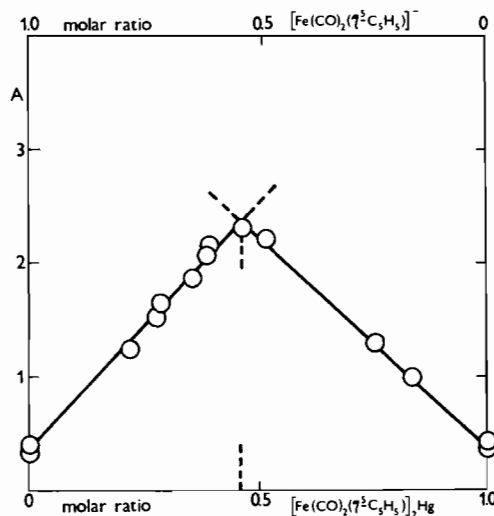


Fig. 4. Jobb analysis of the mixture of  $[Fe(CO)_2(\eta^5-C_5H_5)]_2Hg$  and  $Fe(CO)_2(\eta^5-C_5H_5)^-$ . A = absorbancy at  $\lambda = 496$  nm. Limiting conditions:

$[Fe(CO)_2(\eta^5-C_5H_5)]_2Hg$	$1.14 \times 10^{-3}$ M	0
$Fe(CO)_2(\eta^5-C_5H_5)^-$	0	$2.28 \times 10^{-3}$ M

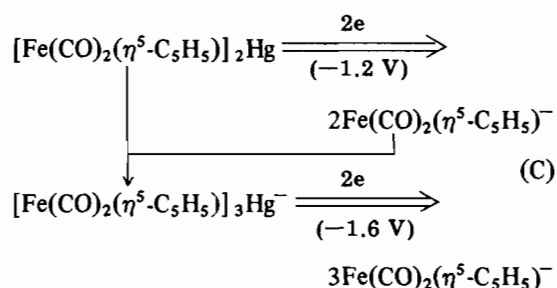
at the ratio of the two components approximately equal 1:1, thus indicating that the product of reaction (1) is predominantly the anion  $[Fe(CO)_2(\eta^5-C_5H_5)]_3Hg^-$  *i.e.*  $x$  in eq. (1) equals 1. The slight deviation from the ratio 1:1 is obviously due to some side reactions. The same polymetallic anion has been described [9, 10] as intermediate in the reduction of  $[Fe(CO)_2(\eta^5-C_5H_5)]_2Hg$  by alkali metals.

In the previous sections it was stated that the exhaustive electrolysis of the anion  $Fe(CO)_2(\eta^5-C_5H_5)^-$  yields the mercury compound as the final product. However, after passage of a small fraction of charge the deep red colour characteristic for the  $[Fe(CO)_2(\eta^5-C_5H_5)]_3Hg^-$  species is observed also during electrolysis of the anion at mercury pool anode. At the same time the reduction wave at  $-1.6$  V appears which can thus be identified as being due to the reduction of the mercury complex containing three iron units. The wave at  $-1.2$  belongs then to the direct reduction of  $[Fe(CO)_2(\eta^5-C_5H_5)]_2Hg$  generating the corresponding anion which inactivates further portions of the depolarizer and prevents thus the reduction wave of  $[Fe(CO)_2(\eta^5-C_5H_5)]_2Hg$  to

reach the overall diffusion controlled limit. Solutions containing  $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_3\text{Hg}^-$  show, except for the reduction wave at  $-1.6$  V, an anodic wave identical with that of simple anion  $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)^-$ . The anodic process proceeds obviously via free simple anions which are in equilibrium with the mercury containing anion.

The direct microscopic observation of mercury drop surface during electrolysis shows the formation of the deep red colour in the vicinity of the drop surface, thus confirming the formation of the mercury-containing anion even under polarographic conditions.

According to this the mechanism of the electrode reaction can be described by the scheme C:



## Conclusions

The detailed study has shown that the previous papers [1, 5, 11] on electrochemistry of the studied compounds detected only the limiting mechanisms

of the electrode processes. In this paper it was shown that the electrode reaction proper is coupled with chemical reactions between products and depolarizers which lead to the formation of electrochemically active intermediates. The mechanism of these processes helps to understand the behaviour of other complexes of the  $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{X}$  series as will be described in subsequent communications.

## References

- 1 R. E. Dessy, F. E. Stary, R. B. King and M. Waldrop, *J. Am. Chem. Soc.*, **88**, 471 (1966).
- 2 R. E. Dessy, P. M. Weissman and R. L. Pohl, *J. Am. Chem. Soc.*, **88**, 5, 117 (1966).
- 3 R. E. Dessy and P. M. Weissman, *J. Am. Chem. Soc.*, **88**, 5, 125 (1966).
- 4 R. E. Dessy and P. M. Weissman, *J. Am. Chem. Soc.*, **88**, 5, 129 (1966).
- 5 S. P. Gubin, *Pure Appl. Chem.*, **23**, 463 (1970).
- 6 S. Herzog and J. Dehmert, *Z. Chem.*, **4**, 1 (1964).
- 7 E. O. Fischer and R. Böttcher, *Z. Naturforsch.*, **106**, 600 (1955).
- 8 J. A. Fergusson and T. J. Meyer, *Inorg. Chem.*, **10**, 1025 (1971).
- 9 J. M. Burlitch, R. B. Petersen, H. L. Conder and W. R. Robinson, *J. Am. Chem. Soc.*, **92**, 1783 (1970).
- 10 S. C. Cohen, S. H. Sage, W. A. Baker, J. M. Burlitch and R. B. Petersen, *J. Organometal. Chem.*, **27**, C44 (1971).
- 11 R. E. Dessy, R. L. Pohl and R. B. King, *J. Am. Chem. Soc.*, **88**, 5, 121 (1966).
- 12 A. Vlček, Jr. and A. A. Vlček, *J. Electroanal. Chem.*, **100**, 867 (1979).
- 13 D. Grešová and A. A. Vlček, *Inorg. Chim. Acta*, **1**, 482 (1967).