

Electrochemistry of $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{X}$ Series. II. Mechanism of Reduction for $\text{X} = \text{Cl, Br, I, SnCl}_3, \text{GeCl}_3$

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Electrochemical reduction of $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{X}$ ($\text{X} = \text{Cl, Br, I, SnCl}_3, \text{GeCl}_3$) proceeds in two one-electron steps. The primary products of the first reduction, the $E_{1/2}$ of which depends slightly upon X , are the anion X^- and the kryptoradical $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2^{\cdot-}$, from which, in a follow-up chemical step, $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2\text{Hg}$ is formed. The second reduction step at -1.54 V corresponds essentially to the reduction of the dimer, $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2$, which is formed in a complicated sequence of chemical reactions coupled with the electrode reaction. The detailed analysis of the electrode process and comparison with homogeneous redox reactions leads to the conclusion that stability of the anion X^- in solution is the most decisive factor governing the concerted electron transfer and bond rupture process taking place in the course of the first reduction step. The detailed mechanism of the reduction of the dimer, $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2$, is elucidated and shown to be identical with that of other $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{X}$ compounds.

Introduction

In the first paper of this series [1] the electrochemical behaviour of $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2$ and $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2\text{Hg}$ was described. Our attempt to rationalize the electrochemical behaviour of the compounds of the type $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{X}$ led us to the reinvestigation of the behaviour of this series of complexes as even the first experiments had shown the mechanism of electrode reactions described in literature [2–6] to be oversimplified and not fully consistent with experimental data. As in the case of compounds described in our previous paper [1], also in the series studied in this communication complicated chemical reactions were found to be coupled with the electrode reaction proper which modify the electrochemical picture and influence the composition of intermediates and products of the electrochemical reduction.

Experimental

Experimental procedure and equipment was that described previously [1].

$\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{I}$ was commercial product of Alpha Inorganics. $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{Cl}$, $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{Br}$, $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{SnCl}_3$ and $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{GeCl}_3$ were prepared by Dr. Pavlík at the Chemical Technical University in Pardubice.

All samples were freshly sublimed before use.

Results and Discussion of Electrode Mechanism

General Pattern of Electrode Behaviour

The polarographic reduction of all compounds of the series $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{X}$ ($\text{X} = \text{Cl, Br, I, SnCl}_3, \text{GeCl}_3$) takes place in two waves (see Table I for values of $E_{1/2}$).

In all cases the first wave is diffusion controlled and corresponds to a one-electron reduction. The second wave, even if also diffusion controlled, is under normal experimental conditions, by about 10% smaller than the first reduction step.

The temperature dependence of the limiting currents shows that the activation energy of the processes governing the limiting values of the first and second wave differ; from the plot $\log i_1 - 1/T$ [8] for the first wave the activation energy is calculated to be $12.1\text{ kJ}\cdot\text{M}^{-1}$ which is a value corresponding to a process fully governed by diffusion [8]. However, a similar plot for the overall limiting current gives the value $16.8\text{ kJ}\cdot\text{M}^{-1}$ for the activation energy of the overall process which indicates that the overall limiting current is partly controlled by a chemical reaction. At elevated temperatures the limiting current of the second wave approaches that of the first reduction step and the overall process corresponds to a two-electron diffusion controlled reduction.

Both electrode processes are irreversible, as follows from the shape of the waves ($\alpha_1 = 0.38$; the plot of $\log i/i_d - i$ vs. E for the second wave consists of

TABLE I. Half-Wave Potentials of $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{X}$ Compounds in THF, 0.1 M Bu_4NClO_4 .

X	${}_1E_{1/2}^*$	${}_2E_{1/2}^*$
Cl	-0.59	-1.54
Br	-0.52	-1.54
I	-0.46	-1.54
SnCl_3	-0.55	-1.54
GeCl_3	-0.95	-1.54

*V vs. SCE.

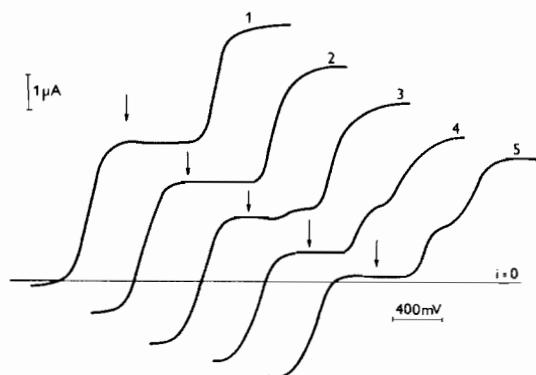


Fig. 1. Polarographic pattern of successive steps of large scale electrolysis at mercury pool electrode. Solution: 1.5×10^{-3} M $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{I}$; 0.1 M Bu_4NClO_4 in THF. Electrolysis potential -0.8 V. Fraction of reduction: curve 1, $n = 0$; 2, $n = 0.3e$; 3, $n = 0.56e$; 4, $n = 0.83$; 5, $n = 0.99e$.

two linear parts of different slopes: 42 mV and 67 mV, respectively). The commutator experiments show that, at generating potential in the region of the limiting current of the first wave, the only electroactive products formed are the corresponding anions X^- . For generating potentials in the region of the overall limiting current, an anodic wave is detected which is identical with that of $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)^-$, as described previously [1]*.

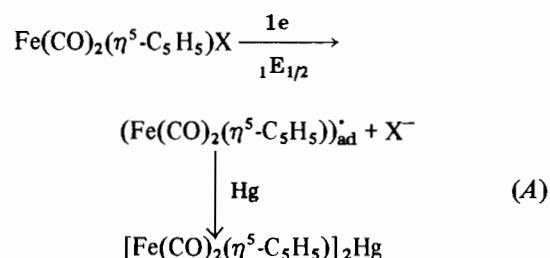
Mechanism of the First Reduction Step

The large scale electrolysis on a mercury pool cathode shows that for complete reduction at potentials in the region of the limiting current of the first reduction wave one electron per particle of depolarizer is consumed. The polarographic picture of the partly reduced solutions depends, however, upon the frac-

tion of reduction (n) (see Fig. 1). For $n < 0.5$ the first reduction wave decreases, the second reduction step remains unchanged and anodic wave of the anion X^- newly appears (in the case of $\text{X} = \text{I}$ a 'pseudo reversible wave' is formed due to the coincidence of half-wave potentials of the first reduction step and that of the anodic wave of iodide). For $n > 0.5$, a wave at -1.2 V appears which increases with increasing n at the expense of the original second reduction step. For $n = 1$, reduction waves characteristic for $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2\text{Hg}$ and the wave of the anion X^- are seen.

The UV-Vis- and IR-spectrophotometric control of the electrolytic reduction indicates, however, that the only product formed at all values of n is $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2\text{Hg}$ in 100% yield.

From these experiments it follows that the mechanism of the first reduction step can be described by Scheme (A):



The 'radical' in scheme (A) is obviously a sort of kryptoradical, *i.e.* a radical strongly attached to mercury surface by a sort of chemical bond (*cf. e.g.* [7]). This kryptoradical is loosened from the surface in a follow-up process. No direct evidence has been obtained for its existence, the temperature dependence of the limiting current of the second reduction steps points, however, to the conclusion that the primary product of the first reduction is not reducible and has to be converted into an electrochemically active species in a chemical step. This step is obviously the formation of the mercury compound from the kryptoradical in a chemical surface reaction.

The polarographic and spectrophotometric evidence quoted above seem, at first sight, to be in contradiction; whereas the spectrophotometric evidence shows unambiguously the formation of the mercury compound at all values of n , the polarographic picture characteristic for this compound appears only for $n > 0.5$.

To clarify this apparent discrepancy we have studied interaction between various species taking part in the electrode process:

1) There is no interaction between $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{X}$ and $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2\text{Hg}$ in solution as follows from spectrophotometric investigation.

*As the behaviour of all compounds of the series was found to be essentially the same, the detailed study was carried out for $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{I}$ only.

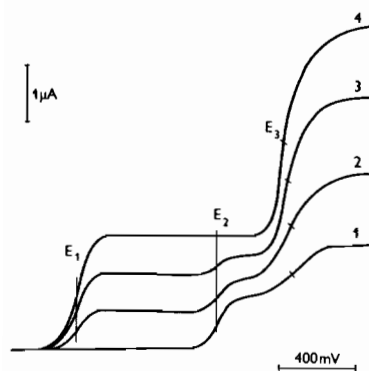
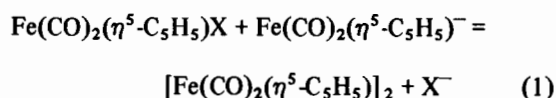


Fig. 2. Influence of $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{X}$ upon the polarographic reduction of $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2\text{Hg}$. $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2\text{Hg}$: $8 \times 10^{-4} \text{ M}$, $0.1 \text{ M Bu}_4\text{NClO}_4$, THF. $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{I}$: curve 1, 0; 2, $4 \times 10^{-4} \text{ M}$; 3, $8 \times 10^{-4} \text{ M}$; 4, $1.6 \times 10^{-3} \text{ M}$.

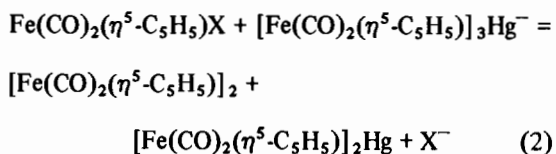
2) Reaction



takes place readily in solution (see [4]).

The same reaction proceeds also in presence of metallic mercury; the corresponding mercury compound is not observed under conditions when all components are present in the solution.

3) Reaction



takes place very readily as follows from spectrophotometric observation.

The above mentioned reactions take place also at the electrode and their incorporation into the reaction sequence explains the dependence of the polarographic pattern upon the fraction of reduction, n .

The same effect has to be observed when $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{X}$ is stepwise added to a solution of $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2\text{Hg}$ (see Fig. 2): Upon the addition of $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{I}$ to the solution of the mercury compound, the wave of the latter at -1.2 V diminishes until it disappears when the molar ratio of the reactants equals 2 (see Fig. 2). The more negative wave of the mercury compound increases at the same time and is slightly shifted towards positive potentials. The overall limiting current equals to the sum of currents of both depolarizers present.

The explanation for the disappearance of the first wave of the mercury compound – and of its non-

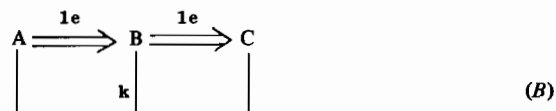
existence in large scale electrolysis experiments for $n < 0.5$ – is as follows: $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2\text{Hg}$ present in the solution, as well as that formed by the reduction of $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{X}$, is reduced at -1.2 V under the formation of the anion, $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)^-$. This, however, when diffusing into the solution reacts according to eqn. (1), consuming a part of the depolarizer before it reaches the electrode. The dimer formed undergoes reduction at more negative potentials [1]. Assuming the diffusion coefficients of both reactants in eqn. (1) to be roughly equal, the reduction current of the mercury compound at -1.2 V is exactly compensated for by the diminished flux of $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{X}$ towards the electrode. The wave of the mercury compound at -1.2 V can thus appear, in presence of $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{X}$, only when the molar concentration of the latter is less than $\frac{1}{2}$ of the concentration of the mercury compound. This explains the appearance of the wave at -1.2 V only for $n > 0.5$ in large scale electrolysis experiments, as well as its total disappearance at molar ratio > 2 in experiments with mixtures of both compounds.

Mechanism of the Second Reduction Step

The second reduction step shows properties which, even if not fully identical, are very nearly those of the reduction of the dimer. The latter is the depolarizer proper in the second reduction step. *The dimer is, however, not formed by the dimerization of the primarily formed radical but by the chemical reaction, eqn. (1), which is essentially a process of reproporationation type.* The overall mechanism is thus of the eec type*, which was analyzed by Ružić [9, 10]. Even if our mechanism is more complex than that calculated by Ružić, the form of the $\log i_1 - i/i - E$ plot as well as the shift of $E_{1/2}$ (-1.54 V as compared with -1.48 V for free dimer) are in qualitative agreement with the theoretical predictions for the assumed mechanism. From the $\log i_1 - i/i - E$ plot the rate constant of the reproporationation reaction $10^5 < k < 10^6 \text{ M}^{-1}\cdot\text{s}^{-1}$ can be estimated, using the criteria given by Ružić [9, 10].

The dependence of the limiting currents upon temperature is, furthermore, indicative for an eec mechanism [11] in which the depolarizer proper of the second reduction step is formed by a chemical

*A reproporationation reaction coupled to an eec mechanism can be depicted as

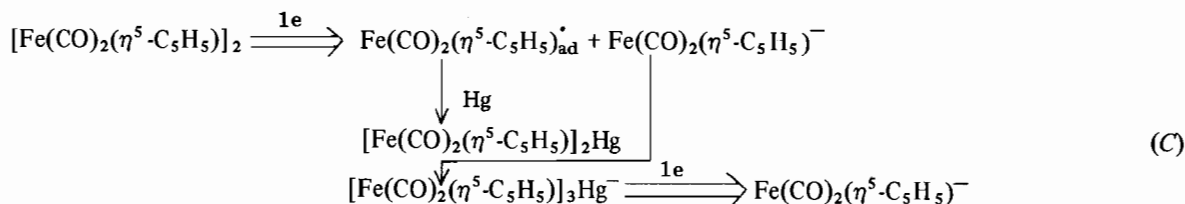


In our case $\text{A} = \text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{X}$, $\text{B} = [\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2$, $\text{C} = \text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)^-$.

reaction from a precursor resulting as primary product of the first reduction (*vide ante*), i.e. the anion $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)^-$ triggering the reproporationation reaction is not formed primarily by the reduction of the dimer but by the reduction of the mercury salt, which is formed from the kryptoradical in a follow-up chemical step. The reduction of the mercury salt starts at -1.2 V, even if no net cathodic current appears, as explained previously.

According to this conclusion the dimer, $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2$, could be expected as the intermediate product of electrode reaction at potentials more negative than about -1.2 V. An attempt was thus made to detect the formation of the dimer in the course of large scale electrolysis at potentials in the region of the second reduction step. The exhaustive electrolysis, controlled polarographically and spectrophotometrically (IR, UV-Vis), shows the only product to be the anion $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)^-$, i.e. 2 electrons ($n = 2$) are consumed per one particle of the depolarizer. For $n < 1$, however, the mercury salt, $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2\text{Hg}$ was detected as the only product even at working potential -1.9 V. For $1 < n < 2$, $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_3\text{Hg}^-$ was detected as an intermediate product. Only at high concentrations of the depolarizer ($>10^{-2}$ M) and under intensive mixing of the solution the mercury compound as well as the dimer were detected in solution for $n < 1$. Under no investigation conditions was the dimer found to be the only product of the partial ($n < 1$) large scale electrolysis.

These results can be compared with those of partial ($n < 1$) large scale electrolysis of the dimer itself which results in the formation of the mercury anion $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_3\text{Hg}^-$. This finding, not understandable from the analysis of the electrode behaviour of the dimer only [1], can be rationalized using the knowledge of the mechanism of the first reduction step of $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{X}$ as described above: the reduction of the dimer proceeds obviously primarily as a *one electron reduction* under the formation of the anion, $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)^-$, and of the kryptoradical, $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)_{\text{ad}}^\bullet$. The latter is converted by a surface chemical reaction into the mercury salt which reacts with the anion under the formation of $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_3\text{Hg}^-$. The full mechanism of the electrode reduction of the dimer can thus be described by Scheme (C), which essentially corresponds also to the mechanism of the second reduction step of $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{X}$ compounds.



The detailed mechanism of the reduction of $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_3\text{Hg}^-$ might be composed of several steps, however, the experimental technique does not make it possible to identify them.

The Overall Mechanism

Previous sections described processes taking part in the first and second reduction steps. Both steps are interconnected by a series of chemical reactions, in the bulk of the solution as well as at the electrode surface, and the overall mechanism is a combination of ece and eec type of mechanism. The first reduction product, the adsorbed kryptoradical, is electrochemically inactive and is converted by a reaction sequence into electrochemically active species, which trigger the eec process characteristic for the second reduction. The main reactions are complicated by further interaction of intermediates leading to the formation of the anion $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_3\text{Hg}^-$. The overall mechanism can thus be depicted by the Scheme (D). The reduction of the dimer, enclosed in the heavy brackets, proceeds *via* mechanism described by Scheme (C).

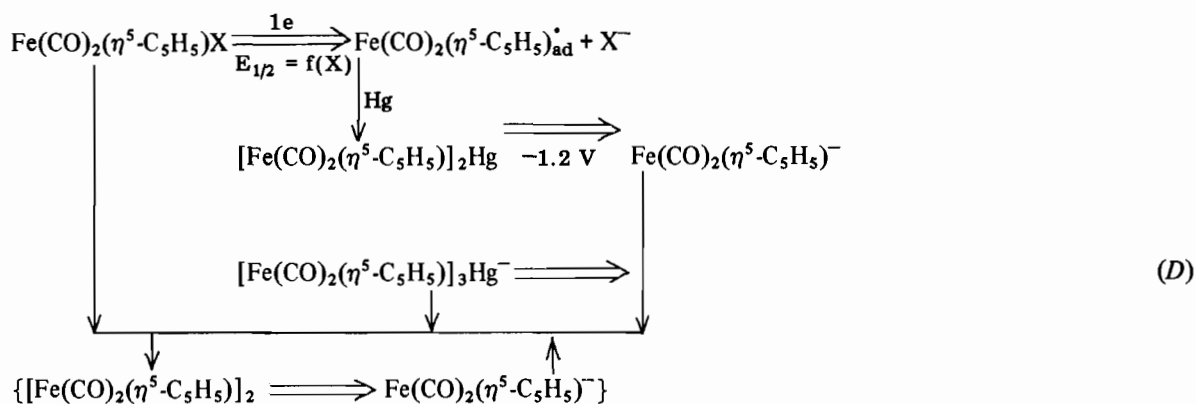
Scheme (D) holds strictly for $\text{X} = \text{Cl}, \text{Br}$ and I . For $\text{X} = \text{SnCl}_3$ and GeCl_3 the anion $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_3\text{Hg}^-$ has not been detected in the course of the large scale electrolysis.

Discussion

From the above described experiments it follows that only the first reduction step of $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{X}$ compounds ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SnCl}_3, \text{GeCl}_3$) depends upon the nature of X , the second step being identical for all compounds studied.

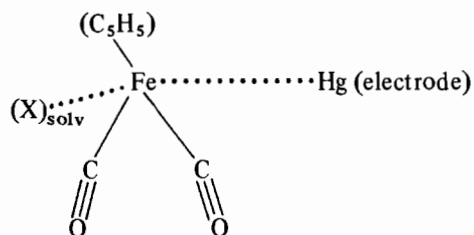
In all cases the first reduction results in the rupture of the iron-X bond and formation of the radical and X-anion. The radical, $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)_{\text{ad}}^\bullet$, is, however, not formed as a solution entity (otherwise the corresponding dimer had to be observed as the final product of the first reduction!) but as a kryptoradical, a species strongly attached to the electrode surface and electrochemically completely inactive.

The reduction is thus a concerted electron transfer and bond rupture process, a type of (e + c) electrode reaction inherently irreversible electrochemically as well as chemically. The factors governing this type of reaction are *i*) the nature of the redox



orbital, *ii*) the stability of the various possible fragments formed.

The redox orbital in the described series is obviously the σ -antibonding orbital of the Fe–X bond. The increase of electron density by one unit in this orbital cannot be compensated for sufficiently by any electron drift to the region outside of the bond and causes thus the instability of the Fe–X bond. Analogous homogeneous reductions result always in the splitting of the X anion and in the formation of the dimer or in the attachment of the reducing agent to the remaining part of the molecule [4]. Whereas the formation of the dimer is a two step reaction, the latter process proceeds most probably as a concerted redox addition and bond rupture reaction. The electrode reaction can be looked upon as a process of the latter type, the redox addition step being a strong interaction between the reacting particle and the electrode. The mechanism of homogeneous reduction also indicates that, even in cases where no redox addition takes place, the electron change in the σ -antibonding orbital results in a drift of electrons towards the X substituent. This comparison between homogeneous and heterogenous electrode reactions leads to the formulation of the activated complex of the electrode reaction as



The weakening of the Fe–X bond in the activated complex is firstly due to a partial transfer of an electron into the corresponding σ -antibonding orbital and, secondly, due to the increased solvation of the substituent X. The electrode reaction is thus governed by the tendency of the ion center towards inter-

action with mercury surface on one side and by the electrofiliicity and solvation stabilization of the X substituent. This explains also the rather small variation of the half-wave potential of the first reduction step with the nature of X. Only for X = GeCl_3 a more negative reduction potential is observed. This might be due to a smaller general stability of the corresponding anion, GeCl_3^- , requiring thus a higher activation energy to achieve the proper activated complex.

These results bring also a deeper insight into the mechanism of the reduction of the dimer, $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2$. This reduction is not an ee process, *i.e.* it does not proceed *via* a consecutive two electron transfer. Contrary, the reduction of the dimer can be looked upon as the reduction of other $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\text{X}$ species, *i.e.* formally as a reduction of $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)^+ \text{---} \text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)^-]$ compound proceeding *via* intermediate formation of the kryptoradical. This result is of fundamental importance elucidating the mechanism of all apparently two electron reduction of organometallics.

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