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Electrochemistry of $Fe(CO)_2(\eta^5\text{-}C_5H_5)X$ Series. III. Mechanism of Reduction for X = $SiPh_3$, $GePh_3$, $SnPh_3$ – Formation of Anion Radicals $Fe(CO)_2(\eta^5\text{-}C_5H_5)MPh_3^{\overline{\cdot}}$

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$Fe(CO)_2(\eta^5\text{-}C_5H_5)MPh_3$ (M = Si, Ge, Sn) compounds were shown to undergo a one electron reversible reduction resulting in the hitherto undescribed anion radicals $Fe(CO)_2(\eta^5\text{-}C_5H_5)MPh_3^{\overline{\cdot}}$. The radicals were characterized by their EPR spectra. The existence of these radicals is explained by the possibility of the interaction of the unpaired electron with the π-system of the phenyl groups system. These anion radicals undergo a further reduction which seems to be a concerted electron transfer and metal–metal bond rupture resulting in the formation of $Fe(CO)_2(\eta^5\text{-}C_5H_5)^-$ and $SnPh_3^-$ or $HGePh_3$ and $HSiPh_3$, respectively.

Introduction

In preceding papers of this series [1, 2] a detailed mechanism of electrochemical reduction for a number of compounds of the type $Fe(CO)_2(\eta^5\text{-}C_5H_5)X$ was described. In all cases previously studied (X = Cl, Br, I, $GeCl_3$ and $SnCl_3$) the redox orbital has been identified as the σ-antibonding orbital of the Fe–X bond. The primary one-electron reduction results in the scission of the Fe–X bond under the formation of the kryptoradical $(Fe(CO)_2(\eta^5\text{-}C_5H_5)\cdot$, attached to the mercury surface, and the corresponding anion X^-. The overall two electron reduction leads to $Fe(CO)_2(\eta^5\text{-}C_5H_5)^-$ and X^-.

The electrochemical behaviour of compounds with X = $SiPh_3$, $GePh_3$ and $SnPh_3$ differs, however, from that mentioned above essentially in the nature of the products of the first reduction step, and is described and analyzed in this paper.

Experimental

Experimental procedures and equipment were as described previously [1].

TABLE I. Half-Wave Potentials of $Fe(CO)_2(\eta^5\text{-}C_5H_5)X$ Compounds (THF; 0.1 M Bu_4NClO_4).

X	$_1E_{1/2}$[a]	$_2E_{1/2}$[a]	N[b]
$SnPh_3$	−1.86	−2.21	2
$GePh_3$	−1.90	−2.40	2
$SiPh_3$	−1.95	−2.93	(2)

[a] V *vs.* SCE. [b] Overall reduction. [c] The wave is distinguished from that of the supporting electrolyte only at concentrations higher than 3×10^{-3} M.

Compounds $Fe(CO)_2(\eta^5\text{-}C_5H_5)X$ (X = $SiPh_3$, $GePh_3$ and $SnPh_3$) were donated by Dr. I. Pavlík of the Chemical Technical University in Pardubice.

Results

The polarographic reduction of all three compounds studied in tetrahydrofurane takes place in two steps (see Table I for values $E_{1/2}$). The overall limiting current (Σi_l) is diffusion-controlled and corresponds to a two-electron reduction, as determined by comparison with structurally analogous pilot compounds, as well as coulometrically. However, the limiting current of the first reduction step ($_1i_l$) is always *higher* than that which would correspond to the diffusion controlled one-electron process ($i_d = ½\Sigma i_l$). The magnitude of this enhancement, expressed as $_1i_l/i_d$, increases non-linearly with increasing concentration of the parent compound.

The dependence of $_1i_l$ upon the parameters of the dropping mercury electrode indicates a combination of diffusion and kinetic control of the magnitude of $_1i_l$.

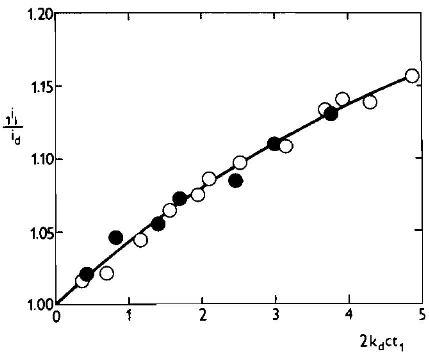


Fig. 1. Dependence of limiting-diffusion current ratio of the first reduction wave of $Fe(CO)_2(\eta^5-C_5H_5)GePh_3$ on $\zeta_1 = 2k_dct_1$ (● t_1 = 2.14 s, variation of c; ○ c = 8 × 10^{-4} *M*, variation of t_1).

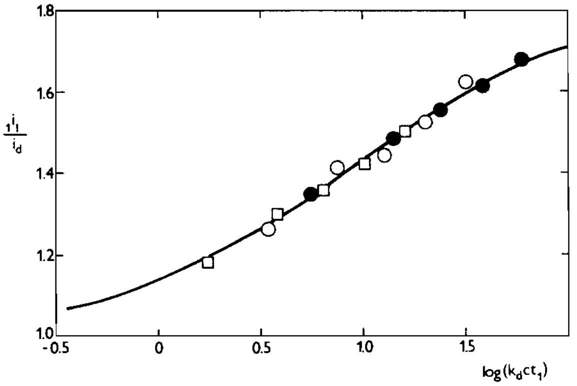


Fig. 2. Dependence of limiting-diffusion current ratio of the first reduction wave of $Fe(CO)_2(\eta^5-C_5H_5)SnPh_3$ on log (k_dct_1) (variation of t_1 for different c): ● c = 3 × 10^{-3} *M*; ○ c = 1.6 × 10^{-3} *M*; □ c = 8 × 10^{-4} *M*.

The value of ${}_1i_1/i_d$ approaches 1 with decreasing temperature, *i.e.* the enhancement of ${}_1i_1$ above the one-electron value decreases with lowering temperature. The log ${}_1i_1$ – 1/T plot [3] indicates the overall activation energy of the mass transport in the first reduction step to be higher than that corresponding to the diffusion controlled process (*e.g.* for X = $SnPh_3$ the measured activation energy is 23.5 kJ mol^{-1} as compared with about 12 kJ mol^{-1} typical for diffusion controlled processes). These facts point to the conclusion that the first reduction steps include a chemical reaction coupled with the electrode reaction proper.

The magnitude of the enhancement of the first reduction step depends upon the nature of the IVB metal and increases in the order Si < Ge < Sn.

The concentration and temperature dependence of ${}_1i_1/i_d$, together with the fact that this ratio approaches 1 under conditions when the rate of coupled chemical reaction is decreased, point to the conclusion that the enhancement of the limiting current of the first reduction wave is due to a ***disproportionation*** reaction of the primary product formed, *i.e.* a second order reaction with respect to the primary product which necessarily results in the dependence of ${}_1i_1/i_d$ upon the concentration of the depolarizer. The electrode process can thus be depicted schematically as given in Scheme I.

TABLE II. Characteristics of Anion Radicals $Fe(CO)_2(\eta^5-C_5H_5)X^{\overline{\cdot}}$.

X	k_d (M^{-1} s^{-1})	EPR Parameters	
		g	H (mT)
$SiPh_3$	[a]	1.988	1.7
$GePh_3$	4.3 × 10^2	1.958	7.7
$SnPh_3$	3.7 × 10^3	1.998[b]	12[b]

[a] The value k_d was not calculated because of the incorrect determination of the diffusion-controlled current of the one-electron process. [b] Stannyl radical anion is too unstable for its EPR signal to be obtained at T = 298 °C at which EPR spectra of silyl and germyl compounds were measured. The present data were measured at T = 253 °K.

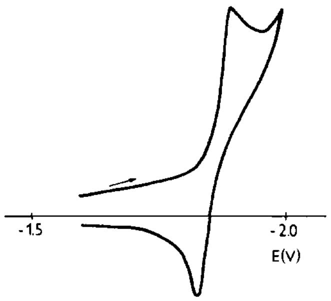
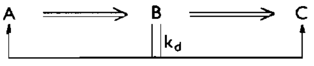


Fig. 3. Cyclic voltammogram of $Fe(CO)_2(\eta^5-C_5H_5)GePh_3$ at platinum electrode in tetrahydrofuran; scan rate = 0.5 V s^{-1}.



Scheme I.

The rate constant of this disproportionation reaction (k_d) has been calculated from the dependence of ${}_1i_1/i_d$ upon the drop time of the mercury electrode and concentration of the depolarizer (see Figs. 1 and 2) using standard methods [4–7]. The corresponding results are summarized in Table II.

To determine the nature of B and C in Scheme I electrochemical, EPR and spectroscopic methods have been used.

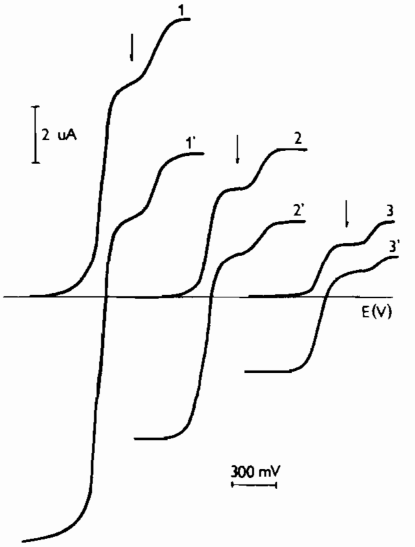


Fig. 4. DC-polarograms (1, 2, 3) and curves, recorded by Kalousek commutator (1', 2' 3'), of $Fe(CO)_2(\eta^5\text{-}C_5H_5)SnPh_3$ at DME in tetrahydrofuran. Auxiliary potential E = −1.95 V (*vs.* SCE); drop time 2.14 s, commutating frequency 12.5 s^{-1}; 1,1': c = 3 × 10^{-3} *M*; 2,2': c = 1.6 × 10^{-3} *M*; 3,3': c = 8 × 10^{-4} *M*.

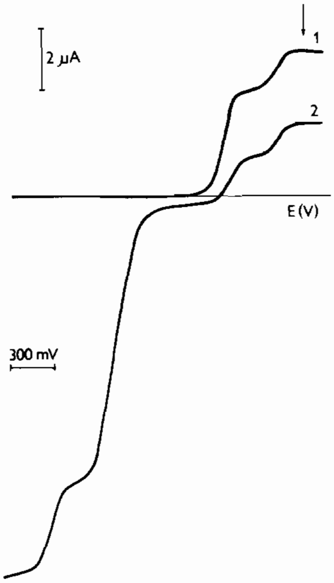


Fig. 5. DC polarogram (1) and curve recorded by Kalousek commutator (2) of $Fe(CO)_2(\eta^5\text{-}C_5H_5)SnPh_3$ at DME in tetrahydrofuran. Auxiliary potential E = −2.4 V (*vs.* SCE), drop time 2.14 s, commutating frequency 12.5 s^{-1}; c = 1.6 × 10^{-3} *M*.

Cyclic voltammetry shows (see Fig. 3) that the electrode reaction of the first reduction step is reversible. However, the ratio of the cathodic and anodic peak currents indicates that the primary product formed (*i.e.* B) is inactivated by a chemical process.

The same results are obtained by using the commutator technique, in which the primary product is generated directly at the electrode at the potential of the limiting current. When the generating potential is located in the region of the limiting current of the first reduction step, a reversible oxidation of the primary product is found (see Fig. 4). However, the magnitude of the corresponding oxidation current is in all cases smaller than that predicted by theory [8] for a simple, reversible, diffusion-controlled process. The relative oxidation current decreases with increasing concentration of the parent compound (see Fig. 4) and with increasing temperature.

In general, the greater the enhancement of the limiting current of the first reduction step, the smaller the portion of the primary product reoxidized under conditions of both cyclic voltammetry and commutator technique. These results are in full agreement with Scheme I and indicate that the primary process (A ⇔ B in I) is a *reversible* one-electron reduction followed by a disproportionation of the product. The primary reduction product (species B in I) can be thus formulated as a radical–anion, $Fe(CO)_2(\eta^5\text{-}C_5H_5)MPh_3^{\overline{\cdot}}$ disproportionating by a bimolecular process to give the original depolarizer (species A in I) and a two-electron reduction product.

The existence of the radical–anion has been proved by controlled potential electrolysis in the EPR cavity. The species formed in the first reduction step show EPR signals, the parameters of which are given in Table II. In all cases simple one-line signals without any hyperfine splitting were found.

The nature of the final product (C in I) was investigated by its generation at the electrode using the commutator technique. When the generating potential is set in the region of the overall limiting current, two anodic steps are observed, at −0.7 and −1.18 V, both for the stannyl and germyl compounds (see Fig. 5). In the case of the germyl compound both oxidation waves are of approximately the same magnitude. For the stannyl compound, however, the wave at −1.18 V is much higher than the corresponding wave of the germyl compound as well as than the second oxidation wave at −0.7 V both for stannyl and germyl compounds. From the study of $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$ [1] it is known that $Fe(CO)_2(\eta^5\text{-}C_5H_5)^-$ produces an anodic wave at −1.18 V. No other anodic wave connected with any possible fragment derived from the $Fe(CO)_2(\eta^5\text{-}C_5H_5)$ moiety has been observed. The oxidation wave at −0.7 V has thus to be attributed to a process connected with the IVB metal fragment.

The reduction of Sn_2Ph_6, investigated under the same commutator conditions, results in the formation of $SnPh_3^-$ which gives two anodic waves, at −1.18 and −0.7 V, respectively. The ratio of the wave of the stannyl compound at −1.18 V to that at −0.7 V unambiguously indicates that in the former case more material undergoes the electrode reaction than in the latter one. In the case of the stannyl compound the wave at –1.18 V is thus attributed to coinciding anodic processes of the anion $Fe(CO)_2(\eta^5\text{-}C_5H_5)^-$ and $SnPh_3^-$, the wave at –0.7 V to oxidation of $SnPh_3^-$ alone.

The electrochemical study of Ge_2Ph_6 [9, 10] shows that the reduction of this species results in the formation of $HGePh_3$. In the commutator experiments with Ge_2Ph_6 an oxidation wave of the reduction product at –0.7 V is found. In the case of the germyl compound the anodic wave is thus solely due to the formation of $Fe(CO)_2(\eta^5\text{-}C_5H_5)^-$ and that at –0.7 V to the formation of $HGePh_3$*.

All these results obtained using the commutator technique are in full agreement with those obtained by cyclic voltammetry.

In no case was direct evidence found for the formation of the dianion $Fe(CO)_2(\eta^5\text{-}C_5H_5)MPh_3^{2-}$. The disproportionation reaction is merely an electron transfer from one monoanion radical $Fe(CO)_2(\eta^5\text{-}C_5H_5)MPh_3^{\bar{\cdot}}$ to another.

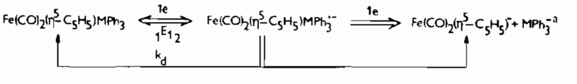
Supposing that this process results in the filling up of the σ-antibonding orbital of the Fe–X bond in one of the reacting units, a concerted electron transfer and bond rupture can be assumed:

$$2Fe(CO)_2(\eta^5\text{-}C_5H_5)MPh_3^{\bar{\cdot}} \longrightarrow Fe(CO)_2(\eta^5\text{-}C_5H_5)MPh_3 + Fe(CO)_2(\eta^5\text{-}C_5H_5)^- + MPh_3^- \qquad (1)$$

For M = Sn the anion $SnPh_3^-$ is stable enough to be detected. On the other hand, $GePh_3^-$ is a very strong nucleophile, reacting extremely rapidly with any available proton donor (*e.g.* solvent, Bu_4N^+, traces of water) with the formation of $HGePh_3$.

The corresponding silicon compound has not been investigated by the commutator technique in detail, due to extreme experimental difficulties when working at the very negative potentials required.

Large scale electrolysis at a mercury pool cathode under coulometric control confirms all the above conclusions. All three compounds investigated are reduced completely by two electrons already at the potential of the first reduction steps. This means that the disproportionation reaction of the radical anions formed converts these primary one-electron reduction products to the original depolarizer and the products of two-electron reduction. While under polarographic conditions the disproportionation reaction leads only to a *partial* conversion of B into A and C (see Scheme I), on the time scale of exhaustive electrolysis the disproportionation reaction necessarily leads to completion. In the electrolyzed solution the presence of the reduction products $Fe(CO)_2(\eta^5\text{-}C_5H_5)^-$ and $SnPh_3^-$, $HGePh_3$ or $HSiPh_3$, respectively, was confirmed by IR and UV–VIS spectra.



a for M = Si, Ge HMPh3 is formed

Scheme II.

On the basis of these results the overall mechanism of reduction of $Fe(CO)_2(\eta^5\text{-}C_5H_5)MPh_3$ can be deduced as given in Scheme II.

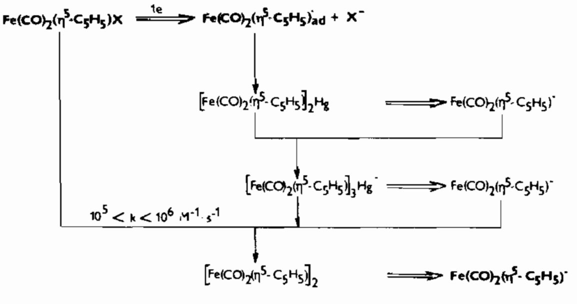
Discussion

The mechanism of electrode reduction of compounds $Fe(CO)_2(\eta^5\text{-}C_5H_5)X$ for X = MPh_3, given in Scheme II, differs from that deduced from formally-analogous compounds with X = Cl, Br, I, $SnCl_3$, $GeCl_3$ (*cf.* Scheme III in which the bold-typed species represent the depolarizer, the primary and final products, [2]) in that in the former case

i) no intermediate interaction with mercury surface is detected,

ii) a stable anion radical is formed as the primary product.

The reduction proceeding via a mercury compound, as described previously [2], requires an adsorption at the mercury surface as the primary step which is followed up by concerted electron transfer and bond rupture. The prerequisite of an adsorption at a mercury surface, resulting in the formation of metal-centered kryptoradical and eventually a mercury compound, $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2Hg$, is the existence of a metal (*i.e.* iron) localized center capable of interacting with mercury. This



Scheme III.

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*The appearance of the anodic wave both for the germyl and stannyl compound at –0.7 V is thus merely a coincidence and has no physical meaning.

condition is obviously fulfilled for X = Cl^-, *etc.*, as the compounds of this type behave chemically as compounds of iron(II) with some positive charge localized on the iron atom. However, compounds with X = MPh_3 are, on the basis of the method of their preparation and their chemical behaviour [11, 12], described as derived from iron d^7 configuration [12], *i.e.* with the σ-bond Fe–M having more electron density in the vicinity of iron. This conclusion is further supported by comparison of ionization potentials of the possible radical fragments:

$\cdot Fe(CO)_2(\eta^5\text{-}C_5H_5)$	7.7 eV	[13]
$\cdot SnPh_3$	6.29 eV	[14]
$\cdot SnCl_3$	9 eV	[14]

From these data it follows that the $SnPh_3$ fragment would be a much better electron donor towards iron as compared with $SnCl_3$.

As the interaction of iron(II) species with mercury surface results in the formation of a fragment essentially of iron(I) character (*i.e.* the kryptoradical $Fe(CO)_2(\eta^5\text{-}C_5H_5)\cdot$, see Scheme III), the increased electron density and thus actually the iron(I) character in the compounds with X = MPh_3 will make the adsorption and interaction with the mercury surface less probable. The activation energy necessary to induce an electron shift towards the $SnPh_3$ group creating the electron configuration around the iron atom appropriate for adsorption and electron transfer to the iron center is obviously very unfavourable. As a result of this, the electrode-assisted fragmentation does not proceed for compounds with X = MPh_3.

The stability of the resulting anion radicals, $Fe(CO)_2(\eta^5\text{-}C_5H_5)MPh_3^{\overline{\cdot}}$, is remarkable. Using simple arguments, applied usually to the explanation of radical stability, an existence of Fe–M π-bond would be expected and the radical–anion would be formulated as one containing the electron in the π-antibonding orbital of the Fe–M bond. However, most of the experimentally-available data [14–17] do not support the existence of the Fe–M π-bond, so that the simple explanation of the anion radical stability cannot be accepted. If the formulation of the σ-bond as developed above is used, the σ-antibonding orbital would be predominantly localized on the MPh_3 fragment and would accept the electron when the anion radical is formed. However, an interaction of this charge with unoccupied orbitals of the MPh_3 moiety (*e.g.* through space interaction) leading to its partial delocalization over the phenyl groups has to take place to account for the relatively high stability of the anion radicals formed. Support for this description is found in the UV spectra of Ge_2Ph_6 and Sn_2Ph_6 which have been interpreted as showing interaction of the π-system of the phenyl groups with the orbitals of the metal–metal system [18–21]. The observed EPR spectra do not give direct evidence for the delocalization of the unpaired spin onto the phenyl rings. However, simulation of EPR spectra shows that any weak interaction could not manifest itself within the broad line observed. Due to the extreme sensitivity and disproportionation reactions, the direct investigation ion of electron configuration of the anion–radicals is very difficult. However, experiments are in progress to test the above hypothesis.

The second reduction step is fully irreversible and seems to involve a bond rupture concerted with the electron transfer, as the overall electronic configuration of the system formed in this process would correspond to the full occupation of the σ-antibonding orbital of the Fe–M bond. As seen from Table I, unlike the first reversible redox potentials, the $E_{1/2}$'s for the second reduction step depend considerably upon the nature of M, being more negative in the order

$$Sn < Ge < Si$$

This order parallels the order of nucleophilicity of the anions, MPh_3^-, which are formed as primary fragments of the electrode process. The increasing nucleophilicity corresponds to increasing need of energy to form the corresponding anion from its precursor. This is obviously reflected in the order of values of $E_{1/2}$ for the second reduction step, even if the strength of the bond to be broken could be expected to decrease in the parent, uncharged compound in the opposite direction, as can be deduced from the data on analogous compounds [14]. For M = Ge and Si the nucleophilicity of the anion, MPh_3^-, is so high that protonation in THF takes place extremely rapidly after being formed, if not even in the cage of solvent molecules after primary fragmentation. Analogous arguments can be applied to the rate of disproportionation process, which fully parallels that of the second step of the electrode reaction.

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