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Redox Reactions of Organometallic Compounds. II[1]. Behaviour of Cr(dipy)$_2\Phi_2^+$ at the Dropping Mercury Electrode

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The ion Cr(dipy)$_2\Phi_2^+$ *undergoes two one-electron reductions (at* -1.11 V *and* -1.65 V*) at the dropping mercury electrode. Both steps proceed rapidly and with retention of the composition of the depolarizing particle. The phenyl group causes a considerable shift of the redox potential to negative values as compared with the* Cr(dipy)$_3^{3+}$ *system.*
At the dropping mercury electrode no direct oxidation of the complex is observed. However, mercurous halide assisted oxidative splitting is found at $+0.1$ V *which results in the formation of* HgΦI*. Conditions for the formation of organomercury compounds from other organometallics are outlined.*

Introduction

The redox reactions of compounds with a metal-carbon σ-bond, although used quite often in preparative work, have not been studied from the mechanistic point of view, especially as regards the splitting of the metal-carbon bond under oxidative or reductive conditions. The knowledge of the factors influencing the ability of the metal carbon σ-bond to get split in the course of a redox process migth help to elucidate several preparative procedures and bring a deeper insight into the nature of the metal-carbon σ-bond and its influence upon the redox behaviour of the complex.

However, the rather high sensitivity of many organometallic species makes such a deeper and systematic study difficult.

Recently a very interesting compound, [Cr(dipy)$_2$-Φ_2]I was prepared by H. Müller[3] who, on the basis of chemical properties, magnetic behaviour, and IR spectra, concluded that the complex unit contains two σ-bonded phenyl groups. The most remarkable property of this compound is its stability towards air oxidation, in the solid as well as in solution. This compound is very convenient for the electrochemical investigation of the metal-carbon bond as the behaviour of analogous tris-dipyridyl as well as bis-dipyridyl complexes with conventional ligands is well known.[4] The influence of the σ-bonded phenyl groups on the reduction of the complex can thus be seen directly from comparison with other structurally analogous complexes.

Experimental Section

Polarographic Measurements were performed on an LP-60 Model self-recording polarograph of Laboratorni přistroje (Prague, Czechoslovakia) using a normal Kalousek vessel with an aqueous $4M$–NaCl calomel electrode or $1M$–Na$_2$SO$_4$ mercurous sulphate electrode. All data in this paper are given against the calomel electrode. All measurements were carried out in nitrogen atmosphere. For the study of the mechanism of the electrode processes, the Kalousek[5] commutator was used.

For all experiments ethanol was used as the most suitable solvent. Pure absolute ethanol was refluxed with metallic sodium before use. The electrolytes, LiNO$_3$, LiCl, tetrabutylammonium-iodide and chloride, were checked polarographically for impurities before use. In all experiments 0.1 M solutions of the electrolyte were used. In spite of the stability of the solutions of the complex, always only solutions prepared in the electrolytic vessel directly before the experiment were investigated.

Results and Discussion

Cr(dipy)$_2\Phi_2^+$ shows under all conditions investigated two reduction waves. Its ability to undergo an anodic process, however, depends strongly upon the medium.

The Cathodic Process. The more positive reduction is well developed with the half-wave potential -1.11 V (satd. aqueous cal. electrode, 0.1 M TBACl in ethanol). The limiting current is fully diffusion controlled and linearly dependent upon the concentration of the complex. The complex consumes 1 electron per one particle as follows from the comparison with the reduction process of π–Cr(diphenyl)$_2^+$, which is used as a pilot compound for the determination

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[1] First paper of the series: D. Grešová, A. A. Vlček, *Inorg. Chim. Acta, 1*, 482 (1967).

[2] Permanent address: Forschungsstelle für Komplexchemie der DAW zu Berlin, Jena.

[3] H. Müller, Forschungsstelle für Komplexchemie der DAW zu Berlin, Jena, private communication. The anion is easily exchangeable via hydroxide species.

[4] (a) A. A. Vlček, *Nature, 189*, 393 (1961). (b) L. Kišová, P. Tvaružek, *Coll. Czech. Chem. Commun., 30*, 3565 (1965). (c) B. R. Barker, B. D. Mehta, *Inorg. Chem., 4*, 848 (1965).

[5] M. Kalousek, *Coll. Czech. Chem. Commun., 13*, 105 (1948).

of the number of electrons as well as for fixing the potential scale. The ratio of the limiting currents of the latter species to that of the complex investigated being 1:0.85 under comparable conditions.

The shape of the wave, defined by the log[i/(i_d–i)]–E plot, depends to a great extent upon the concentration of the depolarizer and the nature of the cation of the supporting electrolyte. In solutions of lithium salts and at concentrations of the complex higher than 4×10^{-4} *M* the wave is asymmetric, the slope of the log — plot up to i$\sim$2/3i_d being 25-35 mV, for i>3/4i_d approaching 60 mV, the value for a reversible, one electron process. At concentrations of the complex below 3×10^{-4} *M* and especially when tetrabutylammonium salts are used, the log — plot is a straigh line with a slope of 58-61 mV, *i.e.* the wave has the shape corresponding to a reversible one-electron process. In solutions of tetrabutylammonium salts the reversible shape of the wave is observed up to higher concentrations of the depolarizer ($\sim10^{-3}$ *M*). This type of behaviour is typical for such electrode processes the product of which is sparingly soluble and covers the electrode surface hindering thus the electrode reaction proper. At low concentrations of the depolarizer or in the presence of the adsorbable cation the layer of the product does not fully develop at the surface so that the electrode reaction proceeds without any hindering effects. However, at higher concentrations and in the absence of adsorbable cations, the sparingly soluble product formed slows down the electrode reaction proper. As the potential of the electrode becomes more negative the adsorption of the product is less effective and the electrode process reaches rapidly the rate corresponding to a free surface. This effect explains thus the low values of the log-plot slope observed in lithium salts at higher depolarizer concentrations.

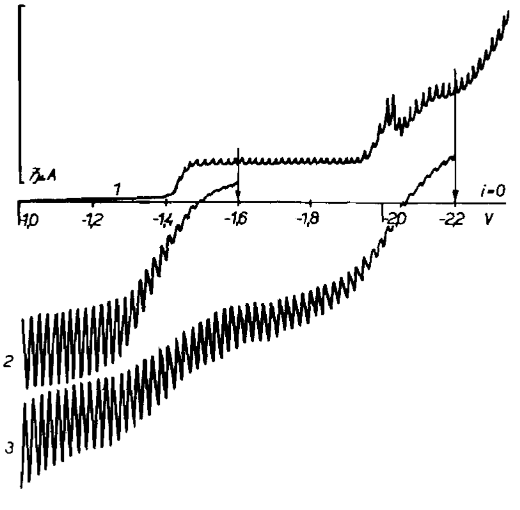

Figure 1. Oxidation of the Product of the $Cr(dipy)_2\Phi_2^+$ Reduction Generated by the Commutator. 10^{-3} *M*$[Cr(dipy)_2\Phi_2]I$ in 0.1 *M* LiCl in ethanol, mercurous sulphate electrode. Curve 1, original wave; curve 2, commutated wave with the generating potential –1.6 V, curve 3, commutated wave with the generating potential –2.2 V.

The experiments with the Kalousek commutator (Figure 1) show that the product of the reduction process is fully oxidized at the potential identical with that of the reduction process. This finding confirms thus the reversible nature of the electrode process and points to the conclusion that the reduction proceeds without any change in the composition of the particle.

The reduction product of $Cr(dipy)_2\Phi_2^+$, obtained in a preparative way has the composition $Cr(dipy)_2\Phi_2$ [3] and is so sparingly soluble in all suitable solvents [3] that it was not possible to prove its identity with the product of the electrode reaction. However, the properties of the latter, strong absorption at the electrode and reversible oxidation without any change in composition, show that such an identity is very probable.

At more negative potential a second reduction step of $Cr(dipy)_2\Phi_2^+$ appears in all solutions investigated. The limiting value and the properties of the current corresponding to this step depend, however, strongly upon the composition of the solution.

In LiCl-solutions the wave with a small maximum has a $E_{1/2}$ = –1.65 V. This value is about 70 mV more positive than the reduction potential of α,α'-dipyridyl under the same conditions. The limiting current of the second reduction step is partly reaction-rate controlled and is (in dependence upon the height of mercury column) 1.3 to 1.7 higher than the diffusion limiting current of the first reduction step. The analysis of the dependence of the limiting current upon the height of mercury column shows that the diffusion controlled component of the limiting current corresponds approximately to one-electron reduction. The experiments with the Kalousek commutator (see Figure 1) point to the conclusion that the product of the reduction is oxidized in two steps, *reversible* to the corresponding step.

In $LiNO_3$ solutions the position of the second step is the same as in the previous case. However, the limiting current is fully reaction-rate controlled and 4 to 5 times higher than the diffusion limiting current of the first wave.

These results point to the conclusion that the complex $Cr(dipy)_2\Phi_2^+$ is able to undergo altogether a two electron reduction without any decomposition (*cf.* the reversible two-step oxidation of the final product!). However, the product thus formed is very reactive and is reoxidized by components of the solution (traces of water in the case of LiCl solutions or probably even nitrate ions in the case of $LiNO_3$ solutions). This process increases the limiting current of the second reduction step.

As can be seen from data in Table I, the reduction potential of $Cr(dipy)_2\Phi_2^+$ falls into the general pattern of the $Cr(dipy)_2X_2^{n+}$ complexes: the substitution of one dipyridyl molecule by two anions shifts the half-wave potential to negative values, the shift being the greater the stronger the ligand field strength of the ligand X. This *seems* to be a general pattern for complexes in which the redox process is localized in an orbital localized to a substantial extent on the central metal atom, which is thus directly influenced by the presence of the ligand X. This condition is

Table I. Properties of the First Reduction Steps of Some Chromium Complexes

Complex	$E_{1/2}$ [a]	n	k_o [b]	Ref.
$Cr(dipy)_3^{3+}$	-0.36	1	3.7×10^{-2}	c
$Cr(dipy)_2Cl_2^+$	-0.71	1	5×10^{-3}	d
$Cr(dipy)_2\Phi_2^+$	-1.11	1	2×10^{-2}	this paper
$Cr(dipy)_2(CN)_2^+$ [f]	-1.2_5	1	—	d
π—$Cr(diphenyl)_2^+$	-0.72	1	2×10^{-2}	e

[a] Against aqueous saturated calomel electrode; [b] rate constant of the electrode process at equilibrium potential, cm s^{-1}; [c] ref. 4a, 4b; [d] A. Rusina, A. A. Vlček, to be published; [e] A. A. Vlček, *Z. Anorg. Chem. 304,* 109 (1960) and new unpublished experiments; [f] depolarizer proper in solution of $Cr(dipy)_2Cl_2^+$ containing cyanide ions, unpublished studies.

fulfilled by the orbitals derived from the set of d-orbitals of the central metal atom. (*cf. e.g.* $\Delta E^\circ\{Fe(phen)_3^{3+/2+}-Fe(phen)_2(CN)_2^{+1/0}\} = -0.28$ V, $\Delta E^\circ\{Fe(dipy)_3^{3+/2+}-Fe(dipy)_2(CN)_2^{+1/0}\} = -0.24$ V.[6,7] Localization of the redox process into the pure π-antibonding orbitals of the dipyridyl ligands (*i.e.* orbitals with no direct interaction with the metal orbitals) would show, as indicated by comparison with other systems,[8] much smaller dependence upon the nature of the X which would arise from second order effects only. According to this it can be concluded that the first reduction is predominantly localized in orbitals arising from d_ε-orbitals of chromium and that the phenyl groups behave as anionic ligands with high ligand field effects. This influence of the σ-bonded phenyl groups upon the *reversible* potential has to be distinguished from the influence the carbon-metal σ-bond exerts upon slow reduction processes.[8]

The localization of the second reduction step is most probably primarily the same. However, to obey the general principle of compensation of the charge changes caused by a redox process[8] it has to be assumed that the d_ε-orbitals are delocalized to a considerable extent. The σ-bonded phenyl groups do not obviously function as rigorous σ-donors[8] and seem to partake, at least partially, in the mechanism of compensation of the charge change. The analogous complex $Cr(dipy)_2Cl_2^+$ decomposes already after the first reduction, or in presence of high Cl^- concentration after the second electron is accepted.[9] The Cl^- ligand cannot accommodate any considerable electron density from the central metal atom, its compensating effect being primarily limited to the change in the polarity of the σ-bond. The phenyl groups seem to stabilize the lower oxidation states of the complex much more effectively, most probably due to the interaction of their π-systems with the d_ε-orbitals of the central metal atom.

No reduction of dipyridyl ligands is observed up to potentials about 200 mV more negative than the potential of free dipyridyl. This shows that dipyridyl in the complex is stabilized towards reduction by bonding in the complex and by the increased electron density due to the shift of electrons from the metal via the π-bond system.

The Anodic Process. $[Cr(dipy)_2\Phi_2]$NC in $LiNO_3$ solutions gives a poorly developed wave at positive potentials ($E_{1/2}\sim+0.3_5$ V) (*cf.* Figure 2, curve 2). The nature of the process giving rise to this oxidation current is not quite clear. As this poorly developed wave cannot be studied in sufficient detail, it is not possible to distinguish between the direct oxidation and mercury assisted splitting. Preliminary studies on platinum rotating electrode indicate, however, the possibility of direct oxidation. Results of these studies will be reported later.

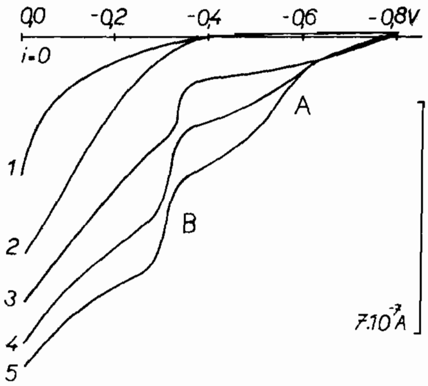

Figure 2. Influence of Iodide Ions on the Behaviour of $[Cr(dipy)_2\Phi_2]NO_3$ at the Dropping Mercury Electrode. Curve 1, 0.1 *M* $LiNO_3$ in ethanol, mercurous sulphate el., curve 2, 3×10^{-4} *M*$[Cr(dipy)_2\Phi_2]NO_3$, curve 3 to 5, successive additions of tetrabutylammonium iodide. 3: 0.91×10^{-4} *M* TBAI, 2.72×10^{-4} *M* complex; 4: 1.67×10^{-4} *M* TBAI, 2.5×10^{-4} *M* complex; 5: 2.3×10^{-4} *M* TBAI, 2.3×10^{-4} *M* complex.

The addition of iodide ions results in the appearence of two anodic waves (see Figure 2). The wave with $E_{1/2} = -0.16$ V (A) is identical with the wave observed in solutions of iodide ions alone.[10] The wave at about $+0.1$ V (see below) (B) is unambiguously connected with the presence of the complex. It is, however, not observed in solutions of the complex *without* iodide ions nor in solutions of iodide containing π—$Cr(diphenyl)^+$ or $Cr(dipy)_3^{3+}$. It has thus to be concluded that the wave B is due to the simultaneous presence of $Cr(dipy_2)_2\Phi_2^+$ and iodide ions. For $[I^-]\leqslant[Cr(dipy)_2\Phi_2^+]\leqslant3\times10^{-4}$ *M* the

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(6) R. J. Campion, N. Purdie, N. Sutin, *Inorg. Chem.*, 3, 1091 (1964).

(7) It has to be noted that this is an empirical rule which does not follow from the consideration of ligand field stabilization energy. A detailed analysis of this effect will be published shortly by A.A.V.

(8) A. A. Vlček, *Rev. Chim. Minérale*, 5, 299 (1968).

(9) A. Rusina, A. A. Vlček, unpublished results.

(10) Iodide ions give one anodic wave at -0.16 V, directly proportional to the concentration and diffusion controlled only at concentrations below *ca.* 4×10^{-4} *M*. At higher concentrations a double wave appears coinciding with the processes corresponding to the complex. All experiments discussed were carried out at concentrations of iodide ions below 3×10^{-4} *M*.

wave B is directly proportional to the concentration of iodide ions (the concentration of the complex being constant) the ratio of the wave A and B being 1:1. The wave B reaches the limiting value for $[I^-] = [Cr(dipy)_2\Phi_2^+]$ and remains constant with further increase of the iodide concentration. At constant concentration of iodide ions the wave B is directly proportional to the concentration of the complex and has about the same magnitude as the first reduction wave at −1.1 V. The limiting current of wave B is diffusion controlled. The half-wave potential depends slightly upon the concentration of iodide ions: at $[I^-] = 9 \times 10^{-5} M$ $E_{1/2}$ equals +0.07 V, $[I^-] = 1.7 \times 10^{-4} M$ $E_{1/2} = +0.09$ V and at $[I^-] = 3 \times 10^{-4} M$ $E_{1/2} = +0.12$ V (against aqueous saturated calomel electrode).

The addition of chloride ions, the anodic wave of which is more positive than that of iodide ions, does not cause the appearance of a new wave. The wave, analogous to the B-wave in presence of iodide ions, coincides in this case with the chloride wave. The increase of the chloride wave caused by the addition of the complex is strinctly additive and directly proportional to the concentration of the complex.

This behaviour represents a new type of electrode process in which the electrode reaction of one substance does not proceed without a simultaneous reaction of another substance at the electrode. In our specific case the formation of mercurous iodide (or chloride) is the necessary condition for the reaction of the complex giving rise to the wave B. The experimental results are consistent with the following sequence of reactions:

$$I^- + Hg - e \longrightarrow \frac{1}{2} Hg_2I_2 \qquad \text{(wave A)}$$

$$Cr(dipy)_2\Phi_2^+ + \frac{1}{2} Hg_2I_2 - e \longrightarrow \frac{1}{2} Hg\Phi I \qquad \text{(wave B)}$$

The process occuring in wave B is thus *mercurous halide assisted oxidative splitting of* metal-carbon σ-bond. This type of behaviour, which is also observed with some other complexes with metal-carbon σ-bond,[8] specifies conditions under which mercury-aryl or alkyl compounds (or mixed halide-alkyl or aryl compounds) can be obtained from other organometallics.

The reaction between mercury and an organometallic compound needs oxidative conditions and is strongly enhanced by the presence of halide ions. Attempts are now being made in this laboratory to use this principle for electrochemical preparation of organomercury compounds.

Conclusion

The behaviour of the complex $Cr(dipy)_2\Phi_2^+$ can be summarized in the following way:

$$\begin{tikzcd}
Cr(dipy)_2\Phi_2^+ \arrow[r, leftrightarrow, "e"'] \arrow[d, "e"', "Hg_2I_2"] & Cr(dipy)_2\Phi_2 \arrow[r, leftrightarrow, "e"'] & Cr(dipy)_2\Phi_2^- \arrow[d, dash] \\
Hg\Phi I & {} & {} \arrow[l, "X"']
\end{tikzcd}$$

It has to be emphasized that only one phenyl group reacts in the oxidative splitting (in the case of simultaneous mercury and mercurous halide assisted splitting both phenyl groups seem to be involved). The detailed mechanism of this process (which might involve either the intermediate formation of Φ-radical or a group transfer attack) is not known and is under investigation.