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EFFECT OF COORDINATION WITH THE METAL ON THE REACTIVITY OF π-BONDED ORGANIC LIGANDS
II. REVERSIBLE POLAROGRAPHIC REDUCTION OF ACETOPHENONE, FREE AND COORDINATED WITH THE $Cr(CO)_3$ GROUP

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SUMMARY

The reversible polarographic reduction of acetophenone, free and coordinated with the $(CO)_3Cr$-group in aprotic media was investigated. The analogy between the polarographic data for coordinated and non-coordinated acetophenone leads to the conclusion that the electronic density changes in the acetophenone part of the complex during the reduction on the dropping mercury electrode. Coordination with $Cr(CO)_3$ is likely to decrease the energy of the lowest unoccupied molecular orbital of acetophenone by over 0.5 eV.

In a previous communication[1] concerning the oxidation–reduction reactions of the quinone–rhodium and –iridium complexes, the effect of coordination with the metal on the reactivity of π-bonded carbocyclic ligands was discussed in detail. Examples were considered where ligands behave as strong electron-acceptors, and essential charge transfer from the metal to the π-ligand occurs during the formation of the complex. When combined in a complex, quinone was found to be more difficult to reduce than when non-coordinated, and the energy of the lowest vacant orbital of the ligand was shown to increase by approximately 1 eV.

Examples are also known in the chemistry of the transition metal π-complexes where the metal and its adjacent ligands behave as the electron-withdrawing groups, and the coordination involves a considerable charge transfer from a π-bonded ligand to the metal. It can be assumed that the most significant electron displacement in this direction should occur in complexes with metal carbonyl fragments, where the CO-groups are known to display properties of strong π-acceptors in complexes. In the present paper we investigated in aprotic media the reversible polarographic reduction of acetophenone free and coordinated with the $Cr(CO)_3$-group*: We found that in absolute acetonitrile as medium acetophenonechromiumtricarbonyl[1], as well as free acetophenone[11], give clear diffusive one-electron waves of reversible reduction together with a second diffusive wave (Fig. 1). The dependence of log $[i/(i_d-i)]$ on E

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* Dabard *et al.*[2] recently described the reduction of the acetophenonechromium tricarbonyl complex in protic media.

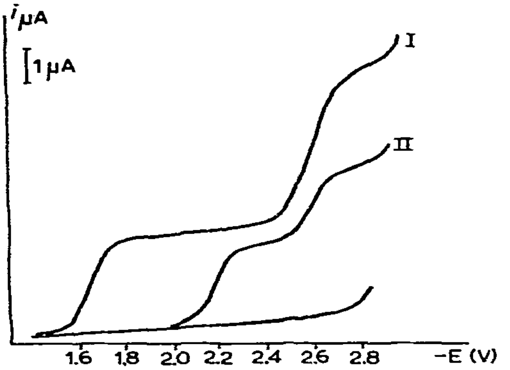
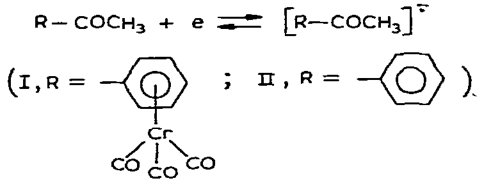


Fig. 1. Polarographic reduction waves of coordinated and non-coordinated acetophenone: (I) $C_6H_5COCH_3Cr(CO)_3$; (II) $C_6H_5COCH_3$; CH_3CN, 0.1 *N* $(C_2H_5)_4NClO_4$.

for the reduction waves is a linear function. For the first waves, the slopes somewhat exceed the theoretic values* found for the reversible processes, but are almost equivalent for (I) and (II); (II) is known to be reduced reversibly in aprotic solvents[4]. Investigations conducted on the Kalousek commutator confirmed the reversibility of the first stages in the reduction of (I) and (II).

Thus the first reduction stage for (I) and (II) can be represented by the following scheme:



$$R{-}COCH_3 + e \rightleftharpoons [R{-}COCH_3]^{\overline{\cdot}}$$

The characteristics of the reduction waves are shown in Table 1. It can be seen from this Table that unlike (II), the first reversible reduction stage for compound (I) occurs at more positive potentials. The essential shift of the first reduction wave ($\Delta E_{\frac{1}{2}} = 0.5$ V) testifies to the withdrawal of electron density from the ligand to metal; as a result, the addition of the first electron is essentially facilitated.

The half-wave potential of the second wave, corresponding to the addition of the second electron to an anion-radical, changes very slightly with coordination. Thus the difference between the potentials of the first and second reduction waves changes from 0.37 for (II) to 0.77 V for (I). This can be interpreted as a stabilization of an anion-radical generated at the first reduction stage as the electron density on the $Cr(CO)_3$-group delocalizes. The reactivities of free and coordinated arenes were compared for some arenechromium tricarbonyl complexes[5-7]. Our approach however seems to be more correct for a quantitative comparison of the reactivities of both coordinated and free ligands. First, we deal with an equilibrium; hence the difference in the reactivities observed should not be associated with the differences in the character of the transi-

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* We used a rapidly dropping capillary provided with a forced dropping system. The limits of reversibility or irreversibility of the polarographic waves are known to depend on the dropping period of the capillary[3].

TABLE 1

POLAROGRAPHIC CHARACTERISTICS OF ACETOPHENONE, FREE AND COORDINATED WITH THE $Cr(CO)_3$-GROUP (C, $1 \cdot 10^{-3}$ mol·l^{-1}; SCE: 0.1 N $(C_2H_5)_4NClO_4$, CH_3CN)

Compound	1st wave			2nd wave		
	$-E_{\frac{1}{2}}$ (V)	i_d (μA)	$2.3RT/\alpha nF$ (mV)	$-E_{\frac{1}{2}}$ (V)	i_d (μA)	$2.3RT/\alpha nF$ (mV)
$C_6H_5COCH_3Cr(CO)_3$(I)	1.61	2.9	74	2.37	4.5[a]	94
$C_6H_5COCH_3$(II)	2.10	2.4	71	2.47	2.4	104
$C_6H_6Cr(CO)_3$				2.28	2.2	91

[a] The second reduction wave of coordinated acetophenone is imposed on the reduction wave of arene-chromium tricarbonyl.

tion state in reactions of coordinated and non-coordinated ligands. Secondly, from the study of one-electron transfer processes having exceptionally fast rates and negligible activation energies[8], one may assume that when passing from the non-coordinated to the coordinated state, the changes observed should result from "purely" electronic interactions, whereas the differences in solvating, steric and other effects are minimal. Thirdly, the reversible reduction potential differences between non-coordinated and coordinated ligands, measured under the same strictly maintained conditions (as was shown repeatedly) may be quite reliably equated to the differences between the energies of the corresponding ligand orbitals[9]. This provides a quantitative determination of the results of the coordination. According to the calculations available[10], the lowest vacant orbital of acetophenone belongs to the B_{2u} type. It is usually assumed that the addition of an electron occurs on this orbital. As a result of our earlier discussion[1] we concluded that the energy of this orbital decreases by approximately 0.5 eV after coordination with the $Cr(CO)_3$-group.

According to Brown[11], on coordination with the $Cr(CO)_3$-group the vacant orbital of B_{2u} symmetry should interact with the occupied metal orbital ($3d_{xy}$ or $3d_{x^2-y^2}$). As a result, two orbitals appear, one of which (vacant) should be located above the vacant ligand orbital that took part in the interaction. Experiment gives the opposite picture—the energy of the lowest vacant level decreases considerably upon coordination. The ligand field theoretical interpretation of this result seems to be more convenient. MO calculations show an essential effective positive charge (+0.558) at the chromium atom in $C_6H_6Cr(CO)_3$ resulting generally from the strong π-electron-withdrawing effect of the CO-groups. It can be assumed that each of the six coordinated phenyl carbons resides in the field of the $Cr(CO)_3$-group chromium atom bearing the effective positive charge. In terms of the Huckel approximation this can be expressed by an absolute increase of the coulomb integrals for each carbon AO together with increasing resonance integrals of the C–C bonds. Both occupied and vacant MO's constructed taking account of the AO changes mentioned should be located below the corresponding orbitals of the non-perturbed (non-coordinated) molecule.

Further investigations should show how much can be learned from the 0.5 eV decrease in the orbital energy to explain the changes observed in arene reactivity upon coordination with the $Cr(CO)_3$-group.

EXPERIMENTAL

Compounds

Acetophenonechromium tricarbonyl was prepared by a procedure already described[5], and had the following characteristics: m.p. 84–85°. (Found: C, 51.82; H, 3.34; Cr, 20.46. $C_{11}H_9O_4Cr$. calcd.: C, 51.57; H, 3.15; Cr, 20.30%).

Polarographic measurements

Polarograms were taken on a PE-312 electronic polarograph. Measurements were conducted using a dropping mercury electrode with a forced dropping system ($m=0.77$ mg·sec^{-1}, $\tau=0.50$ sec). Use was made of a cell thermostatted at 25±0.1°, provided with two external saturated aqueous calomel electrodes (references electrode and anode). $E_{\frac{1}{2}}$-values corrected for the ohmic potential drop in solution are given in Table 1. A sample of analytically pure acetophenonechromium tricarbonyl was dissolved in absolute acetonitrille, free from oxygen, and mixed with a supporting electrolyte (also free of oxygen) in a cell. Polarograms were recorded immediately, since after 10–15 min they showed the reduction wave of acetophenone resulting from complex decomposition.

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