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THE EFFECT OF COORDINATION WITH A METAL ON REACTIVITY OF π-BONDED ORGANIC LIGANDS

I. REDOX PROPERTIES OF SOME RHODIUM- AND IRIDIUM-QUINONE COMPLEXES

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SUMMARY

The coordination with a metal *versus* the reactivity of π-bonded organic ligands has been studied for π-C_5H_5–Rh and –Ir complexes with quinones by polarographic methods. It was observed that in an acetonitrile solution of the coordinated quinones the reversible reduction waves of the above complexes shifted to the negative potentials with respect to the non-coordinated ligands. The analogy of the polarographic data for both coordinated and non-coordinated quinones allows the conclusion that the electronic density changes in the quinone part of the complex during the reduction on the mercury-dropping electrode. The coordination with $-RhC_5H_5$ is likely to increase the energy of the $2b_{2g}$ orbital of the quinone by over 0.9 eV and over 1.1 eV in the case of $-IrC_5H_5$.

INTRODUCTION

At present there seems no doubt that coordination with a metal has some effect on the reactivity of a ligand. In general, the effect of a metal on the reactivity of a π-bonded organic ligand may be due to the following particular phenomena: electronic effects or displacement of electron density along the metal–ligand bond; the promotion of lability of a π-electron cloud in a ligand; a variety of steric effects: *e.g.*, stabilisation of a geometric configuration improper to a non-coordinated ligand, an increase in the stability, during the reaction, of one of the possible steric forms, or steric hindrance preventing the reactant attacking the reaction centre of the ligand. All these possibilities could be illustrated by appropriate experimental fact. Thus, for example, it was shown that the coordination of the phenyl nucleus with the $Cr(CO)_3$-group (*i*) increases the acidity of benzoic acid[1]; (*ii*) increases the activity of chlorine in chlorobenzene in nucleophilic substitution reactions; (*iii*) evens out the effect of the alkyl groups in alkylbenzenes on the reactivity of *ortho*-, *para*- and *meta*-positions in the Friedel–Crafts acylation reaction[3], etc. The isolation of stable cyclobutadienyliron complexes[4], the conversion of 1,3-cyclooctadiene into the 1,5-isomer on coordination with rhodium[5], the high reactivity of *exo*-alcohols of the α-ferrocenylmethyl series with respect to the corresponding *endo*-isomers[6], and other analogous examples clearly testify to the significance of effects that are described as steric effects.

In order to understand the nature of the bonding between a metal and a π-ligand it is important not only to state the existence of the reactivity change during the coordination process but also to estimate it quantitatively by means of a strict comparison between the reactivities of the coordinated and non-coordinated ligands. Such comparisons were made, for example, for redox reactions of aromatic ketones coordinated with the $Cr(CO_3)$-group[7]. However, since the reduction processes investigated were irreversible, the interpretation of the processes studied was difficult.

In the present paper we have chosen some redox reactions of quinones, coordinated with rhodium or iridium, as reactions for the quantitative investigation of coordination effects on reactivities of some π-bonded organic ligands. Complexes of this type were first prepared and described by Schrauzer and Dewhirst[8].

EXPERIMENTAL

Rhodium and iridium complexes with duroquinone (Table 1, numbers 1 and 3) were synthesized and characterized by the methods of Schrauzer and Dewhirst[8]. The same procedure was applied for the rhodium complex of 2,6-di-tert-butylbenzoquinone-1,4 (Table 1, number 2).

π-Cyclopentadienylrhodium-2,6-di-tert-butylbenzoquinone-1,4

3.0 g of 2,6-di-tert-butylbenzoquinone-1,4 and 1.12 g of $RhCl_3 \cdot 3\,H_2O$ in 100 ml of ethanol were refluxed for 4 h. The solvent was removed in vacuo and the residue dried by azeotropic distillation with benzene. Exhaustive washing of the dry material with petroleum ether (40–60°) and subsequent drying gave 1.3 g of a yellowish-pink product. The IR spectrum contains two absorption bands of C=O groups at 1667 and 1550 cm^{-1}, while the C=O groups of the initial quinone absorb at 1657 and 1595 cm^{-1}. To a solution of 1.2 g of the product in 200 ml of THF, was added a solution of 0.0091 mole of cyclopentadienyl sodium (from 0.35 g Na and 1 ml of cyclopentadiene) in 30 ml of THF. After 3 h, the solvent was removed in vacuo, the glittering dark-brown solid was exhaustively extracted in an argon atmosphere with small portions of methylene chloride until the extracts became colourless. After removal of the solvent, the residue was recrystallized from petroleum ether. 0.5 g (38.5%) of yellow product was obtained, m.p. 266–267° (dec.). (Found: C, 58.81, 58.92; H, 6.60, 6.65. $C_{19}H_{25}RhO_2$ calcd.: C, 58.76; H, 6.49%.)

The IR spectrum contains a wide band in the carbonyl area at 1638–1613 cm^{-1}, corresponding to a C=O absorption in the coordinated quinone, as well as bands at 3094, 1437, 1100, 1010 and 830 cm^{-1}, characterizing the C_5H_5-ring.

Polarographic measurements

Polarograms were recorded using PE-312 and PA-3 electronic polarographs. A capillary with a forced dropping had the following characteristics: $m = 1.53$ $mg \cdot sec^{-1}$ and $\tau = 0.30$ sec (at -0.9 V, $H = 50$ cm). The measurements were carried out at 25 ± 0.1° in an argon atmosphere saturated with vapours of the solvent. When the experiments were conducted in acetonitrile medium, a 0.1 N solution of $(C_2H_5)_4$-$NClO_4$ was used as a supporting electrolyte. In water and water–alcohol (1 : 1) media,

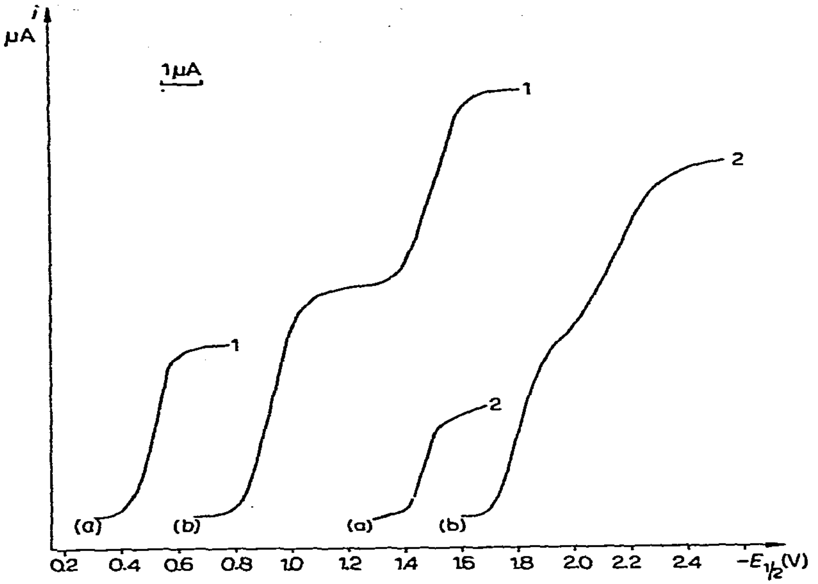

Fig. 1. Polarographic reduction waves for coordinated and non-coordinated quinones. (a) 1, duroquinone; 2, π-cyclopentadienylrhodiumduroquinone in ethanol–water (1 : 1) medium, 0.1 *N* KCl; (b) 1, duroquinone; 2, π-cyclopentadienylrhodiumduroquinone in acetonitrile, 0.1 *N* $(C_2H_5)_4NClO_4$.

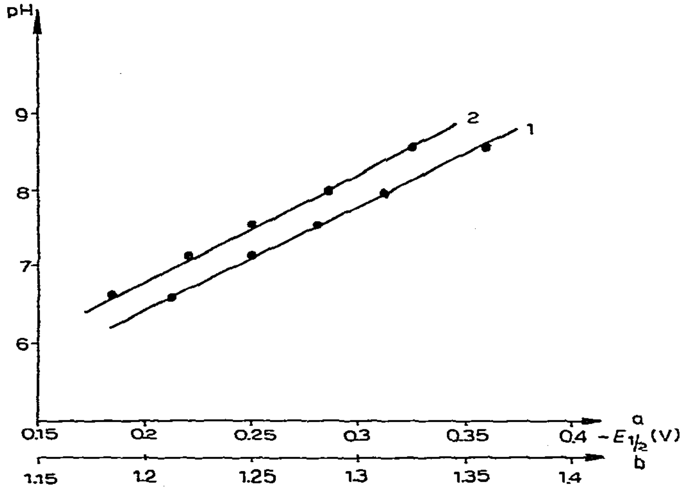

Fig. 2. The dependency of $E_{\frac{1}{2}}$ on pH for coordinated and non-coordinated quinones (phosphate buffer–ethanol, 1 : 1). 1, duroquinone; 2, π-cyclopentadienylrhodiumduroquinone. (a), $E_{\frac{1}{2}}$-values for duroquinone; (b) $E_{\frac{1}{2}}$-values for π-cyclopentadienylrhodiumduroquinone.

the supporting electrolyte was KCl (0.1 *N*) solution. The potential values given are referred to the aqueous saturated calomel electrode and calculated from a dependency of log $(i/i_d - i)$ on *E*. The *E*-values were corrected for IR-drop by measuring the cathode potential with an auxiliary calomel electrode. For measuring the dependencies of $E_{\frac{1}{2}}$

on $\sqrt{H}$, on C and on pH, a capillary having following characteristics was applied: $m=0.39$ mg·sec^{-1} and $\tau=0.44$ sec (with the broken electric chain, $H=55$ cm). For the definition of the dependency of $E_{\frac{1}{2}}$ on pH, phosphate and acetate buffer solutions were used.

RESULTS

The reduction of non-coordinated quinones

Quinone–hydroquinone systems are classical organic oxidation–reduction couples. Since the time of Michaelis the electron exchange in such systems has been repeatedly studied both potentiometrically and polarographically. It was established that this process consists of two reversible one-electron stages in each of which a proton participates:

$$Q+e^- \rightleftharpoons Q^{\cdot -}+H^+ \rightarrow QH^{\cdot} \qquad (1a)$$

$$QH^{\cdot}+e^- \rightleftharpoons QH^-+H^+ \rightarrow QH_2 \qquad (1b)$$

In electrochemical reductions at the dropping mercury electrode, the above redox processes are complicated by absorption on the electrode surface of the initial compounds as well as of the reaction products. Moreover, the kinetics of the electrode processes may be significantly affected by the addition of protons to the products of electrochemical reactions[10].

In aprotic solvents, where the protonation stage of the semiquinone radical is prohibited, we have observed two distinctive one-electronic waves of quinone reduction.

The first reduction stage under these conditions is reversible (Fig. 1(1b)): the half-wave potential does not depend upon the concentration or drop-time of the electrode; the cot α values are somewhat above the theoretical values for reversible one-electron processes. For duroquinone, for example, we have shown that, if electrolysis was carried out in a cell mounted in the resonator of an ESR spectrometer, it has been possible to observe a signal characteristic of the durosemiquinone radical at the limiting current potential of the first wave (1.2 V)[11]. As expected, two tert-butyl groups have less electron-donating power than four methyl groups. Thus, the first reduction wave for 2,6-di-tert-butylbenzoquinone-1,4 is observed at more positive potentials (over 0.11 V) than the same stage for duroquinone (Table 1). On the other hand, probably owing to the strong steric screening of the two *ortho*-tert-butyl groups, the addition of a second electron to the semiquinone radical is more difficult in the latter case, than the same processes for duroquinone.

In aqueous media, the reduction process for quinones is complicated. Since the electron affinity of the protonized semiquinone[9] is much higher than that of the initial compound, the potential-determining stage is the first stage of the process. One diffusion wave was observed in the polarogram (Fig. 1(1a)), corresponding (by its height) to the addition of two electrons, but having the characteristics of a one-electronic reversible process: the half-wave potential does not depend upon the concentration or drop-time of the electrode, the cot α values are somewhat above the theoretical values for a reversible one-electron process. These deviations for the series *para*-benzoquinone, 2,6-di-tert-butylbenzoquinone-1,4, duroquinone increase regularly. In the pH-range 6.61–8.58, a linear dependency of half-wave reduction potential for duroquinone is observed with a slope of 76 mV/pH unit (Fig. 2(1a)).

The reduction of π-quinonerhodium-π-cyclopentadienyls

The reactivity investigations for π-duroquinonerhodium-π-cyclopentadienyl in the present work, have shown that this compound does not participate in any reaction characteristic of non-coordinated duroquinone and quinones in general actions. We have studied the effects of hydroxylamine, diazomethane, butyllithium etc. In all cases, together with the decomposition products, considerable amounts of the starting materials were isolated. Only with strong reducing agents (sodium amalgam) does a change in color from orange to red occur, but after decomposition of the mixture, only the initial compound was isolated.

We have found, however, that π-cyclopentadienylrhodium-π-duroquinone and other analogous complexes can be reduced on the dropping mercury electrode at comparatively negative potentials. In acetonitrile solution, two diffusion waves of equal height with a poorly defined limiting current plateau for the first wave, were observed in the polarograms (Fig. 1(2b)). The main characteristics of these waves are rather similar to those for the non-coordinated quinone, except for the $E_{\frac{1}{2}}$-values which are essentially shifted into a more negative area thus causing a considerable decrease in the potential difference between the waves: from 0.52 for the non-coordinated quinone to 0.27 V for its complex.

In aqueous medium with 0.1 *N* KCl as supporting electrolyte, one well-defined diffusion wave was observed (Fig. 1(2a)): the limiting current of this wave is proportional to the concentration and varies linearly with $\sqrt{H}$. The half-wave potential does not vary with the depolarizator concentration and does not depend upon the drop-time of the electrode, while another criterion of reversibility—the value of cot α—as in the case of non-coordinated quinones is somewhat above the theoretical value for a one-electron reversible reduction process. The half-wave potential shifts towards negative values with an increase in pH from 6.61 to 8.58. This shift is linear (Fig. 2(2b)) and corresponds to 70 mV/pH unit which shows that one proton participates in the electrode reaction. Thus, in aqueous medium, the main characteristics of the waves again do not differ essentially from those of the non-coordinated quinones. We have carried out the reduction of complex 1 (Table 1) in acetonitrile in the cell mounted in the resonator of the ESR spectrometer. With electrolysis potentials between 1.5 and 5 V there was no apparent ESR signal.

The tert-butylquinone complex 2 could be reduced more easily in acetonitrile than its duroquinone analogue. In this process not only the first, but also the second reduction stage, occur at somewhat more positive potentials than in the case of duroquinone complexes. The potential difference between the first and second reduction stages decreased from 0.71 to 0.32 V during the coordination process and became of the same order as the corresponding difference for the duroquinone complex. In aqueous medium, both these complexes as well as the non-coordinated quinones could be reduced in one stage at practically the same potentials, and they have very similar wave characteristics.

The reduction of duroquinoneiridium-π-complex

We have also investigated the behaviour of π-duroquinoneiridium-π-cyclopentadienyl 3 (the iridium analogue of complex 1) at the dropping mercury electrode. In acetonitrile solution, one diffusion wave was observed, which was twice as high as any reduction wave for non-coordinated duroquinone or for its rhodium complex 1. Thus a tendency for the reduction waves for duroquinone to coalesce, that actually started with the rhodium complexes, was completed by blending of the two waves into one for the iridium complex. The half-wave potential is shifted by 0.23 V to more negative values compared to the rhodium complex 1 and varies little with the depolarisator concentration (by 0.1 V when C varies from $1 \cdot 10^{-2}$ to $6.25 \cdot 10^{-4}$ M). The value of cot α (130 mV) is substantially different from its theoretical value for reversible processes.

In aqueous medium, the characteristics of the diffusion reduction waves for the iridium complex resemble those of a reversible process (cot $\alpha = 83$ mV; $E_{\frac{1}{2}}$ does not depend upon concentration) and differ little from those for the rhodium complex 1. The half-wave potential, however, is shifted to more negative values by 0.26 V with respect to the rhodium complex 1.

DISCUSSION

Localization of electronic changes

In our opinion, in the reduction processes of rhodium- and iridium-quinone complexes, the electronic changes are localized on the quinone carbonyl groups; in other words, these changes occur first of all in the ligand coordinated. This is supported by the close analogy between the polarographic reduction characteristics of both coordinated and non-coordinated ligands: the number of waves, their heights and other characteristics, pH variation effect, solvent effect—all these characteristics undoubtedly indicate the identity of the reduction processes. Moreover, a fact, favouring the above suggestion, is that the potential difference between the first reduction stages for both duroquinone and 2,6-di-tert-butylbenzoquinone-1,4 (0.11 V), governed by electronic and structural differences, is also retained in their coordination with rhodium (0.09 V).

On the other hand, coordination with a metal, owing to a possibility of carbonyl groups moving out of the ring plane, compensates for the steric effects inhibiting the second reduction stage for non-coordinated 2,6-di-tert-butylbenzoquinone-1,4 in comparison with duroquinone: for complex 2, the second reduction stage proceeds at even more positive potentials than that for complex 1.

The fact, that we failed to obtain a signal in the ESR spectrum for the coordinated semiquinone-radical (unlike the non-coordinated ligand), is probably not associated with an alternative reaction mechanism and: either we could not observe the signal owing to a negligible difference in potentials between the first and second reduction stages for complex 1, or, in complexes of monovalent rhodium, there is absolutely no possibility of obtaining a signal from the unpaired electron as, for example, in the case of ferricinium salts[13].

For a final decision about the localization of electronic changes we have applied the procedure of Vlček[14]. In attempts to make an approximate estimation of the contributions of the metal and ligand to the orbital of the complex, in which some electronic changes occur, we have obtained the reduction potential differences for two structurally identical ligands and their complexes. Using our first reversible reduction potentials for duroquinone and 2,6-di-tert-butylbenzoquinone-1,4 and their rhodium complexes, we have calculated for the highest orbital occupied ($2b_{2g}$) the mixing coefficient of the anion-radical generated at the first stage in the reduction. This value was shown to be equivalent to 0.82, *i.e.*, there is 80% electron transfer from metal to quinone ligand. The known considerable electron transfer from metal to quinone ligand[15] in the complexes of type 1 was also supported by the fact that the cyclopentadienyl ring in this complex is inert under conditions of aromatic substitution, and is characteristic, for example, of ferrocene (Friedel–Crafts' acylation and acylation with acetic anhydride in the presence of polyphosphoric acid, metallation with butyllithium, etc., have been recently investigated).

A considerable back-donation from metal to quinone causes a decrease in electron density in the cyclopentadienyl ring and makes it inactive under conditions of aromatic substitution. Thus, the investigation of redox transformations has shown that the electronic changes occur in the orbital localized mainly on the quinone part of the complex molecule.

Quantitative estimation of coordination effect on reactivities of quinones investigated

According to the energy level diagram, the lowest inoccupied molecular orbital in quinone is the $2b_{2g}$ orbital in which the electronic changes occur during the redox process[16]. The redox potential of the first reversible reduction stage for quinones in acetonitrile medium is proportional to the energy change in the molecule caused by the addition of one electron. The change in the π-electron energy during the transfer from quinone to the semiquinone-anion-radical makes a significant contribution to the redox potential[17]. In aprotic solvents, this value should also involve changes in solvation energy and, probably changes in the energy of σ-electrons during the redox processes.

In the coordination of the quinone molecule with a transition-metal atom, the energy of this orbital is heighted owing to the back-donation from the $3d_{xz}$–$4p_x$

TABLE 1

POLAROGRAPHIC CHARACTERISTICS OF RHODIUM AND IRIDIUM COMPLEXES WITH QUINONES ($C=2\cdot10^{-3}$ M; S.C.E.)

	Compound	$CH_3CN/0.1$ N $(C_2H_5)_4NClO_4$			$C_2H_5OH:H_2O$ (1:1)/0.1 N KCl		
		$-E_{\frac{1}{2}}$ (V)	i_d (μA)	cot α (mV)	$-E_{\frac{1}{2}}$ (V)	i_d (μA)	cot α (mV)
1	π-cyclopentadienyl-rhodium-duroquinone[a]	1.76 2.03	5.1 4.6	82 156	1.44	2.7	68
2	π-cyclopentadienyl-rhodium-2,6-di-tert-butylbenzoquinone-1,4	1.67 1.99	4.5 4.2	96 185	1.40[b]	3.4[b]	60[b]
3	π-cyclopentadienyl-iridium-duroquinone	1.99	9.2	130	1.67[b]	5.5[b]	83[b]
4	Duroquinone	0.87 1.39	6.5 5.7	100 104	0.48	4.7	78
5	2,6-di-tert-butylbenzoquinone-1,4	0.76 1.47	5.0 4.7	100 110	0.46	2.7	71

[a] In water, $E_{\frac{1}{2}}=-1.41$ V, $i_d=3.8$ A, cot $\alpha=67$ mV. [b] In aqueous solution.

metal orbitals[18]. The magnitude of this effect has been calculated using the potentials of the first reversible stages in the reduction of quinones and their complexes. The difference between the half-wave potentials, measured under strictly the same conditions, may readily be shown to be equivalent to the difference between the standard redox potentials of the respective reversible processes. It can be seen from the data of Table 1 that this difference, as expected, depends neither upon the nature of the quinone nor upon the character of the solvent used. For complexes of rhodium, this value was equal to 0.9 V. This value, may also involve other values apart from the main contribution: the change in the solvation energy difference between quinone and the semiquinone-anion-radical in both coordinated and non-coordinated states, as well as some value associated with distortions of the molecular geometry of duroquinone during the coordination process as already suggested[8]. We assume that the total contribution of these values should not exceed 10%.

A satisfactory linear dependency has been shown to exist (with a slope of about 45°) between the reduction potentials of quinones and the energies of their lowest inoccupied orbitals[17]. The fact that such dependencies do exist, shows that for two quinones the reduction potential difference (in volts) should be equivalent to that between the energies of their lowest inoccupied orbitals (in electron-volts). The application of this idea to the quinones and complexes investigated in the present work, indicates that the energy of the $2b_{2g}$ orbital in quinone increases by about 0.9 eV during the process of coordinating with the RhC_5H_5 radical and by 1.1 eV on coordination with its iridium analogue.

The increase in the negative shift of the reduction potential for iridium with respect to that for rhodium should be regarded as an increased tendency for the metal to back-donation in iso-structural complexes passing downwards along the Periodic Table. Usually this is not obviously the case although there are some other examples[19] of stimulation of back-donation from heavier metals to a ligand orbital in which some electronic changes occur during redox reactions. However, our experiments agree with a theory of Schrauzer that π- and δ-bondings are more important for the heavier metals, which he arrived at using calculated values of overlap integrals between corresponding metal and ligand orbitals.

A degree of back-donation from metal to quinone depends not only upon the nature of the metal but, for the same metal, also upon the nature of the bonding with other ligands. A detailed investigation of the ligand effect on the redox properties of some metal π-complexes of quinones, is now in progress.

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