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The Mercury–Iridium Complexes Generated by Electrolysis of *trans*-Chlorocarbonylbis(triphenylphosphine)iridium(I) on Mercury Electrodes

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Electrolysis of $IrCl(CO)(PPh_3)_2$ (further abbreviated as Irk) on anodically polarized mercury electrodes in CH_2Cl_2 using tetrabutylammonium perchlorate as supporting electrolyte leads to the formation of a mixture of species with the stoichiometry $(Irk)_3Hg^{2+}$ and $(Irk)_4Hg^{2+}$ (as perchlorate salts). In presence of tetraethylammonium nitrate the species $(Irk)_2Hg(NO_3)_2$ is formed. All three species are converted by the action of halide ions into the complex $(Irk)HgX_2$ (X = Cl, Br, I). Electrochemical and spectral (visible and IR) characterization of the products is given.

Introduction

In connection with the study of the redox* addition mechanism to d^8 square planar complexes it is of importance to attempt a separate insight into the oxidation and the addition step. Therefore we undertook a study of electrochemical oxidation of the complex $IrCl(CO)(PPh_3)_2$ in presence of perchlorate ions which, as rather poor ligands, might be supposed not to play any important role in the redox addition, and for comparison in presence of ligands with higher coordination ability (NO_3^-, halide ions). The present paper deals with results obtained on mercury electrodes.

Experimental

The polarographic experiments were performed using the Radelkis Model OH 102 instrument. The dropping mercury electrode had the following characteristics: t_1 = 2.85 sec and m = 1.96 mg sec^{-1} at a height of the mercury column of 64 cm and the applied voltage 0.0 V *vs.* aqueous saturated calomel electrode (SCE) in the supporting electrolyte 0.1*M* tetrabutylammonium perchlorate in CH_2Cl_2. In all electrochemical measurements the three-electrode system in potentiostatic circuiting was used. The large-area electrolyses were performed with a Jaissle 1000 T potentiostat. The charge consumed in the electrolyses was measured by an Amel Integrator M 558 coulometer.

The absorption spectra were recorded using the Unicam SP-800B spectrophotometer for the visible and UV region, and the Perkin–Elmer Model 257 instrument for the IR region.

The dichloromethane (Uvasol–Merck) was refluxed and distilled with anhydrous calcium chloride and potassium carbonate under inert atmosphere prior to use. The complex $IrCl(CO)(PPh_3)_2$ was prepared by a standard procedure[1]. The tetraalkylammonium salts were recrystallized from a ethanol–water mixture and dried over P_2O_5 *in vacuo.* All experiments were carried out under an inert atmosphere of argon or nitrogen purified on the BTS catalyst (BASF) column and dried over P_2O_5.

Results and Discussion

The complex $IrCl(CO)(PPh_3)_2$ (further abbreviated as Irk) in 0.1*M* tetrabutylammonium perchlorate (TBAP) in CH_2Cl_2 yields a single anodic polarographic wave with $E_{1/2}$ = +0.695 V (SCE) when using the mercury dropping electrode. A similar wave of the same height but slightly different half-wave potential is obtained also in 0.1*M* $(C_2H_5)_4NBF_4$ ($E_{1/2}$ = +0.700 V) or 0.1*M* $(C_4H_9)_4NPF_6$ ($E_{1/2}$ = +0.710 V) in CH_2Cl_2. The limiting current is diffusion controlled and corresponds to the exchange of 0.58 e (mean value of 10 experiments with a scatter of ±0.02 e, obtained by comparison with the 1-electron oxidation wave of ferrocene). The experiments with the Kalousek commutator and cyclic voltammetry have shown that the electrode process is totally irreversible. The half-wave potential is dependent on the height of the mercury column and shifts to positive potentials with increasing concentration of the complex (the $E_{1/2}$ values given above apply to h = 85 cm and $c_{Irk} = 5 \times 10^{-4} M$). This anomalous behaviour is due to the adsorption of the

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* The term "redox addition" seems to us more appropriate than the term "oxidative addition" frequently used in the literature since in the process of addition a formal redox reaction between the reaction partners occurs.

electrode reaction product at potentials corresponding to the ascending part of the wave as can be seen from the shape of the corresponding i–t curves. However, at potentials corresponding to the limiting current of the wave both the i–t curves and the mercury column dependence indicate a strict diffusion character of the limiting current. Since our main interest in this work was to get information on the nature of the products of electrode reaction which can be derived from the limiting current, no further attention was paid to a detailed analysis of the entire wave and to the nature of the mentioned adsorption.

By a large-area potentiostatic electrolysis using the mercury pool electrode at potentials of the limiting current of the wave a dark greenish–blue solution is obtained (solution A). This solution shows a drawn-out cathodic polarographic wave with $E_{1/2} = +0.15$ V (SCE), the limiting current of which is diffusion controlled. This wave is presumably composed of two waves with close half-wave potentials. The original complex Irk is completely consumed (and accordingly the anodic wave disappears) after passing 0.56 F/mol Irk (mean value of 6 experiments showing a scatter of ±0.015 F/mol Irk). In turn, by a large-area electrolysis of the solution A at potentials of the limiting current of its cathodic wave the complex Irk is quantitatively recovered on passing the same amount of charge that was necessary for its anodic generation (0.56 F/mol Irk). Solution A in 0.1*M* TBAP–CH_2Cl_2 shows absorption bands in the visible region ($\lambda_{max} = 634$, 619 and 500 nm, molar extinction coefficients exceeding 10^4, see Fig. 1) and the carbonyl stretching vibration bands at 2005 and 2020 cm^{-1}.

The electrolytic product A was isolated in the following way. The solution A was evaporated to dryness and the residue extracted with benzene; after evaporating the benzene extract a deep blue solid was obtained which was recrystallized from dichloromethane (product A). A qualitative chemical analysis shows that product A contains mercury. A solution of the product A in CH_2Cl_2 shows the same absorption bands in the visible region and carbonyl stretching vibration bands as the original solution A. The same CO frequencies were obtained with the isolated product A in nujol mulls.

To get information on the composition of the product A its solutions were reacted with various anions. With tetraethylammonium nitrate ($TEANO_3$) added to the solution A the original Irk and a new substance (B) are formed as indicated by the appearance of the anodic wave typical for Irk, and of a new IR ν_{CO} band at 2030 cm^{-1} and reduction wave at +0.23 V. The amount of the liberated Irk corresponds approximately to one half of the amount of Irk originally present in the system. A more exact information about the composition of the species B is obtained from the electrochemical behaviour of Irk in $TEANO_3$ medium. In 0.1*M* $TEANO_3$ the complex Irk yields a diffusion controlled anodic wave with $E_{1/2} = +0.36$ V, the limiting current of which corresponds to the uptake of 1 electron. By the large-area electrolysis on the mercury-pool electrode at potentials of the limiting current of this wave the species B is obtained (as found by the IR spectra and polarography) and the complete electrolysis consumes 1F/mol Irk. From this solution the solid product B was obtained in the same way as described above with the species A. A qualitative chemical analysis shows that product B also contains mercury.

If to the TBAP solution of Irk the $TEANO_3$ is gradually added the anodic wave with $E_{1/2} = +0.36$ V is also stepwise developed at the expense of the wave with $E_{1/2} = +0.695$ V, the increase of the more negative wave being always larger than the decrease of the more positive one (see Figure 2; the full height of the wave in TBAP media corresponds to 0.58 e

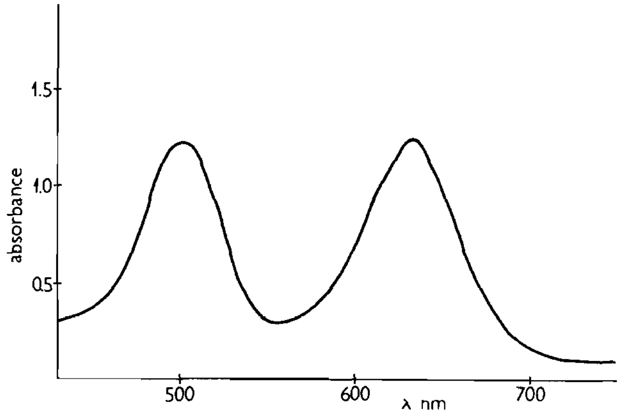

Figure 1. Electronic spectrum of the solution. 5×10^{-4}*M* Irk in 0.1*M* TBAP–CH_2Cl_2 solution electrolyzed at mercury-pool electrode polarized to +0.73 V (SCE).

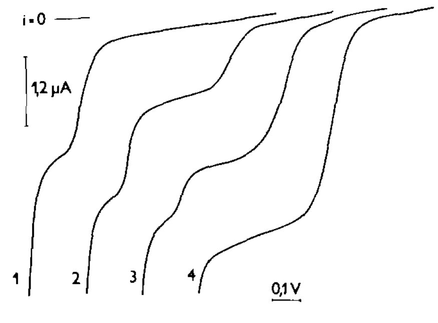

Figure 2. Effect of $TEANO_3$ additions on polarographic behaviour of Irk in TBAP–CH_2Cl_2. 5.25×10^{-4}*M* Irk in 0.1*M* TBAP–CH_2Cl_2; $TEANO_3$ concentration: 1, 0; 2, 2.35×10^{-4} *M*; 3, 4.05×10^{-4}*M*; 4, 5.5×10^{-4}*M*. Polarographic curves recorded from 0.0 V *vs.* SCE towards positive potentials.

whilst that of the wave in $TEANO_3$ corresponds to 1 e – see above). In these addition experiments the more negative wave is fully developed and the positive one completely disappears when the molar ratio $TEANO_3$: Irk reaches the value of 1. From these results and from the knowledge that only divalent mercury[2] is incorporated into the adducts with Irk it follows that the overall electrode process corresponding to the anodic wave with $E_{1/2} = +0.36$ V can be described as

$$2\mathrm{Irk} + \mathrm{Hg} + 2\mathrm{NO_3^-} - 2\,\mathrm{e} \rightarrow (\mathrm{Irk})_2\mathrm{Hg}(\mathrm{NO_3})_2 \qquad (1)$$

and accordingly product B has the stoichiometric composition $(Irk)_2Hg(NO_3)_2$.

If to solution A obtained electrolytically from the known amount of Irk, halide ions (in form of tetrabutylammonium salts) are added the greenish–blue solution turns yellow. At the same time substance A disappears and in the solution free Irk and a new species (C) is formed, as shown from the appearance of the cathodic wave with $E_{1/2} = -0.070$ V, –0.15 V, –0.23 V and of the IR band with $\nu_{CO} = 2035$, 2035 and 2040 cm^{-1} for the chloride, bromide and iodide added, respectively. These values are identical with those obtained[3] on species $IrkHgX_2$ prepared according to the procedure described by Nyholm *et al.*[2]

The composition of substance C was determined independently in the following way. The solution of A (obtained by electrolysis of a known amount of Irk) was titrated with halide ions up to complete disappearance of the cathodic wave corresponding to product A (Figure 3). From the difference between the original amount of Irk used for generation of A and that liberated after the addition of the halide the ratio Irk : X in product C was determined. Typical data of this experiment (average from 3 measurements) were: original quantity of Irk used for the electrolysis *m* mol (this quantity was different in various experiments), quantity of Irk liberated in the titration 0.72 *m* mol (*i.e.* 0.28 *m* mol was left in the species C), the consumption of the halogen 0.55 *m*, from which it follows that the ratio Irk : X in the species C equals to 1 : 2. These quantitative data were obtained from the height of the corresponding polarographic waves. If the titration was followed spectrophotometrically from the decrease of the absorption bands (see Figure 1) it was seen that the band at 500 nm decreases much more rapidly than that at 634 nm, indicating that solution A contains at least two species which are eventually converted to the species C giving, however, the same molar ratio Irk : Hg : X in C. On addition of a large excess of iodide ions (1*M* solution) product C is completely decomposed[3] with regeneration of the original amount of Irk, and mercuric ions contained in C are quantitatively converted to HgI_4^{2-}. Spectrophotometric determination[4] of HgI_4^{2-} in CH_2Cl_2 ($\lambda_{max} = 334$ nm, $\varepsilon_{max} = 2.75 \times 10^4$ $lmol^{-1}$ cm^{-1}) afforded the mercury contents in C and it was found that the molar ratio of all three components Irk : Hg : X in C was 1 : 1 : 2 which is in agreement with the above identification of product C as $(Irk)HgX_2$.

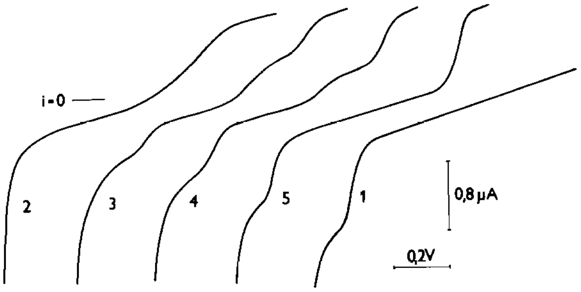

Figure 3. Polarographic pattern in the titration of the solution A with TBACl. $2.7 \times 10^{-4}M$ Irk in 0.1*M* TBAP–CH_2Cl_2; 1, Irk prior to electrolysis; 2, after electrolysis (solution A); 3, 4, 5, $0.67 \times 10^{-4}M$, $1 \times 10^{-4}M$, $1.5 \times 10^{-4}M$ TBACl added to solution A, respectively. Polarographic curves recorded from –0.2 V *vs.* SCE towards positive potentials.

TABLE I. Electrochemical and Spectroscopic Characterization of the Irk Complexes.

Species	$E_{1/2}$[V] (process)[a]	λ_{max}[nm][b]	ν_{CO}[cm^{-1}][b]
$IrCl(CO)(PPh_3)_2$ (Irk)	+0.695 (*a*; 0.1*M* TBAP) +0.700 (*a*; 0.1*M* $TEABF_4$) +0.710 (*a*; 0.1*M* $TBAPF_6$) +0.360 (*a*; 0.1*M* $TEANO_3$)	340; 386; 438	1965
A: $(Irk)_4Hg^{2+} + (Irk)_3Hg^{2+}$	+0.15 (*c*; 0.1*M* TBAP)	500; 619; 634	2005; 2020
B: $(Irk)_2Hg(NO_3)_2$	+0.23 (*c*; 0.1*M* $TEANO_3$)		2030
C: $IrkHgCl_2$	–0.070 (*c*; 0.1*M* TBAP)	290	2035
$IrkHgBr_2$	–0.15 (*c*; 0.1*M* TBAP)	290; 335	2035
$IrkHgJ_2$	–0.23 (*c*; 0.1*M* TBAP)	290; 315; 367	2040

[a] The electrode process is denoted *a* or *c* depending on whether the corresponding polarographic wave is anodic (oxidation) or cathodic (reduction), respectively; further data in the brackets refer to the concentration and kind of supporting electrolyte. [b] ν_{CO} and λ_{max} measured in CH_2Cl_2.

Supposing that all the mercury present in product A remains in product C, then it follows from the titration data given above that the ratio Irk : Hg in product A is 3.6 : 1. It is improbable that product A as a single species contains a fractional number of Irk molecules and therefore it has to be assumed that A is a mixture of perchlorate salts of the species $(Irk)_3Hg^{2+}$ and $(Irk)_4Hg^{2+}$ in the ratio 2 : 3 (0.66). This result agrees also quantitatively with the number of electrons exchanged in the anodic electrode reaction of Irk on mercury electrodes in perchlorate media (0.58 e from the height of the polarographic wave and 0.56 F/mol from the large-area electrolysis – see above) and qualitatively with the finding that in the titration of A with halide ions the spectral bands corresponding to product A are decreased with unequal rates.

Electrochemical and spectroscopic characterization of the individual species is summarized in Table I. Further information about the Hg–Irk adducts was obtained from the study of chemical reactions of Irk with mercuric ions which is described elsewhere[5].

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