Decomposition of Redox Addition Complexes Ir(CO)YX(PPh₃)₂ HgX by Halide Ions and Their Electrochemical Properties

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The compounds of the type Ir(CO)YX(PPh₃)₂HgX (X, Y = Cl, Br, I) formed by redox additions of HgX₂ to Vaska complexes Ir(CO)Y(PPh₃)₂ are decomposed in presence of halide ions with formation of the Vaska complexes and mercury(II) halo complexes. The nature of the halide in the decomposition products is influenced by rapid substitution reactions of the halide ions in which these ions are preferentially coordinated to the iridium central atom in the sequence I < Br < Cl. The decomposition reaction being in a sense a reverse of the redox addition can be denoted as redox* elimination. The mentioned complexes are reduced electrochemically in the tetrabutylammonium perchlorate (TABP) – dichloromethane medium in a diffusion controlled one-electron process followed by a chemical disproportionation reaction. A large difference in the reduction potential was observed when using mercury and platinum as electrode material.

Introduction

As was shown in a preceding paper [1] the complex Ir(CO)Cl(PPh₃)₂ is oxidized at the mercury electrode in the 0.1M TBAP–CH₂Cl₂ medium with formation of a mixture of complexes with the stoichiometry $[Ir(CO)Cl(PPh_3)_2]_nHg^{2+}$ (n = 3, 4). Both complex cations are quantitatively converted by the action of halide ions into complexes Ir(CO)ClX-(PPh₃)₂HgX (X = Cl, Br, I). These complexes which can be prepared also by the redox addition of HgX₂ to Ir(CO)Cl(PPh₃)₂ are decomposed by the action of an excess of halide ions with regeneration of the original complex Ir(CO)Cl(PPh₃)₂. In a similar way the complexes Ir(CO)ClX(PPh₃)₂HgX react with bases such as triphenylphosphine, pyridine or NH₃ with formation of the complex Ir(CO)Cl(PPh₃)₂ in addition to mercury complexes containing the

corresponding bases as ligands [2]. The decomposition reaction of complexes containing the iridium–mercury bond by bases has been denoted as reductive elimination [3]. The present contribution deals with a more detailed study of the decomposition reactions by means of halide ions and with the electrochemical properties of the adducts containing the iridium–mercury bonds.

Experimental

The decomposition and substitution reactions were followed spectrophotometrically using a Unicam SP 800B spectrophotometer in the UV and visible region and a Perkin–Elmer Model 257 for the IR region. The polarographic and voltammetric experiments were carried out with a Radelkis Model OH 102 instrument. The mercury dropping electrode had the following characteristics: t_1 = 2.85 s, m = 1.96 mg s⁻¹ at the mercury level of 64 cm and the applied voltage 0.0V against aqueous saturated calomel electrode in the 0.1M TBAP–CH₂Cl₂ supporting electrolyte. Against this electrode all potentials were measured. In all measurements a potentiostatically controlled three-electrode system was used. The large-area electrolyses were carried out with a Jaissle 1000T potentiostat. The charge transferred in the course of the electrolyses was measured by means of an Amel Integrator M 558. The dichloromethane was refluxed and distilled under inert atmosphere with anhydrous calcium chloride and potassium carbonate prior to use. The complexes Ir(CO)Y(PPh₃)₂ were prepared by a standard procedure [4]. The complexes of the type Ir(CO)ClX(PPh₃)₂HgX (X = Cl, Br, I) were prepared according to the described method [2]. The complexes of the type Ir(CO)YX(PPh₃)₂HgX (X = Cl, Br, I; Y = Br, I) were prepared *in situ* by the titration of 5 × 10⁻⁴ M Ir(CO)Y(PPh₃)₂ in dichloromethane with 1 × 10⁻³ M HgX₂ in ether.

The tetrabutylammonium salts were recrystallized from an ethanol–water mixture and dried over P₂O₅ *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 P₂O₅.

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*The expression "redox elimination" seems to be more appropriate than the "reductive elimination" often used in the literature since, similarly as with the redox addition, a formal redox change is associated with the process.

TABLE I. Spectroscopic Characterization of the Complexes $Ir(CO)(halide)(PPh_3)_2$.

Complex	λ_{max} [a] [nm]	ϵ_{max} [M^{-1} cm^{-1}]	ν_{CO} [b] [cm^{-1}]
$Ir(CO)Cl(PPh_3)_2$	386	3.10×10^3	1954
$Ir(CO)Br(PPh_3)_2$	390	3.42×10^3	1955
$Ir(CO)I(PPh_3)_2$	398	2.71×10^3	1958

[a] λ_{max} measured in CH_2Cl_2.   [b] ν_{CO} measured in Nujol.

TABLE II. Halides in the Complexes $Ir(CO)(halide)(PPh_3)_2$ Resulting from the Decomposition of $Ir(CO)YX(PPh_3)_2HgX$ with TBAZ.

X, Y	Z = Cl	Br	I
Cl, Cl	Cl	Cl	Cl
Cl, Br	Cl	Cl	Cl
Cl, I	Cl	Cl	Cl
Br, Cl	Cl	Cl	Cl
Br, Br	Cl	Br	Br
Br, I	Cl	Br	Br
I, Cl	Cl	Cl	Cl
I, Br	Cl	Br	Br
I, I	Cl	Br	I

Results and Discussion

In dichloromethane the originally colourless or slightly yellow 5×10^{-4}M solution of the complexes $Ir(CO)YX(PPh_3)_2HgX$ (X, Y = Cl, Br, I) turns deep yellow immediately after addition of an excess of the tetrabutylammonium halide (TBAZ; Z = Cl, Br, I). The change in colour intensity corresponds to the formation of the product $Ir(CO)(halide)(PPh_3)_2$ characterized on the basis of visible and IR spectra which were measured in CH_2Cl_2 solution and in nujol mull spectra (see Table I). The nature of the halide ligand in the product is dependent on the nature of the halides X, Y and Z in the starting reaction mixture. From the complex of the type $Ir(CO)YX(PPh_3)_2HgX$ in combination with three different TBAZ 27 possible reaction mixtures were prepared. The products were 19 times $Ir(CO)Cl(PPh_3)_2$, 7 times $Ir(CO)Br(PPh_3)_2$ and once $Ir(CO)I(PPh_3)_2$ (see Table II).

$Ir(CO)Cl(PPh_3)_2$ was formed from those combinations of $Ir(CO)YX(PPh_3)_2HgX$ with TBAZ in which at least one of the halides X, Y and Z was the chloride. $Ir(CO)Br(PPh_3)_2$ resulted in the case where X, Y and Z corresponded to the bromide or bromide and iodide. The complex $Ir(CO)I(PPh_3)_2$ as product was formed only in the reaction of $Ir(CO)I_2(PPh_3)_2$-HgI with TBAI. From these results it follows unambiguously that the lighter halides are preferentially coordinated in the reaction product. This preference reflecting the expected energy of the
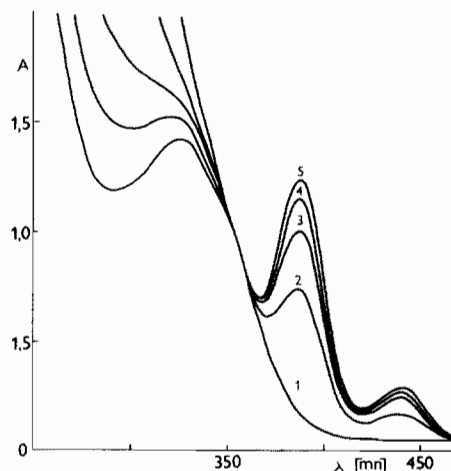

Figure 1. Spectrophotometric titration of $Ir(CO)Cl_2(PPh_3)_2HgCl$ with TBACl in CH_2Cl_2.
1) 4.5×10^{-4} M $Ir(CO)Cl_2(PPh_3)_2HgCl$;
2) 2.5×10^{-3} M TBACl added;
3) 5.0×10^{-3} M TBACl added;
4) 7.5×10^{-3} M TBACl added;
5) 10.0×10^{-3} M TBACl added.

metal–chloride and metal–bromide bonds in comparison with the metal–iodide bond [5] was described in connection with the study of halide exchange reactions in the system $Ir(CO)I(PPh_3)_2$–Cl^- in 1,2-dichloroethane [6].

The spectrophotometric titration of the $Ir(CO)I(PPh_3)_2$ solutions with TBACl and TBABr, carried out in our laboratory, has shown that in the dichloromethane medium the same substitution of iodides by chlorides or bromides takes place according to equation 1 (X = I; Y = Cl, Br)

$$Ir(CO)X(PPh_3)_2 + Y^- \rightleftharpoons Ir(CO)Y(PPh_3)_2 + X^-$$
$$(1)$$

The exchange proceeds practically instantaneously and is quantitative within the error given by the small differences in the position of the followed absorption bands before and after the reaction ($\Delta\lambda_{max} \sim 7$ nm). Therefore it can be assumed that similar reactions proceed also in the course of the described decomposition and influence the composition of the products.

A more detailed information on the influence of the halide ions on the decomposition of the complexes $Ir(CO)YX(PPh_3)_2HgX$ (X, Y = Cl, Br, I) was

TABLE III. Dependence of the Concentration of Liberated Irk on TBAZ and IrkHgX₂ at Equimolar Concentration of the Reactants ($4.5 \times 10^{-4} M$).

| IrkHgX₂	TBAZ	$C_{Irk} \times 10^4$
IrkHgI₂	TBAI	3.25
IrkHgBr₂	TBAI	2.80
IrkHgCl₂	TBAI	2.35
IrkHgI₂	TBABr	2.10
IrkHgBr₂	TBABr	1.75
IrkHgCl₂	TBABr	1.05
IrkHgCl₂	TBACl	0.75
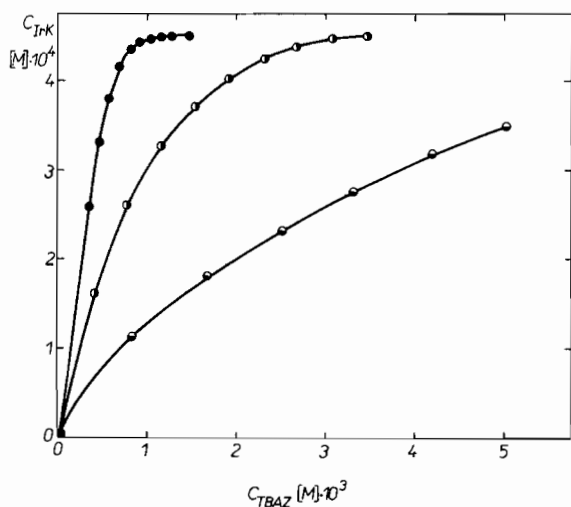
Fig. 2. Dependence of the concentration of Irk liberated in the decomposition of IrkHgCl₂ on the TBAZ concentration. Medium CH₂Cl₂. ● Z = I; ◑ Z = Br; ◐ Z = Cl.

obtained by spectrophotometric titrations of Ir(CO)-ClX(PPh₃)₂HgX (further abreviated as IrkHgX₂ where Irk = Ir(CO)Cl(PPh₃)₂) with halide ions followed in the IR, UV and visible region. In the course of the titration of IrkHgX₂ with TBAZ (Z = Cl, Br, I) the IR carbonyl stretching bands and absorption bands corresponding to the complexes IrkHgX₂ are gradually replaced by those corresponding to the complex Irk. The titration of IrkHgCl₂ with TBACl is shown in Fig. 1.

If the titration is carried out with the iodide ions then with the 100 fold excess of TBAI the mercury-(II) tetraiodo anion (HgI_4^{2-}) was identified on the basis of its pronounced absorption band in the UV region (λ_{max} = 334 nm, ϵ_{max} = 2.75 $\times$ 10⁴ l mol⁻¹ cm⁻¹. The formation of HgI_4^{2-} as a product is in analogy with the decomposition reactions in the presence of other bases, *e.g.* triphenylphosphine [2] in which case HgI₂(PPh₃)₂ is formed.

In the course of the titration beside the mercury-(II) halo complexes and Irk no other product was detected spectrophotometrically and hence the decomposition reaction can be described by the overall equation

$$\text{IrkHgX}_2 + n\text{Z}^- \rightleftharpoons \text{Irk} + [\text{HgX}_2\text{Z}_n]^{n-} \; (n = 1,2)$$

(2)
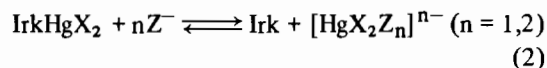
With higher concentration of TBAZ the mixed mercury halo complexes undergo substitution reactions according to the equilibrium constants of these complexes which increase in the sequence Cl < Br < I. Hence it follows that in the case of Z = I in excess of TBAZ the final product is HgI_4^{2-} as was described above.

The concentration of Irk set free according to equation 2 and determined spectrophotometrically (λ_{max} = 380 nm; ϵ_{max} = 3.10 $\times$ 10³ l mol⁻¹ cm⁻¹)

TABLE IV. Electrochemical and Spectroscopic Characterization of IrkHgX₂ and TBAZ.

Species	Mercury Dropping Electrode[a]		Platinum Rotating Electrode[a]		λ_{max}[c] [nm]	ν_{CO}[c] [cm⁻¹]
	$E_{1/2}$ [V][b]	n	$E_{1/2}$ [V][b]	n		
IrkHgCl₂	−0.07	1.1	−1.43	1.0	290	2035
IrkHgBr₂	−0.15	1.1	−1.40	1.1	290; 335	2035
IrkHgI₂	−0.23	1.2	−1.41	1.1	290; 335; 367	2040
TBACl	−0.07	1	+1.5	1		
TBABr	−0.15	1	+0.82	1		
TBAI	−0.23	1	+0.4	1		
HgCl₂	−0.07	1	2 waves: + 0.24; −0.07	sum of 2 waves 1		
HgBr₂	−0.15	1				
HgI₂	−0.23	1				

[a]Electrochemical measurements carried out in 0.1*M* TBAP–CH₂Cl₂ [b]$E_{1/2}$ measured against aqueous saturated calomel electrode. [c]ν_{CO} and λ_{max} measured in CH₂Cl₂.

was found to be dependent under comparable conditions (equimolar addition of halide ions and constant starting concentration of $IrkHgX_2$) on the nature of halide Z in TBAZ and X in $IrkHgX_2$. From Fig. 2 and Table III it is evident that under the above conditions the concentration of Irk set free increases with the use of different halide ions in the sequence $Cl < Br < I$, *i.e.* in the sequence in which the nucleophillic properties of the halides and the stability constants of the mercury(II) halo complexes in non-aqueous media increase [7, 8]. Even if these stability constants in dichloromethane medium are not known (their calculation from the data of the Table III or Fig. 1 is difficult due to the formation of the mixed halide mercury complexes – see eq. 2) on the basis of the analogous polarographic behaviour of the halides in dichloromethane, dimethylformamide and acetonitrile it can be assumed that the relative sequence of stability constants of the mercury(II) halo complexes will be the same in dichloromethane as in acetonitrile and dimethylformamide [9]. The corresponding half-wave potentials of the anodic waves of the halides are given in Table IV.

From Table III it follows further that the concentration of Irk set free increases in the sequence $X = Cl < Br < I$, *i.e.* the dependence on the change of X follows the same trend as on the change of Z. The dependence on X may be due as in the preceding case to the changes in stability constants of the mixed halide complexes of mercury, but on the other hand it can reflect also the stability of the complexes $IrkHgX_2$ which increases in the reverse sense in the sequence $X = I < Br < Cl$. In this connection exchange of HgX_2 in the $IrkHgX_2$ complexes was followed. On addition of $HgCl_2$ to slightly yellow solutions of $IrkHgBr_2$ or $IrkHgI_2$ the resulting solutions turn immediately colourless, the absorption bands corresponding to the original complexes disappear and the absorption band corresponding to $IrkHgCl_2$ ($\lambda_{max} = 290$ nm – see Table III) remains. The product $IrkHgCl_2$ was also characterized after isolation from the solution. A similar reaction is observed also between $HgBr_2$ and $IrkHgI_2$ where $IrkHgBr_2$ was identified spectrophotometrically as the product. The results show that in the systems $IrkHgX_2$–HgX'_2 exchange reactions proceed in which the heavier halogens are preferred in HgX_2 whilst the more electronegative (lighter) halogens are preferred in the HgX_2 coordinated in the complex $IrkHgX_2$.

Further information on the complexes containing the iridium–mercury bond was obtained by an electrochemical study of the $IrkHgX_2$ complexes. The experiments were carried out in the medium of $0.1M$ tetrabutylammonium perchlorate (TBAP) in dichloromethane. All complexes are reduced at the mercury dropping electrode in a single cathodic wave the half-wave potentials of which are given in Table IV. The limiting currents are diffusion controlled and corres-

pond to a one-electron electrode reaction (this value was obtained by comparison with the one-electron wave of ferrocene). Experiments with the Kalousek commutator and cyclic voltammetry showed that the electrode processes with all the complexes are reversible. By a large-area potentiostatic electrolysis using the mercury electrode at the potential of the limiting current of the cathodic wave yellow solutions were obtained. Spectrophotometrically it was found that the yellow colour is due to Irk. The solutions after electrolysis yield anodic polarographic curves with diffusion controlled limiting currents and half-wave potentials identical with those of the corresponding halides (see Table IV) indicating that the further products of electrolysis are the corresponding halides Cl^-, Br^- and I^-, respectively. The height of the anodic waves with respect to the original cathodic waves of $IrkHgX_2$ before electrolysis is approximately twofold. In the more positive region a further anodic wave appears corresponding to the liberated Irk.

The charge necessary for the complete electrolysis of the complexes $IrkHgX_2$ is 2.0 F/mol $IrkHgX_2$. In the course of the electrolysis a diffuse grey turbidity is observed which does not correspond to any of the mentioned products and which ceases with time. This finding together with the difference in the number of electrons consumed in the electrode process at the dropping mercury electrode (1e) and in the large-area electrolysis (2e) leads to the conclusion that the primary one-electron electrode process is followed by a slower disproportionation reaction:

$$IrkHgX_2 \rightleftharpoons IrkHgX + X^-$$
$$2IrkHgX \longrightarrow Irk + Hg + IrkHgX_2 \tag{4}$$
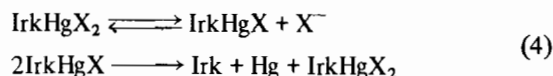
The primary electrode process need not be reversible although the electrochemical results show its reversibility. It is probable that the complexes $IrkHgX_2$ are reduced at the mercury electrode at more positive potentials but the halide ions set free in this process cause a current of the opposite direction so that the zero current observed before the appearance of the cathodic wave corresponds to mixed currents. Hence follows the identity of the half-wave potentials of reduction of the complexes $IrkHgX_2$ with those of the anodic waves of TBAZ (Table IV) and also the "reversible" behaviour of the cathodic waves. This mechanism is substantiated by the fact that the mercuric halides HgX_2 show an identical behaviour at the mercury electrodes as $IrkHgX_2$ (see Table IV).

When using the platinum rotating electrode with which the above mentioned mixed currents cannot occur the complexes of the type $IrkHgX_2$ are reduced also in a single cathodic wave shifted to more negative potentials. In all cases the limiting current is diffusion controlled with a linear dependence on the complex concentration, the wave is irreversible (cyclic voltammetry) and by comparison with the ferrocene wave it was found that the electrode process corres-
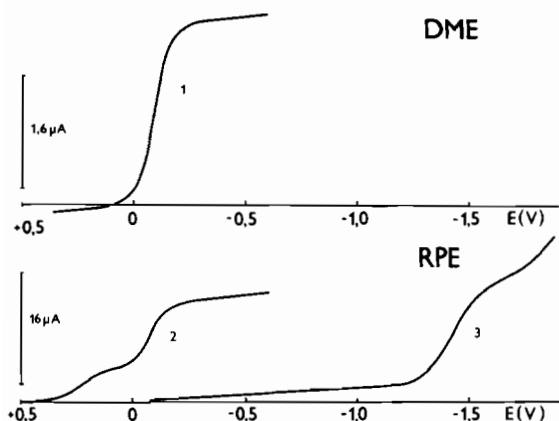
Figure 3. Polarographic behaviour of IrkHgCl₂ and HgCl₂ at the dropping mercury electrode (DME) and the rotating platinum electrode (RPE). Supporting electrolyte: $0.1M$ TBAP in CH_2Cl_2. 1) $5 \times 10^{-4}M$ IrkHgCl₂ or $5 \times 10^{-4}M$ HgCl₂ using DME; 2) $5 \times 10^{-4}M$ HgCl₂ using RPE; 3) $5 \times 10^{-4}M$ IrkHgCl₂ using RPE.

ponds to the one-electron transfer. A coulometric determination of the charge transferred on a large-area platinum electrode was not possible due to a rapid inhibition of the electrode process. A gray layer was observed visually at the surface of the electrode. The half-wave potentials of the complexes are considerably sensitive to the prior history of the electrode. Reproducible results can be obtained only after polishing of the electrode prior to each measurement (Cr_2O_3, Al_2O_3, SiC). Under these conditions the obtained values of the half-wave potentials of all complexes are very close to each other and in comparison with those obtained with the mercury electrodes are considerably shifted to more negative values (see Table IV). The reduction pattern of HgX₂ and IrkHgX₂ is not identical at platinum electrodes as is the case with mercury electrodes (Fig. 3). *E.g.* HgCl₂ is reduced at the platinum rotating electrode in 2 waves, the $E_{1/2}$ of the second one being identical with that obtained with the mercury electrodes. The sum of both waves corresponds to the uptake of 1 electron (Table IV). The separation of the one-electron reduction into 2 waves is presumably due to the coating of the platinum electrode surface by mercury during the electrode process. The large diffrence in half-wave potentials of IrkHgX₂ obtained with mercury and platinum electrodes is not sufficiently elucidated as yet and is subject to further study.

The non-reproducibility of the results obtained with the rotating platinum electrode without polishing before each measurement is due presumably to a partial coating of the electrode with mercury. Experimental evidence of the deposition of mercury at the electrode during the electrode process was obtained with the use of the inverse voltammetry carried out in the following way. The platinum rotating electrode was maintained under the potential of the limiting

current for a certain time (2–5 min) and then a slow potential sweep (2mV sec⁻¹) was applied towards positive potentials (+2.0V). At the anodic side a peak was observed at the potential of mercury dissolution in the given medium (+0.9V), the height of which at constant rotation rate of the electrode and constant time of electrolysis was dependent on the nature of the halide X in the complex IrkHgX₂. The peak height and thus the amount of mercury deposited at the electrode increases in the sequence X = Cl < Br < I. The amount of mercury corresponding to the peak area is, however, very low and for IrkHgI₂ it corresponds only to about 5% of the charge consumed during the electrolysis. This is a further evidence that the complexes IrkHgX₂ are reduced as a whole in a primary one-electron process, the products of which undergoes a disproportionation according to eqn. 4. The disproportionation reaction can proceed both in the bulk at a certain distance from the electrode and in the adsorbed state on the surface of the electrode, and its rate depends on the nature of X.

Since the formation of IrkHgX₂ from Irk and HgX₂ is considered as a redox addition, the decomposition reaction studied in this work which proceeds according to the described results by nucleophillic attack of halides on mercury can be characterized as a redox elimination. This reaction belongs thus to the group of redox elimination reactions which proceed under normal conditions [10–12] in presence of Lewis bases [13] or are thermally [14, 15] or photometrically activated. The intrinsic mechanism of these reactions is hitherto not fully elucidated. The complexes with the iridium–mercury bond show in several respects an analogous behaviour as the organometallic compounds with the carbon–mercury bond which is evidently due to the covalent character of these bonds and to the electrophillic properties of mercury [17–19].

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