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Electrochemical Studies of $[Rh_2\{(S)\text{-}C_6H_5CHOHCOO\}_4(H_2O)_2]$

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Binuclear rhodium(II) complexes $[Rh_2(RCOO)_4\text{-}L_2]$ (Fig. 1) have been the subject of intensive studies because of their unusual electronic structure and their application in catalytic organic synthesis [1].

The electrochemistry of these complexes has also been examined, for a better understanding of their electronic structure and reactivity [1, 2]. The oxidation potentials were found to be dependent upon the electronic factors of the R groups, and equally, upon the ligands coordinated along the Rh–Rh axis. The oxidation potential grows with the increase of the electronegativity of R.

Rhodium(II) amidates $[Rh_2\{R'NC(O)R\}_4]$ undergo electrochemical oxidation much easier than carboxylates. The greater is the donor number of a solvent [2–5], the easier proceeds the oxidation of binuclear $[Rh_2(OOCR)_4]$ compounds.

Herewith we present the results of the electrochemical studies of the $[Rh_2\{(S)\text{-}C_6H_5CHOHCOO\}_4\text{-}(H_2O)_2]$ complex. This complex is interesting for us because it acts as a catalyst of olefin reduction and as a precursor of the effective catalysts of the unsaturated hydrocarbons and ketones hydrogenation in methanol solutions. We believe that it could find practical application as a catalyst in the synthesis of asymmetric compounds; our goal was to explain how the presence of the –OH group at the α-carbon in carboxylate ligand would change the electrochemical properties of the complex $[Rh_2\{(S)\text{-}C_6H_5CHOH\text{-}COO\}_4(H_2O)_2]$.

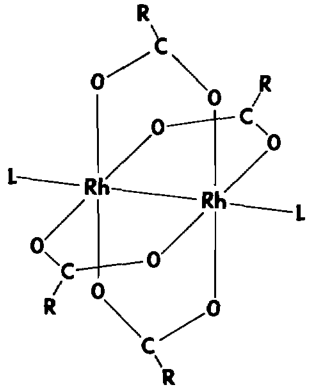

Fig. 1. Structure of $[Rh_2(RCOO)_4(L)_2]$.

Results and Discussion

$[Rh_2\{(S)\text{-}C_6H_5CHOHCOO\}_4(H_2O)_2]$ was synthesized as described in refs. 6 and 7. In a 0.1 M solution of $NaClO_4$ in methanol it is stable for a couple of days. The adsorption electronic spectrum of the solution did not change during this period. A typical cyclic voltammogram of the oxidation of $[Rh_2\{(S)\text{-}C_6H_5CHOHCOO\}_4(H_2O)_2]$ solution in dry CH_3OH (3×10^{-4} M), containing 0.1 M $NaClO_4$ at a static mercury electrode *versus* SCE at 295 K is shown in Fig. 2. The oxidation process of $[Rh_2\{(S)\text{-}C_6H_5\text{-}CHOHCOO\}_4(H_2O)_2]$ is quasi-reversible on the mercury electrode. The measured potentials are: $E_{p,a} = 265$ mV, $E^{I}_{p,c} = 160$ mV for $\nu = 50$ mV s^{-1} and $\Delta E = 95 - 120$ mV for $\nu = 50\text{–}500$ mV s^{-1}. At $\nu = 20\text{–}50$ mV s^{-1} $i^{I}_{p,c} > i_{p,a}$ and at fast scan rates $i_{p,a}/i^{I}_{p,c} \rightarrow 1$. At the potential $E^{II}_{p,c} = 65$ mV (for $\nu = 50$ mV s^{-1}), the second irreversible reduction process takes place and $i^{II}_{p,c}$ is proportional to $\nu^{1/2}$ at all scan rates.

The bulk electrochemical oxidation of $[Rh_2\{(S)\text{-}C_6H_5CHOHCOO\}_4(H_2O)_2]$, carried out in the apparatus with separated cells at the controlled Pt electrode potential (260 mV *versus* SCE), allowed us to obtain the compounds whose electronic spectrum shows bands at 970, 589 and 445 nm. The band at 970 nm is characteristic for $[Rh_2(RCOO)_4]^+$ dimers [1, 8–9] with rhodium in the 2.5 oxidation state.

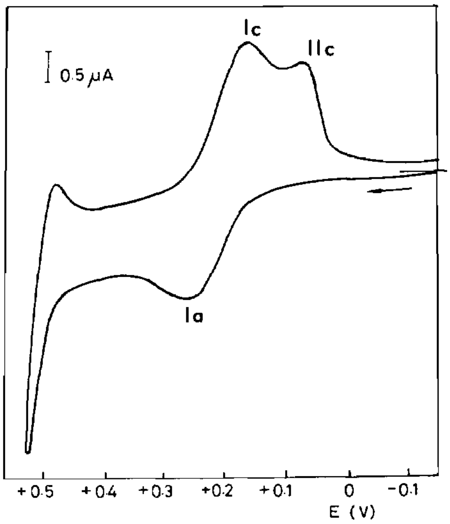

Fig. 2. Cyclic voltammogram of 3×10^{-4} M $[Rh_2\{(S)\text{-}C_6H_5CHOHCOO\}_4(H_2O)_2]$ in CH_3OH/0.1 M $NaClO_4$ scanned between 0.00 and +0.5 V. Scan rate 50 mV s^{-1}.

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An increase in intensity of the band at 445 nm and its shift relative to the band characteristic for Rh(II) complex (at 453 nm) are indicative of the Rh(III) compound as the second oxidation product, because in the range 400–430 nm the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition should appear in octahedral Rh(III) complexes. Hence it follows that processes of the one- and two-electron oxidation probably proceed simultaneously, however disproportionation of the Rh(II)–Rh(III) complex with formation of $[Rh_2(PhCHOHCOO)_4]$ and $[Rh_2(PhCHOHCOO)_4]^{2+}$ is also possible:

$$[Rh_2(C_6H_5CHOHCOO)_4(solv.)_2] \overset{e^-}{\rightleftharpoons} [Rh_2(C_6H_5CHOHCOO)_4(solv.)_2]^+ + [Rh_2(C_6H_5CHOHCOO)_4(solv.)_2]^{2+}$$

$$2[Rh_2(C_6H_5CHOHCOO)_4(solv.)_2]^+ \rightleftharpoons [Rh_2(C_6H_5CHOHCOO)_4(solv.)_2] + [Rh_2(C_6H_5CHOHCOO)_4(solv.)_2]^{2+}$$

At the potential $E^{II}_{p,c} = 65$ mV, the Rh(III) complex $[Rh_2(C_6H_5CHOHCOO)_4(solv.)_x]^{2+}$ is probably reduced to the Rh(II) complex. Electrochemical reduction of $[Rh_2\{(S)\text{-}C_6H_5CHOHCOO\}_4(solv.)_2]$ is an irreversible process. A typical cyclic voltammogram for the solution of the same composition as during oxidation (Fig. 3) shows that the complex undergoes two reduction processes at $E^{I}_{p,c} = -945$ mV and $E^{II}_{p,c} = -1620$ mV at $v = 50$ mV s^{-1}. The calculated values are $\alpha n^I = 0.73$ and $\alpha n^{II} = 0.46$ [10].

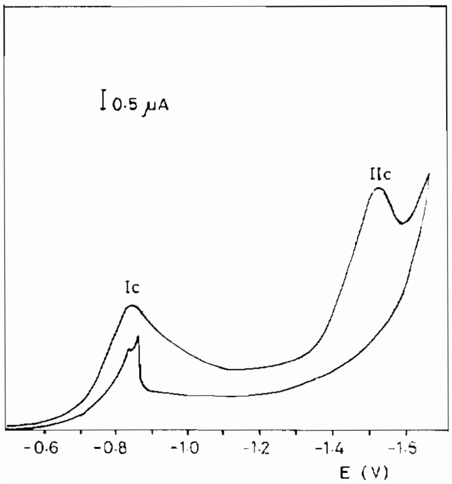

Fig. 3. Cyclic voltammogram of 3×10^{-4} M $[Rh_2C_6H_5CHOHCOO)_4(solv.)_2]$ in $CH_3OH/0.1$ M $NaClO_4$ scanned between -0.6 and -1.7 V. Scan rate 100 mV s^{-1}.

If the cathodic sweep direction is reversed at any point beyond $E^{I}_{p,c}$, the current returns through a cathodic or inverted peak at approximately the same potential as the forward peak. Tetramandelatodirhodium(II) is adsorbed on the electrode before reduction will take place. A reasonable explanation for the inverted current of the reverse cyclic sweep is that $Rh_2(C_6H_5CHOHCOO)_4$ is either desorbed or reoriented at potentials beyond the $E^{I}_{p,c}$ potential and then readsorbed and reduced when the potential is made more positive again [11]. At -945 mV, the complex is most probably reduced to the Rh(I)–Rh(II) compound $[Rh_2(C_6H_5CHOHCOO)_4(solv.)_2]^-$ and at -1620 mV to the Rh(I) complex $[Rh_2(C_6H_5CHOHCOO)_4(solv.)_2]^{2-}$.

The bulk electrolytic reduction of a complex, carried out at the controlled potential of the Pt electrode ($E^{I}_{p,c} = -940$ mV *versus* SCE) produced the new Rh(I) complex. It was evidenced by the intensity decrease of bands characteristic for $[Rh_2(S)\text{-}C_6H_5CHOHCOO_4(H_2O)_2]$ [6, 7] during reduction and by the lack of the new bands in the range 1000–500 nm, indicative of the presence of $[Rh_2(C_6H_5CHOHCOO)_4]^-$.

The irreversibility of the reduction of $[Rh_2\{(S)\text{-}C_6H_5CHOHCOO\}_4(H_2O)_2]$ was confirmed by ESR spectra of the Rh(I)–Rh(II) complex $[Rh_2(PhCHOHCOO)_4]^-$, obtained by γ-irradiation of a methanol solution of tetramandelatodirhodium(II) at 77 K. The ESR spectra showed that $[Rh_2(PhCHOHCOO)_4]^-$ decomposes at 175–195 K [12]. These results were confirmed also by the study of the $[Rh_2(MeCOO)_4]^-$ complex obtained at the low temperature (77 K), in liquid nitrogen. $[Rh_2(OOCMe)_4]^-$ is very unstable; at 130 K there is first the break of the Rh–O–CMe–O–Rh bridge bondings, followed by dissociation to the monomeric compounds. Reduction of $Rh_2(PhCHOHCOO)_4$ at room temperature leads most probably to the immediate formation of the mono- or binuclear rhodium(I) complex $\{[Rh(PhCHOHCOO)_x(solv.)_{4-x}]^{1-x}\}_m$, $x = 1, 2$ owing to the disproportionation of the Rh(I)–Rh(II) compound.

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