Electrochemical activity of rhodium complexes supported on fibrous-carbon material

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The redox properties of heterogenized Rh^{I}, Rh^{II}, and Rh^{III} complexes with different, particularly organophosphorus, ligands were studied by cyclic voltammetry (CVA). The support is a carbon-paste electrode based on a fibrous-carbon material and activated carbon. The electrochemical reduction of Rh^{III} produces Rh metal, which further catalyzes hydrogen evolution. After the reduction of water-soluble binuclear Rh^{II} complexes, the CVA curves exhibit peaks of electrocatalytic hydrogen evolution and irreversible $Rh^{I} \rightarrow Rh^{II}$ oxidation. The Rh^{II} complexes with organophosphorus ligands are characterized only by the peak of $Rh^{I} \rightarrow Rh^{II}$ oxidation. After reduction, the Rh^{I} complexes behave as a pseudo-reverse Rh^{0}/Rh^{I} pair. The electron-donating properties of the ligand determine the reversibility of the system. The degree of structurization of the carbon matrix and the presence of phosphorus(v) atoms in it affect the electrochemical activity of the Rh^{II} and Rh^{I} complexes.

Key words: rhodium complexes, organophosphorus ligands, fibrous-carbon support, electrochemistry.

Rhodium complexes are widely used in catalysis of organic reactions.[1] Redox properties of rhodium compounds have been studied by electrochemical methods, mainly in solutions, using mercury, platinum, rhodium, graphite, and carbon Pyroceram electrodes.[2–9]

In this work, we studied electrochemically the redox properties of Rh^{I}, Rh^{II}, and Rh^{III} complexes, precursors of the hydroformylation[10] and cyclopropanation[11,12] catalysts heterogenized on the carbon-paste electrode,[13] which is based on phosphorus-doped fibrous-carbon material (FCM).[14,15]

The following compounds were studied: $RhCl_3 \cdot 3H_2O$ (**1**), $Rh_2(AcO)_4$ (**2**),[16] $Rh_2(NaCO_3)_4 \cdot 2.5H_2O$ (**3**),[17] $Rh_2(AcO)_4[P(OCH_2)_3CEt]_2$ (**4**),[18] $Rh_2(AcO)_4[P(OCH_2)_3CEt]_2 \cdot 8P(OCH_2)_3CEt$ (**5**),[18] $Rhacac(CO)_2$ (**6**),[19] $Rhacac(CO)[P(OCH_2)_3CEt]$ (**7**),[10] $Rhacac(CO)PPh_3$ (**8**),[20] and $P(OCH_2)_3CEt$ (**9**).[21]

Experimental

Compounds **1**—**9** differ sharply in solubility, and the experimental conditions should be standardized for comparison of their electrochemical behavior. For this purpose, compounds **1**—**9** were supported on the carbon-paste electrode by impregnation with different solvents. Complexes **1**—**8** and phosphite **9** were supported on FCM[14,15] or AR-3 active carbon (AC) prewashed with 10% HNO_3 and distilled water and dried at 130 °C in a vacuum desiccator for 2 h. For the preparation of solutions of compounds **1** and **3**, bidistilled water was used; for compound **2** and compounds **4**—**9**, methanol and methylene dichloride, respectively, were used. Methanol and methylene dichloride were purified by the known methods.[22]

Preparation of the carbon-paste electrode. The starting materials, FCM and AC, were preliminarily dried at 90 °C in a vacuum oven for 3 h and then stored in a vacuum desiccator above $CaCl_2$. Weighed samples of the materials thus prepared (100 mg of FCM or 300 mg of AC) were impregnated with solutions of compounds **1**—**9** (2 mg in 2 mL of the corresponding solvent in the case of FCM or 6 mg in 6 mL of the solvent for AC). The suspensions were thoroughly stirred and then dried in a vacuum oven (aqueous suspensions, at 90 °C; methanol suspensions, at 40 °C; and methylene dichloride, at ~20 °C) for 3 h. The prepared samples of FCM and AC with supported compounds **1**—**9** were stored in a vacuum desiccator with $CaCl_2$. The paste was prepared immediately prior to measurements by the addition of 500 and 600 mg of Nujol to FCM- and AC-supported samples, respectively, and the resulting samples were thoroughly stirred. The paste was placed in the tube of the pre-washed and dried electrode.[13]

Prior to packing, the electrode was disposed in such a manner that its sensitive part was directed upward. The paste was pressed by a spatula until air bubbles and excess oil were removed. The surface was leveled by a slide. The paste layer thickness was ~5 mm.

Electrochemical studies were carried out by the three-electrode scheme using a carbon-paste working electrode, a saturated Ag/AgCl reference electrode, and a platinum auxiliary electrode (plate surface area of ~10 cm^2) in a thermostatted (25 °C) 60-mL cell with a magnetic stirrer. The cell contained 30 mL of 0.1 *N* H_2SO_4 (the acid (reagent grade) in bidistilled water) pre-deaerated with nitrogen (special-purity grade) for 10 min. Measurements were performed by the CVA method[23] using a PI-50-1.1 potentiostat controlled by a PR-8 programmer. Curves were recorded on a PDA-1 X-Y-recorder.

When the electrochemical activity was studied, CVA curves were recorded in the range from 0 to +1.0 V (relative to

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Ag/AgCl, saturated KCl). In particular cases, the range was shifted toward negative potentials. The sweep rate v_s = 100 mV s^{-1}; the pause duration at the beginning and end of the sweep t_p = 1 s.

Electrochemical reduction of samples was performed by cyclic cathodic treatment in the range from 0 to −1.0 V at v_s = 100 mV s^{-1}; t_p = 1 s; the number of cycles n = 5. Hydrogen bubbles were observed on the working electrode. Prior to measuring CVA curves in the region of positive potentials, these bubbles were removed from the electrode surface by intense stirring with a magnetic stirrer. A stationary working electrode was used for measurements.

In the case of water-soluble complexes, measurements with the EPV-1 platinum working electrode (from the set of an EV-74 ionometer) were performed for comparison. For this purpose, a $1 \cdot 10^{-3}$ M solution (100—300 mL) of a complex in 0.1 N H_2SO_4 was added by a Gilson micropipet to a cell containing a solution of the supporting electrolyte (30 mL of 0.1 N H_2SO_4).

Results and Discussion

Rh^{III} compound (1) (Fig. 1, *a*, *b*). Under conditions of CVA measurements in the region of positive potentials, the as-prepared **1**/FCM electrode exhibited no extreme electrochemical activity either before or after reduction (Fig. 1, *a*, curves *2* and *3*). For sweeps to the region of negative potentials (Fig. 1, *b*, curves *5* and *6*), anodic peaks were observed on both direct and reverse branches of the curve within the potential range from −0.05 to −0.10 V. According to the published data,[9] the peaks can be interpreted as those of the current of hydrogen desorption from the surface of rhodium metal formed from Rh^{III} at potentials below −0.4 V. This is confirmed by the fact that after the reduction of the complex, the intensity of the anodic peak (−0.10 V) during successive sweeps from +0.6 to −0.4 V and backward decreased as the number of cycles increased. The sharp increase in the cathodic current at $E < -0.4$ V corresponds to the catalytic hydrogen evolution.

It is noteworthy that the peaks in Fig. 1, *a*, *b* are strongly broadened as compared to the standard peak of H_2 desorption on metallic rhodium.[24] This phenomenon is most likely due to the blocking effect of Nujol used in our experiments as the binding material. It is known that saturated hydrocarbons are chemisorbed on the platinum group metals.[25,26] The strong cathodic polarization results in the partial desorption of Nujol, which explains the broadening of the hydrogen desorption peak on curves *5* and *6* in Fig. 1, *b*. Nujol exerts a blocking effect as well as the support (FCM or AC). This results in the relative broadening of the corresponding redox processes on these supports, which is illustrated by the CVA curves considered below.

Figure 1, *a*, *b* also shows the CVA curves of the electrode based on nonmodified FCM (curves *1* and *4*) obtained by the procedure described above but without treatment with rhodium compounds. Similar reference curves are necessary for the estimation of the contribution of a support to the electrochemical activity. It is seen that under our experimental conditions, FCM does not possess extreme electrochemical activity, *i.e.*, the characteristic oxidation and/or reduction peaks are absent.

The CVA curves for Rh^{III} heterogenized on AC (see Fig. 1, *c*, curve *1*, region of positive potentials) show that the characteristic extreme electrochemical activity is absent as in the case of FCM (see Fig. 1, *a*, curves *2*

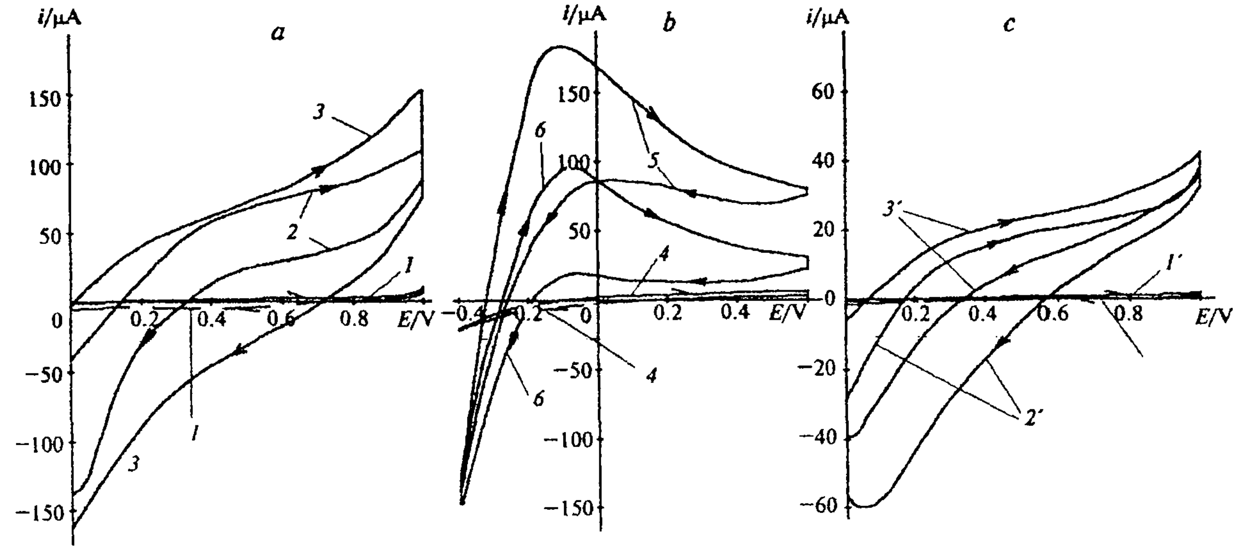


Fig. 1. Cyclic voltammograms of $RhCl_3 \cdot 3H_2O$/FCM (*a*, *b*) and $RhCl_3 \cdot 3H_2O$/AC (*c*): *a*, sweep from 0 to +1.0 V; *b*, sweep from +0.6 to −0.4 V; *1*, *4*, reference FCM sample (without modification by Rh compounds); *2*, *5*, starting $RhCl_3 \cdot 3H_2O$/FCM sample; *3*, *6*, sample after reduction; *1′*, reference AC sample (without modification by Rh compounds); *2′*, starting $RhCl_3 \cdot 3H_2O$/AC sample; *3′*, sample after reduction.

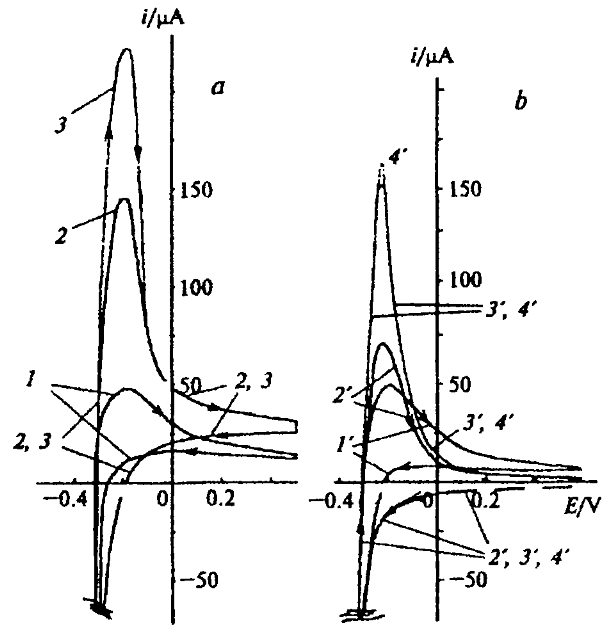


Fig. 2. Cyclic voltammograms of $RhCl_3 \cdot 3H_2O$ (*a*) and $Rh_2(NaCO_3)_4 \cdot 2.5H_2O$ (*b*) in a 0.1 *N* solution of H_2SO_4 on the Pt working electrode; sweep from +0.5 to −0.5 V: *1, 1′*, $c_0 = 0$, background curve; *2*, $c_1 = 3.33 \cdot 10^{-6}$ mol L^{-1}; *2′*, $c_1 = 1.0 \cdot 10^{-5}$ mol L^{-1}; *3*, $c_2 = 1.33 \cdot 10^{-5}$ mol L^{-1}; *3′*, $c_2 = 2.0 \cdot 10^{-5}$ mol L^{-1}; *4′*, $c_3 = 3.0 \cdot 10^{-5}$ mol L^{-1}.

and *3*). However, the currents are much lower than those in the case of FCM, probably due to a higher specific resistance of AC as compared to that of FCM. It is also seen that the current somewhat decreases after the reduction of the sample. This is related to a decrease in the working surface of the electrode probably due to the partial loss of the material during stirring of the solution. A similar phenomenon was also observed for another sample.

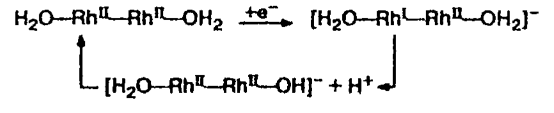
By analogy to Fig. 1, *a*, *b*, Fig. 1, *c* exhibits the CVA curve of the electrode based on nonmodified AC (curve *1′*). It is seen that the AC support possesses no extreme electrochemical activity under our experimental conditions.

Since rhodium chloride is water-soluble, it is partially washed out of the carbon matrix during measurements. Therefore, it was of interest to study its electrochemical properties in a 0.1 *N* solution of H_2SO_4. The CVA curves for Rh^{III} on the stationary platinum electrode without preliminary reduction with a sweep in the range from +0.5 to −0.5 V are presented in Fig. 2, *a*.

Probably, a sharp increase in the cathodic current at $E < -0.3$ V corresponds to the catalytic hydrogen evolution. The anodic peak at a potential of −0.2 V corresponds to hydrogen desorption. An increase in the intensity of this peak (see Fig. 2, *a*, curves *2* and *3*) at different Rh^{III} concentrations (relative to the intensity of the similar peak for the supporting electrolyte, see curve *1*) is associated with the formation of rhodium metal on the platinum surface at potentials lower than −0.3 V. As all noble metals, rhodium sorbs hydrogen at the moment of its catalytic evolution. It is known[24] that the potential of the peak of the current of hydrogen desorption on rhodium in 1 *M* H_2SO_4 is equal to 0.08 V relative to the reversible hydrogen electrode, *i.e.*, −0.14 V relative to the Ag/AgCl electrode. Therefore, according to the published data,[9,24] the anodic peak at −0.2 V can be assigned to the current of H_2 desorption.

Rh^{II} complexes (2—5). Compounds **2—5** are binuclear Rh^{II} complexes. It is known[8] that binuclear rhodium acetate catalyzes hydrogen evolution on the mercury electrode in an acidic medium (pH < 3). It is assumed that one of the atoms of the Rh—Rh pair serves as the electron carrier and is reduced first to Rh^{I} and then re-oxidized to Rh^{II} according to Scheme 1 (acetate ligands are not shown).

Scheme 1



The CVA curves for complex **2** heterogenized on FCM are presented in Fig. 3 (the anhydrous compound was used). At the initial state, the electrochemical activ-

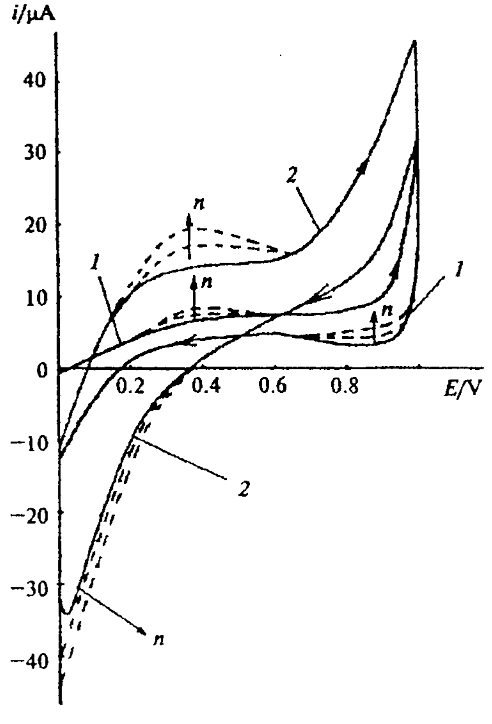


Fig. 3. Cyclic voltammograms of $Rh_2(AcO)_4$/FCM: *1*, starting sample; *2*, sample after reduction (hereinafter the arrow indicates an increase in the number of cycles (*n*) of potential sweep).

ity of the complex is negligible (see Fig. 3, curve *1*). The weak cathodic peak in the region of +0.9 V can be attributed to the desorption of oxygen sorbed at a potential of +1.0 V during the pause t_p = 1 s. The weakening of this peak with an increase in the number of cycles is most likely related to a change in the composition of the surface layer, which is indicated by the appearance of a peak in the region of +0.45 V, assigned to the current of the irreversible oxidation $Rh^I \rightarrow Rh^{II}$. In our opinion, the increase in the cathodic current indicates the enhancement of the catalytic hydrogen evolution involving presumably the Rh^I/Rh^{II} pair. The shape of curve *2* in Fig. 3 (the sample after reduction) indicates an increase in the electrochemical activity of the complex, accumulation of a considerable amount of Rh^I, and a higher intensity of the electrocatalytic hydrogen evolution.

A similar situation was observed for the Rh^{II} carbonate complex (compound 3).

The CVA curves for complex **3** heterogenized on FCM (Fig. 4, *a*) and on AC (Fig. 4, *b*) show that the behavior of complex **3** on AC (see Fig. 4, *b*) more resembles that of complex **2** on FCM (see Fig. 3) than that of complex **3** on FCM (see Fig. 4, *b*). For the rhodium carbonate complex on FCM, a plateau of oxygen desorption (+0.75 to +0.85 V) was observed in the first CVA cycle; however, no peak of the current of $Rh^I \rightarrow Rh^{II}$ oxidation was observed. All evidence of electrocatalysis is observed for complex **3** on AC: after reduction, both the current of peak at +0.35 V (irreversible oxidation $Rh^I \rightarrow Rh^{II}$) and the cathodic current increase. This difference in the behavior of the same complex at different supports can be explained by a higher affinity of the rhodium carbonate complex to the amorphous structure of activated carbon than to the more ordered structure of FCM. In addition, the FCM used contains a trace of phosphorus(v), which should also affect, most likely, the electrochemical activity of the complexes.

Since complex **3** is water-soluble, we obtained for it CVA curves in a 0.1 *N* solution of H_2SO_4 on the stationary platinum electrode (see Fig. 2, *b*), which are analogous to those for Rh^{III} on the platinum electrode (see Fig. 2, *a*). At $E < -0.35$ V, catalytic hydrogen evolution was observed. The peak at −0.22 V corresponds to H_2 desorption. The increase in its intensity with an increase in the Rh^{II} concentration indicates the participation of rhodium metal in electrocatalysis. It is of interest that the behavior of Rh^{II} is quite similar to that of Rh^{III}. Thus, Rh^{II} in an acidic medium on the platinum electrode, as well as Rh^{III}, is reduced to Rh metal (at $E < -0.4$ V), which then catalyzes the H_2 evolution.

The CVA curves for the heterogenized Rh^{II}-based systems (**4**, **5**, and organophosphorus ligand **9**) are presented in Fig. 5.

Complex **4** in the initial state possesses no extreme electrochemical activity (see Fig. 5, *a*, curve *1*). The plateau of oxygen desorption is absent, and no evidence of electrocatalysis is observed. After reduction (curve *2*), the CVA curve exhibits the characteristic peak at +0.29 V, corresponding, in our opinion, to the irreversible oxidation $Rh^I \rightarrow Rh^{II}$. The standard electrode potential of the Rh^I/Rh^{II} redox pair in an aqueous solution is equal to +0.38 V (relative to the Ag/AgCl electrode).[24] Since in our case the rhodium complexes are supported on the carbon support, a decrease in the potential of irreversible oxidation $Rh^I \rightarrow Rh^{II}$ (+0.29 V) as compared to the reference value can be explained by adsorption interaction of the Rh complexes with the support.

A similar situation was observed for the system with complex **5** (see Fig. 5, *b*) containing excess phosphite. However, in this case the initial curve has a weak peak at +0.35 V, which can be explained by two reasons: (1) the presence of some amount of Rh^I in the starting

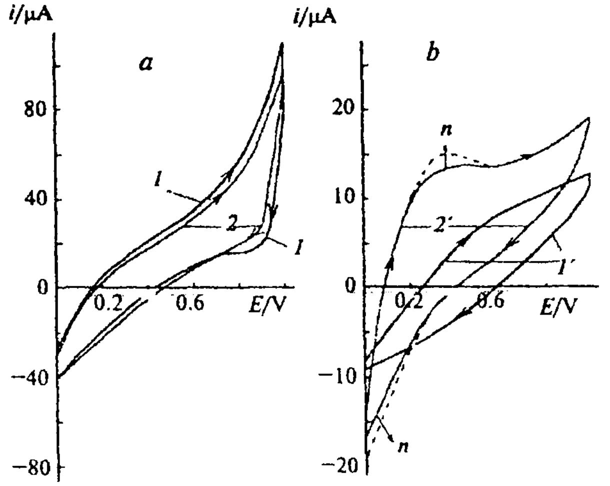


Fig. 4. Cyclic voltammograms of $Rh_2(NaCO_3)_4 \cdot 2.5H_2O$/FCM (*a*) and $Rh_2(NaCO_3)_4 \cdot 2.5H_2O$/AC (*b*): *1*, *1'*, starting sample; *2*, *2'*, sample after reduction.

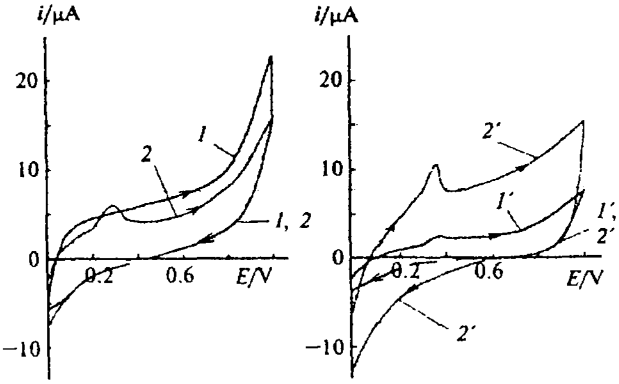


Fig. 5. Cyclic voltammograms of $Rh_2(AcO)_4[P(OCH_2)_3CEt]_2$/FCM (*a*) and $Rh_2(AcO)_4[P(OCH_2)_3CEt]_2 \cdot 8P(OCH_2)_3CEt$/FCM (*b*): *1*, *1'*, starting sample; *2*, *2'*, sample after reduction.

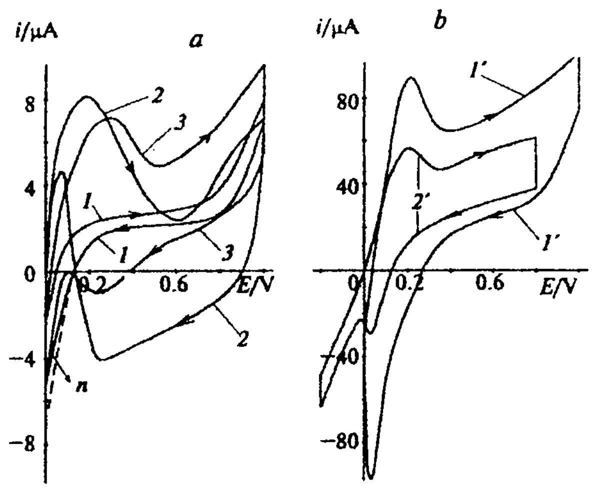


Fig. 6. Cyclic voltammograms of Rhacac(CO)$_2$/FCM immediately (*a*) and 5 days after reduction (*b*): *1*, starting sample; *2*, sample immediately after reduction; *3*, sample 10 min after reduction; *1'*, sweep from 0 to +1.0 V; *2'*, sweep from −0.2 to +0.8 V.

sample, for example, due to the partial reduction of Rh^{II} by excess ligand; and (2) the oxidation of the ligand. To rule out the second version, CVA curves of FCM-supported bicyclophosphite **9** were obtained.

Compound **9** possesses no extreme electrochemical activity either in the initial state or after reduction. In addition, the sample is characterized by extremely low currents, which indicates the shielding effect of phosphite as a dielectric on the carbon matrix. Thus, the peak at +0.36 V on the initial CVA curve for the system with complex **5** is most likely due to an admixture of some amount of Rh^{I} formed by the interaction of complex **2** with excess phosphite **9**, which agrees with the published data.[18]

A decrease in the current after the reduction of the samples containing complexes **4** and **5** (see Fig. 5, *a*) is explained by a partial loss of the material (see above).

Rh^{I} complexes (6—8) (Figs. 6 and 7). Complex **6** differs sharply in behavior from the compounds considered previously. On the initial CVA curve (see Fig. 6, *a*, curve *1*), evidence of electrocatalysis was observed already at zero potential (an increase in the cathodic current with an increase in the number of cycles). An anodic peak at +0.20 V, a weak cathodic peak at +0.23 V, and a very characteristic anodic peak in the cathodic region of the curve (i_a, in the reverse sweep course) at +0.08 V were observed after the reduction (curve *2*). This peak is absent on curve *3* recorded after 10 min, but the cathodic peak at +0.24 V increases, and the anodic peak is shifted to +0.29 V. This shape of curves is characteristic of reversible redox systems. Curve *3* is stable within ~3 h.

This shape of the curves can be explained as follows. When the sample is reduced during a fivefold sweep toward low potentials (to −1.0 V), Rh^{I} is partially reduced to the metal. Metallization of the support (FCM) changes its structure, and then we must deal with the Rh^0/FCM system. A considerable portion of Rh^{I} is reduced to Rh^0, which remains in the ligand surroundings. Thus, a stable reversible (more exactly, pseudoreversible) Rh^0/Rh^{I} system appears during the subsequent cycles in the region of positive potentials (0 to +1.0 V). In this case, the anodic peak in the cathodic region (+0.08 V on curve *2* in Fig. 6) can be assigned to the desorption of hydrogen from the surface of rhodium metal, which agrees with the disappearance of this peak on curve *3*. Then the anodic peak on curve *3* (+0.29 V) corresponds to Rh^0 → Rh^{I} oxidation, and the cathodic peak (+0.24 V) corresponds to Rh^{I} → Rh^0 reduction. Therefore, the parameters presented in Table 1 for the **6**/FCM system are related, in fact, to the system containing Rh^0 and Rh^{I}.

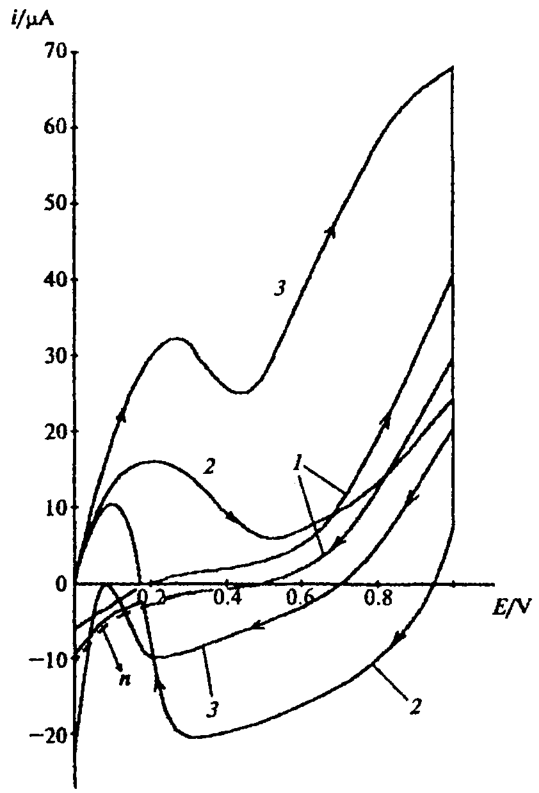


Fig. 7. Cyclic voltammograms of Rhacac(CO)[P(OCH$_2$)$_3$CEt]/FCM: *1*, starting sample; *2*, sample immediately after reduction; *3*, sample 10 min after reduction.

In this case, it is unlikely to be a perfectly reversible system, for which the ΔE value should correspond to ~$59/n_e$ mV, where n_e is the number of electrons participating in the reaction and $i_a/i_c = -1$. Even when it is accepted that the system under question is perfectly reversible, the conditions of its existence (arrangement on the Rh^0/FCM matrix) can strongly affect its parameters. Therefore, it is more correct to consider the

Table 1. Electrochemical activity of FCM-supported Rh^I complexes

Compound	CVA		E_a [a]	E_c [b]	E^0 [c]	ΔE [d]	i_a [e]	i_c [f]	i_a/i_c [g]
	Fig.	Curve	V			/mV	μA		
$Rhacac(CO)_2$	6, *a*	*3*	+0.29	+0.24	+0.265	50	+7	−1	~−7
$Rhacac(CO)_2$	6, *b*	*1'*	+0.24	+0.04	+0.14	200	+90	−96	~−1
$Rhacac(CO)_2$	6, *b*	*2'*	+0.22	+0.02	+0.12	200	+55	−28	~−2
$Rhacac(CO)[P(OCH_2)_3CEt]$	7	*3*	+0.23	+0.20	+0.215	30	+32	−10	~−3

[a] Potential of the anodic peak.

[b] Potential of the cathodic peak.

[c] $E^0 = 1/2(E_a + E_c)$.

[d] $\Delta E = E_a - E_c$.

[e] Anodic current.

[f] Cathodic current.

[g] The ratio of reduction—oxidation currents (equal to −1 for the ideal system).

systems as pseudo-reversible. The standard electrode potential of the Rh^0/Rh^I redox pair in an aqueous solution is equal to +0.38 V (relative to the Ag/AgCl electrode).[24] The difference of the E^0 value found (+0.265 V), as in the case of Rh^I/Rh^{II} (see above), should be related to the adsorption interaction.

The CVA curves for complex **6** on FCM recorded 5 days after reduction (the supporting electrolyte was renewed) showed that the currents increased approximately tenfold (see Fig. 6, *b*). Curve *1'* has the anodic peak at +0.24 V, and the corresponding cathodic peak is at +0.04 V. When the sweep range was shifted toward negative potentials (from −0.2 to +0.8 V), the position of peaks remained unchanged, although their intensity decreased (see curve *2'*). Curve *2'* in Fig. 6, *b* resembles the classical curve for the reversible redox system more so than curve *3* in Fig. 6, *a*. The parameters of curves *1'* and *2'* in Fig. 6, *b* are presented in Table 1.

A similar sharp change in the electrochemical activity after 5-day storage can partly be explained by the effect of dissolved oxygen. However, this effect should be studied in more detail.

The extreme electrochemical activity of complex **6** on AC is absent both before and after the reduction.

Since the Rh^{II} complexes with acetate and organophosphorus ligands are electrochemically active on FCM and inactive on AC, and the Rh^{II} carbonate complex, by contrast, is active on AC and inactive on FCM, we may conclude that the nature of the carbon matrix affects substantially the electrochemical activity of the rhodium complexes.

The effect of the carbon support is especially distinct for the Rh^I compounds with organophosphorus ligands. The CVA curves for complex 7 on FCM (see Fig. 7, Table 1) show that complexes 7 and **6** behave in the same manner with the only difference being that the currents on the CVA of 7 are ~4 times higher. As complex **6**, complex 7 on AC is inactive.

The electrochemical behavior of the Rhacac(CO)L complexes depends on the nature of the organophosphorus ligand. For example, when bicyclophosphite was replaced by triphenylphosphine (PPh_3), an anodic peak at +0.30 V appeared on the CVA curve after reduction; however, the corresponding cathodic peak was absent. The peak of hydrogen desorption was not observed immediately after the reduction. Therefore, it can be assumed that, on the one hand, the triphenylphosphine

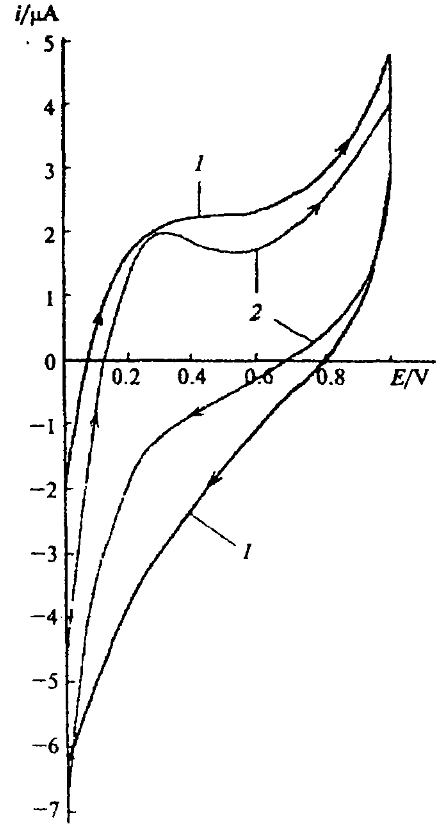


Fig. 8. Cyclic voltammograms of $Rhacac(CO)PPh_3$/FCM: *1*, starting sample; *2*, sample after reduction.

ligand hampers hydrogen desorption and, on the other hand, makes the $Rh^0 \rightarrow Rh^I$ oxidation irreversible due to its higher electron-donor character (Fig. 8).

In conclusion, comparing the electrochemical activity of the Rh^I and Rh^{II} complexes, we can say that no anodic peaks of oxidation are observed on the initial CVA curves of the Rh^{II} complexes (except for complex 5 discussed above). The CVA curves of the Rh^{II} complexes after reduction always contain the anodic peak of irreversible $Rh^I \rightarrow Rh^{II}$ oxidation. Based on this, we can assume that $Rh^I \rightarrow Rh^{II}$ oxidation is possible in the case when two Rh atoms are linked with one another and form a binuclear complex, and only one of these Rh atoms can participate in this transformation, which agrees with the published data.[8]

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