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Reaction of carbon monoxide with dirhodium(II) aqua-cation. New pathway for $Rh_4(CO)_{12}$ synthesis

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Abstract

Reaction of carbon monoxide with an aqueous perchloric acid solution of $Rh_2(H_2O)_{10}{}^{4+}$ produces initially a "$Rh^I(CO)$"$_2$ species, which undergoes further reaction to give $Rh_4(CO)_{12}$ in 70–80% yield as well as some $Rh_6(CO)_{16}$. The reaction was studied at room temperature and atmospheric pressure of CO.

Introduction

Activation of carbon monoxide by transition metal complexes plays a very important role in many chemical processes, e.g. carbonylation, hydroformylation and the Fischer–Tropsch reaction [1]. All reactions between rhodium complexes and CO described in the literature are in practice processes in which rhodium(III) and rhodium(I) participate [2–6]. However James et al. have found that protonation of a suspension of $Rh_2(OAc)_4$ in 1-propanol by aqueous fluoroboric acid gives a $Rh_2{}^{4+}$ species which reacts with carbon monoxide at atmospheric pressure and 75 °C to give $Rh_6(CO)_{16}$ in about 85% yield [7].

These data prompted us to study the reaction between the dirhodium(II) aqua-cation $Rh_2(H_2O)_{10}{}^{4+}$ $\{Rh^{4+}_{2(aq)}\}$ generated by the reduction of $Rh(H_2O)_6{}^{3+}$ with $Cr(H_2O)_6{}^{2+}$ and carbon monoxide.

Results and discussion

Carbon monoxide activation by the Rh^{II} aqua-dimer $Rh^{4+}_{2(aq)}$ in perchloric acid solutions was investigated at the following concentrations: $[Rh^{4+}_{2(aq)}] = 10^{-2}$–$10^{-3}$ M and $[H^+] = 0.1$–3 M.

Introduction of CO to a deoxygenated $Rh^{4+}_{2(aq)}$ solution results in a change of colour from green to yellow. This is accompanied by the decay of the Vis bands characteristic for $Rh^{4+}_{2(aq)}$ at 402 ($\epsilon = 63$ M^{-1} cm^{-1} per Rh) and 648 nm ($\epsilon = 46.5$), by a drastic increase of the absorption above 400 nm and by the appearance of a new UV band at 318 nm.

From reports about the carbonylation reactions of Rh^{III} aqua-halide complexes in HCl aqueous solutions it follows that the first product of these reactions is the

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Rh^I carbonyl complex, which in solution exists as the $[Rh(CO)_2Cl_2]^{1-}$ species. In the UV range it displays a band at 325 nm ($\epsilon = 5700$) [3,4]. Comparison of the data suggests that the formation of the analogous Rh^I complex, "$Rh^I(CO)_2$", containing H_2O molecules and/or OH groups instead of Cl^- ions, is the first stage of the reduction of the $Rh_{2(aq)}^{4+}$ dimer by carbon monoxide.

The change of colour of $Rh_{2(aq)}^{4+}$ solution from green to yellow as an effect of CO treatment is accompanied by clouding of the solution, followed by slow deposition of an orange precipitate. This was filtered off, washed with CO-saturated water and dried *in vacuo*; the resulting solid is easily soluble in methylene chloride, pentane, hexane, heptane and toluene; sparingly soluble in methanol and ethanol; unsoluble in water. The IR spectrum of the "crude" precipitate in CH_2Cl_2 shows intensive bands at 2075, 2040 and 1880 cm^{-1} characteristic for $Rh_4(CO)_{12}$ [8] and a band at 1800 cm^{-1} with relatively low intensity, indicative of the presence of some amount of $Rh_6(CO)_{16}$ [9].

These studies revealed the reduction of $Rh_{2(aq)}^{4+}$ by CO to proceed in two stages:

$$Rh_{2(aq)}^{4+} + CO \rightarrow 2\text{ "}Rh^I(CO)_2\text{"} + CO_2 \qquad (1)$$

$$4\text{ "}Rh^I(CO)_2\text{"} + CO \rightarrow Rh_4(CO)_{12} + CO_2 \qquad (2)$$

(water ligands are omitted).

Reaction 1 leading to the formation of the "$Rh^I(CO)_2$" complex is much faster than the formation of $Rh_4(CO)_{12}$ (2). Under the reaction conditions employed complete reduction of $Rh_{2(aq)}^{4+}$ to "$Rh^I(CO)_2$" was observed after 1–2 h, whereas a 30% yield of $Rh_4(CO)_{12}$ was reached after passing CO through the reaction mixture for about 12 h.

The rate of the colour change and the efficiency of $Rh_4(CO)_{12}$ precipitation are proportional to the concentration of the complex and inversely proportional to the concentration of H^+ ions. Lowering the H^+ ion concentration to below 0.5 *M* before reaction 1 is completed distorts the reaction pathway and lowers the yield of the final product because of the instability of $Rh_{2(aq)}^{4+}$ under such conditions. However, lowering the H^+ ion concentration to ca 0.1 *M* after reaction 1 is completed accelerates reaction 2 and improves the yield of $Rh_4(CO)_{12}$.

Synthesis of the $Rh_{2(aq)}^{4+}$ dimer by the following reduction reaction:

$$2[Rh(H_2O)_5X]^{n+} + 2[Cr(H_2O)_6]^{2+} \rightarrow Rh_{2(aq)}^{4+} + 2[Cr(H_2O)_5X]^{2+} \qquad (3)$$

(where $X = H_2O$, $n = 3$; $X = Cl^-$, Br^-, $n = 2$)

requires a very laborious ion exchange procedure carried out under Ar or N_2 atmosphere in order to isolate the pure $Rh_{2(aq)}^{4+}$ [10–12]. For this reason the reaction has also been studied in the system $\{Rh_{2(aq)}^{4+} + 2Cr(H_2O)_6{}^{3+}\} + CO$ at the following concentrations: $[Rh_{2(aq)}^{4+}] = 0.1–0.3$ *M*, $[Cr^{3+}] = 0.2–0.6$ *M*, $[H^+] = 0.1–1$ *M*. The results obtained indicate that the presence of $Cr(H_2O)_6{}^{3+}$ has no effect on the course of the reaction between $Rh_{2(aq)}^{4+}$ and CO. Similar to when the pure $Rh_{2(aq)}^{4+}$ dimer was used in the presence of $Cr(H_2O)_6{}^{3+}$ a two-step reaction was observed (eqs. 1 and 2). It was also found that reduction 3 could be carried out under CO atmosphere. Using carbon monoxide instead of argon as the medium deoxygenating the $Rh(H_2O)_6{}^{3+}$ solution before the reaction with $Cr(H_2O)_6{}^{2+}$ results in a faster start and shorter duration of the reaction between $Rh_{2(aq)}^{4+}$ and CO.

In reactions with initial concentrations of $Rh^{4+}_{2(aq)} = 0.2$ *M* and $[H^+] = 0.5$ *M* the yield of $Rh_4(CO)_{12}$ after 5 h of carbonylation was ca. 40% and after 12 h ca. 70%. The second reaction product was $Rh_6(CO)_{16}$ formed in an amount of ca 10%. The remainder was the "$Rh^I(CO)_2$" complex.

To our knowledge this is the first report on the activation of carbon monoxide by the pure rhodium aquacomplex.

According to James et al., in contrast to Rh^{III} halogenide complexes, solutions containing the pure aqua complex $Rh(H_2O)_6{}^{3+}$ in 3 *M* perchloric acid do not undergo reduction by carbon monoxide [2].

The first step of the synthesis of the Rh^I carbonyl complexes as products of the reaction between $[RhCl_5(H_2O)]^{-2}$ and carbon monoxide proceeds according to an S_N2 mechanism. This is followed by insertion of the CO group into the Rh–OH bond (formation of $[Cl_4Rh(CO)(OH)]^{2-}$), by the reductive elimination of CO_2 and finally by the formation of Rh^I complex [3]. It seems that the course of the reaction between Rh^{III} aqua-halide compounds and CO is effected by the *trans* effect of Cl^- ions and also by a proper accumulation of electron density on metal, due to the π-donor properties of halides. The lack of these factors in pure $Rh(H_2O)_6{}^{3+}$ prevents the reaction between this complex and carbon monoxide. The results presented in this paper suggest that in the case of the pure dirhodium(II)-aqua species, the reaction with contribution of CO is determined by high electron density on the metal–metal core $[Rh^{II}–Rh^{II}, d^7–d^7]$.

The lack of effect of $Cr(H_2O)_6^{+3}$ on the $Rh^{+4}_{2(aq)}$ reduction carbonylation reaction makes it possible to extend the range of the applied concentrations, which could be important in the application of this procedure to the synthesis of $Rh_4(CO)_{12}$.

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