Direct Carbonylation of Solutions containing Rhodium Salts

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A RECENT Paper[1] prompts us to report our findings on the reaction of carbon monoxide with aqueous solutions of rhodium salts such as rhodium trichloride. In 3M-HCl, under mild conditions (80°, 1 atm. CO), reaction proceeds at a conveniently measurable rate according to the overall stoicheiometry given by the following equation (chloride and water ligands are omitted):

$$\mathrm{Rh^{III}} + 3\mathrm{CO} \rightarrow \mathrm{Rh^{I}(CO)_2} + \mathrm{CO_2}$$

The reaction product is formed as a yellow solution containing the anionic species $[\mathrm{Rh(CO)_2Cl_2}]^-$ which can be precipitated by the addition of a large cation such as tetraphenylarsonium ion. The properties of the isolated solid $\mathrm{Ph_4As[Rh(CO)_2Cl_2]}$ correspond to those reported by Vallarino.[2]

The reduction and carbonylation reaction is of interest in that it exhibits autocatalysis; for reactions carried out at constant pressure the experimental data fit the rate law,

$$\frac{-\mathrm{d[CO]}}{\mathrm{d}t} = 2\,\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{Rh^{I}(CO)_2}] = [\mathrm{Rh^{III}}]\{k_1' + k_2'\,[\mathrm{Rh^{I}\,(CO)_2}]\}$$

which is consistent with the following mechanism:

$$\mathrm{Rh^{III}\text{-}H_2O} + \mathrm{CO} \xrightarrow{k_1} [\mathrm{Rh^{III}\text{-}CO_2H}] + \mathrm{H^+} \qquad (1)$$

$$[\mathrm{Rh^{III}\text{-}CO_2H}] \xrightarrow{\text{Fast}} \mathrm{Rh^{I}} + \mathrm{CO_2} + \mathrm{H^+} \qquad (2)$$

$$\mathrm{Rh^{I}} + 2\mathrm{CO} \xrightarrow{\text{Fast}} \mathrm{Rh^{I}(CO)_2} \qquad (3)$$

$$\mathrm{Rh^{I}(CO)_2} + \mathrm{Rh^{III}(H_2O)} + \mathrm{CO} \xrightarrow{k_2} \mathrm{Rh^{I}(CO)_2} + \mathrm{Rh^{I}} + \mathrm{CO_2} + 2\mathrm{H^+} \qquad (4)$$

k_1' and k_2' are pseudo-constants which correspond to k_1[CO] and k_2[CO] respectively. Step (1) involves a carbon monoxide insertion reaction and has been frequently postulated as the rate-determining step for the reduction of metal ions by carbon monoxide.[3] Stage (3) must be rapid since "unco-ordinated" $\mathrm{Rh^{I}}$ in HCl solution rapidly gives the metal.[4] The detailed path of the autocatalytic stage (4) is not fully understood; the reaction is apparently termolecular, and is similar to other reported $\mathrm{Rh^{I}}$-catalyzed substitution reactions of $\mathrm{Rh^{III}}$ complexes[5] perhaps involving a mixed-valence bridged transition-state $\mathrm{Rh^{I}\cdots X\cdots Rh^{III}}$ (X = CO or Cl) analogous to that involved in the $\mathrm{Pt^{II}}$-catalyzed substitution reactions of $\mathrm{Pt^{IV}}$ complexes.[6] No evidence for rhodium(II) species was obtained although the possibility of (4) going through such an intermediate cannot be ruled out.

At 80° in 3M-HCl, $k_1' = 2{\cdot}5 \times 10^{-4}\,\mathrm{sec.}^{-1}$ and $k_2' = 4{\cdot}5 \times 10^{-2}\,\mathrm{l.mole^{-1}sec.^{-1}}$, and temperature variation experiments yield activation energies of 29 kcal. for $\Delta H_1^{\ddagger}$ and 18 kcal. for $\Delta H_2^{\ddagger}$. The termolecular reaction is more efficient for the reduction because of the lower activation energy. The reaction rates increase markedly at both lower acidities and lower chloride concentrations.

The reaction product $[\mathrm{Rh(CO)_2Cl_2}]^-$, when treated with triphenylphosphine, evolves carbon monoxide and gives an excellent yield of *trans*-$\mathrm{RhCl(CO)(Ph_3P)_2}$ and this provides a general rapid and efficient way of preparing such complexes, giving a better route than the more familiar decarbonylation of alcohols.[7] The similar procedure reported by Chatt and Shaw[1] indicates that their pale yellow solution, resulting from treatment of an alcoholic solution of rhodium trichloride with carbon monoxide, contains the same anionic species. Similar procedures involving direct use of carbon monoxide for the preparation of ruthenium(III) carbonyl complexes containing tertiary phosphines and arsines have also been reported recently.[8]

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