The Binding and Activation of Carbon Monoxide by Rhodium Halide Complexes

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Summary The action of carbon monoxide on aqueous hydrochloric acid solutions of Rh^{III} produces initially $Rh^{III}Cl_5CO^{2-}$, which undergoes a further reductive carbonylation reaction to give $Rh^I(CO)_2Cl_2^-$; the co-ordinated CO in the Rh^I complex is readily oxidized to CO_2 by molecular oxygen.

WE report new findings on the binding of carbon monoxide by solutions of rhodium(III) halides and the subsequent activation of co-ordinated carbon monoxide toward oxidation by molecular oxygen.

The action of carbon monoxide on aqueous, acidic rhodium(III) chloride solutions has been examined recently[1] and found to produce the yellow dichlorodicarbonylrhodium(I) anion, $Rh(CO)_2Cl_2^-$, according to the following overall reaction stoicheiometry (chloride and water ligands omitted):

$$H_2O + Rh^{III} + 3\,CO \rightarrow Rh^I(CO)_2 + CO_2 + 2\,H^+$$

The mechanism suggested as being consistent with the observed kinetics for the reaction postulated, as the rate determining step, the formation of a rhodium(III)–formate ion complex, $[Rh^{III}, CO_2H]$ (by CO insertion into the metal–water bond) which rapidly decomposes to Rh^I, CO_2, and a proton. The Rh^I was then thought to be rapidly carbonylated giving the stable $Rh^I(CO)_2$ species. We have re-examined this reaction recently and find that is proceeds through a previously unknown monocarbonyl chloro-complex of rhodium(III), $RhCl_5CO^{2-}$, and thus can be more correctly written as occurring by at least a two-step process:

$$Rh^{III} + CO \rightarrow Rh^{III}CO \qquad (1)$$

$$H_2O + Rh^{III}CO + 2\,CO \rightarrow Rh^I(CO)_2 + CO_2 + 2\,H^+ \qquad (2)$$

The new $Rh^{III}CO$ species has been isolated and characterized in the following manner. If carbon monoxide is bubbled through a rose-red solution of the salt $Cs_2[RhCl_5(H_2O)]$ in 4M-HCl, at 80°, the colour changes to deep orange within 1·5 hr. Upon cooling the solution to room temperature and evaporating under an air stream, the compound caesium pentachlorocarbonylrhodate(III), $Cs_2[RhCl_5CO]$, is obtained as an orange crystalline solid. The compound gives only three strong, sharp i.r. bands at 2115, 513, and 330 cm.$^{-1}$ which are assignable to the C–O, Rh–C, and Rh–Cl stretching frequencies of the complex, respectively. *X*-Ray powder photographs show the salt to be nearly isomorphous with the Ru^{III} analogue, $Cs_2[RuCl_5CO]$. *Analysis*: Calc. for Cs_2RhCl_5CO: C, 2·10; H, 0·0; Cl, 30·9. Found: C, 2·29; H, 0·0; Cl, 31·1.

The kinetics of the carbonylation of the Rh^{III} aquo-complex, step (1), were followed by visible spectroscopy. At 70°, in 4M-HCl and for a constant concentration of CO (1 atm. pressure) the reaction is first-order in the Rh^{III} aquo-complex (presumably $RhCl_5H_2O^{2-}$) and the pseudo-first-order rate constant for the reaction, which includes the constant concentration of CO, was found to be $3{\cdot}14 \times 10^{-5}$ sec.$^{-1}$. This value of the rate constant was essentially independent of the HCl concentration over the range of 2—4M. Temperature-variation experiments yielded an activation energy, E_a, of 29 kcal./mole. These values of the rate constant and activation energy for the carbonylation of Rh^{III} are similar to those reported recently for the Ru^{III} system.[2]

The kinetics of step (2), the reductive carbonylation of the $Rh^{III}CO$ species to give the $Rh^I(CO)_2$ species, were also studied by visible spectroscopy, but due to the overlapping spectra of the species involved, complete rate data could not be obtained by this method. However, it was clear from the partial data we did obtain that the reaction is complicated and clearly is not first-order in the $Rh^{III}CO$ species. We also note that the previously reported[1] strong acid-dependence of the rate of the overall reductive carbonylation reaction can be identified with this second step since we observed considerably increased reaction rates as the HCl concentration was lowered. More complete rate data on this second step is presently being obtained by gas uptake measurements.

Upon exposure to air, particularly when hot, the final yellow solutions of the $Rh(CO)_2Cl_2^-$ complex, from the carbonylation experiments, rapidly converted into orange solutions, the colour of those observed for the $RhCl_5CO^{2-}$ complex. Qualitative tests indicated that carbon dioxide was evolved in the reaction and that the $Rh^{III}CO$ complex could again be isolated from the solution. These facts suggested that the $Rh^I(CO)_2Cl_2^-$ complex undergoes a novel four-electron oxidative elimination-type reaction with molecular oxygen, in which the rhodium is oxidized from Rh^I to Rh^{III} and one carbon monoxide ligand is oxidized to carbon dioxide according to the following reaction stoicheiometry:

$$2H^+ + Rh^I(CO)_2 + O_2 \rightarrow Rh^{III}CO + CO_2 + H_2O \qquad (3)$$

This reaction sequence was verified by oxidation of known amounts of the Rh^I dicarbonyl complex in HCl solutions with molecular oxygen. The evolved CO_2 was absorbed in a standard $Ba(OH)_2$ solution which was then back-titrated with standard oxalic acid solution.[3] The yields of CO_2 were within 95% of the theoretical expectation.

The kinetics of the oxidation reaction (3) were examined by u.v. spectroscopy. The reaction was too rapid to be followed conveniently at the temperatures or HCl concentrations at which the carbonylations were studied. However, at 25° in 0·66M-HCl and for a constant concentration of O_2 (1 atm. pressure) the reaction is first-order in the $Rh^I(CO)_2$ species and the pseudo-first-order rate constant was found to be $1{\cdot}94 \times 10^{-4}$ sec.$^{-1}$. Temperature-variation experiments yielded an activation energy, E_a, of 2·5 kcal./mole for the oxidation. By analogy with the reaction sequence recently reported for the oxidation of co-ordinated CO in the osmium complex, $OsCl(CO)(NO)(PPh_3)_2$,[4] the mechanism for this oxidation of the $Rh^I(CO)_2Cl_2^-$ complex might be postulated to involve oxidative-addition of O_2 to produce an octahedral intermediate, $[Rh^{III}(CO_3)(CO)Cl_3]^{2-}$, containing co-ordinated carbonate ion, which in the acid media would decompose to give CO_2 and be further anated by Cl^- to form the stable $Rh^{III}Cl_5CO^{2-}$ complex.

The sequence of reactions (1), (2) and (3) is interesting from a practical point of view since it represents a chemical cycle for the oxidation of CO to CO_2, in the presence of the $Rh^{III}CO$ species, with the net consumption of only O_2. Such a cyclic process could have potential as a chemical means for controlling CO concentrations in air.

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[1] B. R. James and G. L. Rempel, *Chem. Comm.*, 1967, 158.

[2] J. Halpern, B. R. James, and L. W. Kemp, *J. Amer. Chem. Soc.*, 1966, **88**, 5142.

[3] M. Katz in "Air Pollution", Vol. 2, Academic Press, New York, 1968, p. 108.

[4] K. R. Lang and W. R. Roper, *Chem. Comm.*, 1968, 1568.