Uptake of Carbon Monoxide and Oxygen by $RhCl(CO)(PPh_3)_2$ and Catalytic Oxidation of Carbon Monoxide and Triphenylphosphine

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Summary The compounds $Rh_2Cl_2(CO)_4$ (II) and $RhCl(CO)_2(OPPh_3)_2$ (III) have been prepared from the reaction of $RhCl(CO)(PPh_3)_2$ (I) with a mixture of carbon monoxide and oxygen; (III) reacts with triphenylphosphine to produce (I).

THE reactions of a number of small molecular species with square-planar d^8 complexes of Rh and Ir have been studied.[1] However, $RhCl(CO)(PPh_3)_2$ (I) has not been found to take up O_2 or CO to a measurable extent under conditions where the iridium analogue $IrCl(CO)(PPh_3)_2$ acts as an oxygen[2] or carbon monoxide[3] carrier.

We have found that $RhCl(CO)(PPh_3)_2$ is converted under a moderate pressure of carbon monoxide and oxygen into $Rh_2Cl_2(CO)_4$ (II), $RhCl(CO)_2(OPPh_3)_2$ (III), and triphenylphosphine oxide (IV)† and that a small amount of carbon dioxide is formed. Application of heat (*ca.* 100°) under pressure (*ca.* 10 kg/cm^2) facilitates co-ordination of oxygen, oxidation of ligands, and carbon monoxide uptake. The complex (III)‡ reacted with triphenylphosphine to yield (I) and (IV), and carbon monoxide was evolved vigorously. Similarly, the co-ordinated dimethyl sulphoxide of $RhCl(CO)(Me_2SO)_2$ (V) was oxidized.

We have extended the reaction of $RhCl(CO)(PPh_3)_2$ and $RhCl(CO)(Me_2SO)_2$ to catalytic oxidation. As shown in the Table, catalytic oxidation of carbon monoxide and triphenylphosphine catalysed by $RhCl(CO)(PPh_3)_2$ was slow. The oxidation of carbon monoxide catalysed by $RhCl(CO)(Me_2SO)_2$ was faster than that by $RhCl(CO)(PPh_3)_2$. The complex $RhCl(CO)(PPh_3)_2$ was recovered unchanged at low conversion of triphenylphosphine into triphenylphosphine oxide, whereas $RhCl(CO)_2(OPPh_3)_2$ was formed at complete conversion. Attempted catalytic oxidation of dimethyl sulphoxide was unsuccessful.

There is a similarity between co-ordination in homogeneous catalysis and chemisorption in heterogeneous catalysis. There have been a number of reports on oxidation reactions on heterogeneous catalysts, and we have at times presented highly speculative schemes. However, the results described above clarify an oxidation mechanism including (1) co-ordination of molecular oxygen (it is easily considered from the iridium analogue), (2) reaction on transition metal, and (3) displacement of the product on the

Catalytic oxidation of CO *and* PPh$_3$ *with* RhCl(CO)L$_2$[a]

Catalyst[b] (mmole)	Solvent	CO (kg/cm^2)	PPh$_3$ (mmole)	Time (hr)	Yield, % (mmole)	
					CO$_2$	OPPh$_3$
(I) (0·065)	C_6H_6	4	0·57	4	0	20 (0·11)
(I) (0·073)	C_6H_6	–	0·80	2	0	10 (0·08)
(I) (0·073)	C_6H_6	4	1·00	45	20 (0·8)	100 (1·00)
(V) (0·10)	C_6H_6	4	—	2	25 (1·1)	—
(V) (0·21)	EtOH	4	—	2	36 (1·6)	—
(V) (0·62)	Me$_2$SO	4	—	2	58 (2·6)	—

[a] In a 25 ml stainless steel autoclave (O_2, 4 kg/cm^2), at 80—105°.
[b] (I): RhCl(CO)(PPh$_3$)$_2$. (V): RhCl(CO)(Me$_2$SO)$_2$.

metal by the new substrate. The above elementary steps correspond to the chemisorption, surface reaction, and desorption of heterogeneous catalysis, respectively. We believe that the present work, a simple reaction catalysed by stable co-ordination compounds, gives a clue to the role of metal in either homogeneous or heterogeneous catalysis.

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