Catalysis of the Water Gas Shift Reaction by $Ru(TPPS)CO^{4-}$ [TPPS = meso-Tetra(4-sulphonatophenyl)porphyrinato]

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The synthesis of the water soluble Ru^{II} porphyrin, $Ru(TPPS)CO^{4-}$ [TPPS = meso-tetra(4-sulphonatophenyl)-porphyrinato], and its ability to catalyse the water gas shift reaction is reported.

Ru(TPP) (TPP = tetraphenylporphyrinato) and Ru(OEP) (OEP = octaethylporphyrinato) have been prepared previously and have been shown reversibly to bind CO and O_2.[1,2] The Ru^{II} porphyrins are also able to expand their co-ordination number from 6 to 7 to accommodate *cis* binding of two groups on one side of the porphyrin plane.[3] This feature is important for the decarbonylation of aldehydes into RH and CO by Ru(TPP) or Ru(OEP).[4] For these reasons it occurred to us that Ru^{II} porphyrins would be good candidates as catalysts for the water gas shift reaction (W.G.S.R.) assuming the Ru^{II}–CO bond is susceptible to nucleophilic addition of OH^- and the normal mechanism for W.G.S.R. activity of metal carbonyl complexes is followed.[5] The porphyrin catalyst should be free from cluster-forming side reactions which reduce the catalytic activity of the mononuclear carbonyl systems $Fe(CO)_5$, $Mo(CO)_6$, $W(CO)_6$,[6–8] or trinuclear cases such as $Ru_3(CO)_{12}$.[9] We have prepared the first water soluble Ru^{II} porphyrin as the $TPPS^{6-}$ [TPPS = meso-tetra(4-sulphonatophenyl)porphyrinato] monocarbonyl complex, $Ru(TPPS)CO^{4-}$. $Na_4TPPS{\cdot}12H_2O$ and $Ru_3(CO)_{12}$ were refluxed in dimethylformamide (DMF) under an Ar atmosphere for 1 to 3 weeks. $Ru(TPPS)CO^{4-}$ was separated from unchanged $Ru_3(CO)_{12}$ and various other derivatives by chromatography on silica gel or alumina. Elution was achieved with $CHCl_3$, $CHCl_3$: MeOH 3 : 1, and finally MeOH. The $Na_4[Ru(TPPS)CO]$ salt may be precipitated from the methanol fraction by slow addition of $CHCl_3$. The Ru^{II} porphyrin is contaminated by other sodium salts and may be converted into the pure Ca^{2+} salt, $Ca_2[Ru(TPPS)CO]{\cdot}12H_2O$ by redissolving the solid in a minimum amount of water and adding to saturated $CaCl_2$ solution, protected from the atmosphere. $Ru(TPPS)CO^{4-}$ has the following maxima (nm) in DMF: 413, 528, 591sh, 641; compared to Ru(TPP)CO in $CHCl_3$: 412, 490sh, 528, 563 or H_2TPPS^{4-} in DMF: 417, 447sh, 508, 543, 586, 643. $Ru(TPPS)CO^{4-}$, ν_{CO} 1940 cm^{-1}; *cf.* Ru(TPP)CO[10] in KBr pellets, 1945 cm^{-1}. Satisfactory analytical data for $Ca_2[Ru(TPPS)CO]{\cdot}12H_2O$ were obtained.

Aqueous solutions of $Ru(TPPS)CO^{4-}$ under a CO atmosphere catalyse the formation of H_2 plus CO_2. The W.G.S.R. was carried out at 100 °C in stirred 100 ml aqueous solutions at equilibrium with 5.0 l of CO at 1 atm. The gas phase was sampled with a gas tight syringe as a function of time over periods of 24 and 48 h (see Table 1). Gas analysis was carried out using a glass column packed with Porpak Q under a He carrier gas flow. The separation of CO, H_2O vapour, O_2 *etc.* from CO_2 was compared with standard authentic mixtures. Under system 1 conditions in Table 1, the $Ru(TPPS)CO^{4-}$ is 6.3 fold more reactive than Ford's $Ru_3(CO)_{12}$ system[9] per mole of Ru. The actual CO_2/H_2 yield is larger, if the gas phase CO_2 analysis is corrected for the amount of CO_2 absorbed by the reactant solution as HCO_3^- and CO_3^{2-}.

Table 1. Catalysis of the W.G.S.R. *via* Ru(CO)TPPS^{4-}.[a]

System no.	Solvent	Ru(CO)TPPS^{4-}/g[b]	NaOH/g	Base/metal mole ratio	Temp./°C	Moles of CO_2[a]/mole of Ru(CO)TPPS^{4-}/h (first CO charge)	$10^2 \times$ total moles CO_2 in 24 h[d]
1	Potassium biphthalate buffer (pH 4.01)	0.0523	0	0	100	10.3[c]	1.12
2	NaOH/H_2O	0.0570	0.1038	52.6	23	0	$\leqslant$0.143
3	NaOH/H_2O	0.0575	0.1092	54.8	100	0.19[c]	0.282
4	H_2O (no base) (pH 7.20)	0.0545	0	0	100	0	*ca.* 0
5	NaOH/H_2O	0.0571	1.0850	547	100	3.75[c]	3.16

[a] Determination of CO_2 produced was based on sample peak areas *vs.* calibrated peak areas. [b] As $Na_4Ru(TPPS)CO$ solid. [c] Gas phase yield. [d] Gas phase plus solution solubility.

These results point to water soluble porphyrin catalysts as a potentially viable scheme for effecting the W.G.S.R. without the cluster- and hydride-forming side reactions.

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