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Hydrogenation of Carbon Dioxide to Formic Acid using Water-soluble Rhodium Catalysts†

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Water-soluble rhodium-phosphane complexes are very efficient catalysts for the hydrogenation of carbon dioxide to formic acid in water–amine mixtures similar to those used for separation of CO_2 from flue gases.

The hydrogenation of carbon dioxide to formic acid has attracted a lot of attention recently as a promising approach to the exploitation of CO_2 as a raw material for chemical synthesis.[1–4] Carbon dioxide is absorbed from flue gases in aqueous solutions of amines on a large scale[1] and the conversion of CO_2 to HCO_2H in these media seems, therefore, especially attractive.

We[4] and others[3] have reported on the formation of HCO_2H from CO_2 and H_2 in organic solvents catalysed by phosphane complexes of group VIII transition metals. In some cases an enhancement of catalytic activity is observed if traces of water are present[3a,c] and some of the catalysts described so far tolerate a water content of up to 20% in volume.[3b] Owing to the insolubility of the catalysts in water, none of these systems may be operated in pure aqueous solutions, however.

We now report that the water-soluble rhodium catalysts **1–3** catalyse the hydrogenation of CO_2 to formic acid very efficiently (Scheme 1). Formic acid concentrations up to 3.63 mol dm^{-3} and turnover numbers up to 3439 may thus be achieved under very mild conditions (Table 1).‡

$[\{(cod)Rh(\mu\text{-}Cl)\}_2]/(C_6H_4\text{-}m\text{-}SO_3^-Na^+)_3P$ (P : Rh = 2.6 : 1)
1

$[\{(cod)Rh(\mu\text{-}H)\}_4]/(C_6H_4\text{-}m\text{-}SO_3^-Na^+)_3P$ (P : Rh = 2.6 : 1)
2

$[\{(C_6H_4\text{-}m\text{-}SO_3^-Na^+)_3P\}_3RhCl]$
3

Sulfonated phosphanes are used successfully as ligands for water-soluble catalysts in many hydrogenation reactions.[5,6]

$$H_2(aq) + CO_2(aq) \rightleftharpoons HCO_2H(aq)$$

Scheme 1 *Reagents and conditions*: H_2O/amine, cat. **1–3**, p° = 40 atm, room temp. Up to 3439 turnovers.

The ligand $(C_6H_4\text{-}m\text{-}SO_3^-Na^+)_3P$ (tppts)§ is most commonly employed, as its sterical and electronical properties are similar to those of the unsubstituted triphenylphosphane Ph_3P (tpp).[6a] Accordingly, catalyst **1** and the corresponding *in situ* system formed with tpp show similar catalytic activity (turnover number 84 and 127, respectively) in the hydrogenation of CO_2 in dimethyl sulfoxide in the presence of triethylamine under conditions developed recently by us.[4] Catalyst **1** can also be employed in a biphasic water–triethylamine mixture, whereby the active rhodium compound is contained almost exclusively in the aqueous layer as judged from the colours of the two phases. The activity of this system is, with 83 catalytic cycles in 18 h, identical to the one observed in dimethyl sulfoxide. The catalyst $[(tppts)_3RhCl]$[6b] **3** shows even higher activity under identical reaction conditions. 264 turnovers within 12 h lead to a formic acid concentration of 1.19 mol dm^{-3}.

As in dimethyl sulfoxide,[4a] the amine plays a crucial role in the stabilisation of the newly formed formic acid. This is emphasised by the fact that no formation of formic acid could be detected by ^1H NMR spectroscopy using an aqueous solution of catalyst **3** in the absence of an amine. Triethylamine may be replaced by dimethylamine yielding homogeneous reaction mixtures. A formic acid concentration of 3.63 mol dm^{-3} was obtained under the conditions summarised in Table 1 using an aqueous solution containing 3.97 mol dm^{-3} dimethylamine and 5.41 × 10^{-3} mol dm^{-3} catalyst **3**. Lowering the rhodium concentration, by a factor of ten, leads to a formic acid concentration of 1.76 mol dm^{-3}, corresponding to the formation of 3439 mol of HCO_2H per mol of rhodium. The latter value represents the highest turnover number reported so far for the hydrogenation of CO_2 to HCO_2H.

It is noteworthy that no other reduction products of carbon dioxide, such as formaldehyde or methanol, could be detected by ^1H NMR spectroscopy. No formation of *N,N*-dimethylformamide[7] was observed if dimethylamine was used as base. Interestingly, the concentration of formic acid did not significantly exceed the amine concentration in all experiments carried out in aqueous media. In contrast, HCO_2H/amine ratios of up to 1.5 may be obtained by hydrogenation of CO_2 in dimethyl sulfoxide.[4a]

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† CO_2-Activation, Part 3—for part 2 see ref. 4*c*.

‡ The high-pressure experiments were carried out as described previously.[4a] The formic acid concentration was determined by integration of the formyl signal in the ^1H NMR spectrum relative to the internal standard dioxan. The number of moles of formic acid was derived from these concentrations *via* a calibration curve.

§ Tppts was prepared in accord with ref. 5*b* and contained 12% of the corresponding phosphane oxide according to ^{31}P NMR.

Table 1 Hydrogenation of CO_2 to formic acid in aqueous solution catalysed by water soluble rhodium phosphane complexes[a]

Cat.	c°(Rh)/ 10^{-3} mol dm^{-3}	P : Rh	Amine	c°(amine)/ /mol dm^{-3}	c°(HCO_2H) /mol dm^{-3}	Turnover number
1	5.81	2.6	NEt_3	1.20	0.45[b]	83
2	0.83	2.6	NEt_3	1.20	0.84[b]	1068
3	4.73	3	NEt_3	1.20	1.19	264
3	5.41	3	—	—	n.d.[c]	—
3	5.41	3	$HNMe_2$	3.97	3.63	733
3	0.54	3	$HNMe_2$	3.97	1.76	3439

[a] Reaction conditions: V° (H_2O + amine) = 6 cm^3, p° = 40 atm, $H_2:CO_2 \approx 1:1$, T = room temp., t = 12 h; [b] t = 18 h; [c] not detectable.

Based on our mechanistic investigations, we proposed clusters of type $[\{(\mathbf{P}_2)Rh(\mu\text{-}H)\}_x]$ ($\mathbf{P}_2$ = two monodentate or one bidentate phosphane) as possible intermediates in the hydrogenation of CO_2 to HCO_2H.[4c] Following these considerations, we used $[\{(cod)Rh(\mu\text{-}H)\}_4]$[8] **4** as precursor for the water-soluble catalyst **2**. Catalyst **2** was 12 times more active than the *in situ* system **1**. This result, which is in agreement with our proposal, is nevertheless rather surprising in view of the high sensitivity towards air and moisture reported for other hydride bridged rhodium complexes.[9] ^1H NMR spectroscopical investigations showed, however, that a solution of **4** in [$^2H_6$]benzene was stable towards H_2O over a period of days and no H/D-exchange was observed in the presence of D_2O. The nature and the reactivity of the complexes formed from **4** and phosphane ligands is currently under investigation.

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