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Activation of carbon dioxide

IV *. Rhodium-catalysed hydrogenation of carbon dioxide to formic acid **

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Abstract

Rhodium catalysts formed *in situ* from suitable precursors and the bidentate phosphane $Ph_2P{-}(CH_2)_4{-}PPh_2$ (**1**) catalyse the reversible formation of formic acid from carbon dioxide and dihydrogen very efficiently. Up to 2200 moles of formic acid may be formed per mole of rhodium with turnover frequencies as high as 375 h^{-1} using $[\{Rh(cod)(\mu\text{-}H)\}_4]$ (**3**) (cod = 1,5-cyclooctadiene) as precursor. In agreement with thermodynamical considerations, the highest yields of formic acid are achieved in polar aprotic solvents in the presence of secondary or tertiary amines. Experiments with various catalyst precursors together with kinetic measurements in a specially designed reactor suggest that neutral rhodium(I) hydride complexes are the actual active species in the catalytic cycle. A mechanism is proposed on the basis of these results that allows explanation of all experimental data including the induction period and the activation of the catalyst by treatment with H_2 or HCO_2H prior to the reaction observed with the precursor $[\{Rh(cod)(\mu\text{-}Cl)\}_2]$ (**2**).

Key words: Rhodium; Phosphanes; Carbon dioxide; Catalysis; Hydrogenation

1. Introduction

The use of carbon dioxide as a C1 building block in organic synthesis seems to be an attractive way of cutting down CO_2 emissions. The amount of carbon dioxide to be fixed that way is, however, very small compared to the huge amount of CO_2 produced by burning fossil fuels. Nevertheless, there is great interest in the use of carbon dioxide as a building block in organic chemistry as it seems to be an ideal raw material for many other reasons as well [1,2]. Carbon dioxide is cheap, easy to handle and nontoxic, to name just a few. The hydrogenation of CO_2 to formic acid appears to be a straightforward approach to the utilisation of carbon dioxide as a chemical feedstock and has attracted additional attention as a possible way of reversibly storing hydrogen [3].

The addition of H_2 to a CO_2 molecule is an endergonic but exothermic process under standard conditions [4]. The equilibrium can be shifted to the right by suitable choice of reaction conditions (elevated pressure, base addition *etc.*) [5,6] or by trapping formic acid as formate esters or formamides [7,8]. There is still a very large kinetic barrier for this reaction, which may however be overcome by a suitable catalyst [5–8]. It is apparent from these considerations that two more or less (*vide infra*) independent problems have to be tackled in order to make the hydrogenation of carbon dioxide an economically interesting process. Firstly, the reaction must be high yielding, *i.e.* the equilibrium must be shifted as far to the right as possible. Secondly the catalyst must show sufficiently high activity, *i.e.* the equilibrium should be reached as fast as possible.

$$H_2(g) + CO_2(g) \xrightleftharpoons[]{\substack{\Delta H^\circ_{298} = -31.6\ \mathrm{kJ/mol} \\ \Delta G^\circ_{298} = +32.9\ \mathrm{kJ/mol}}} HCO_2H(l) \qquad (1)$$

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* For Part III see ref. 6c.

** Dedicated to Prof. E.O. Fischer on the occasion of his 75th birthday.

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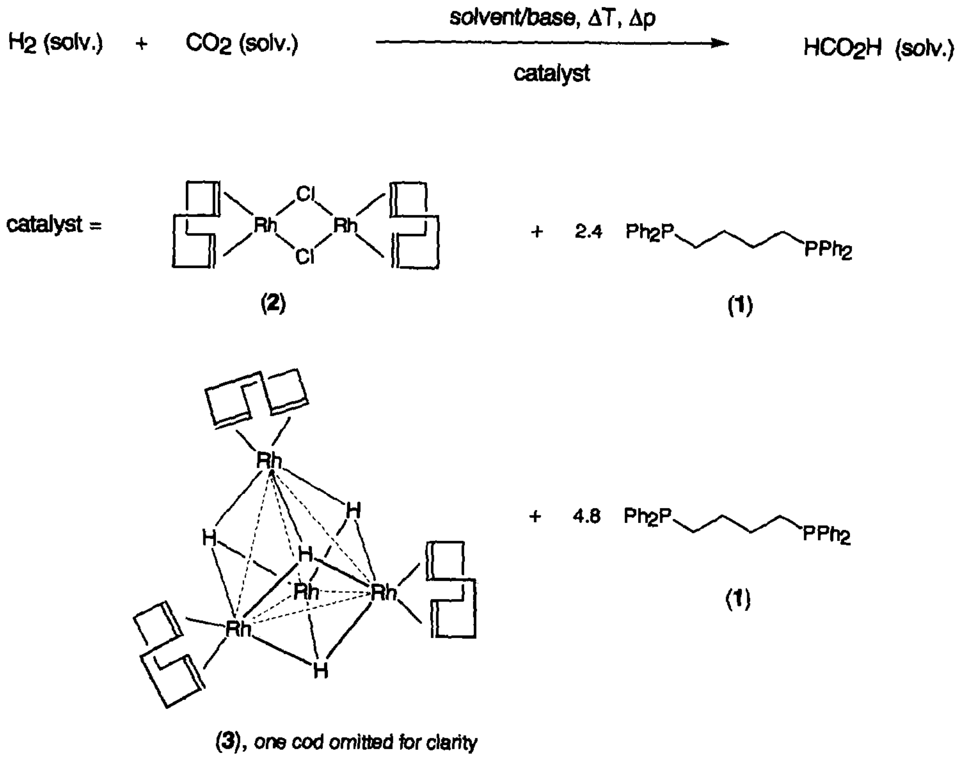

Scheme 1. Rhodium-catalysed hydrogenation of CO_2 to formic acid in organic solvents.

Rhodium(I) phosphane complexes like Wilkinson's catalyst $[Rh(PPh_3)_3Cl]$ were reported as early as 1976 to catalyse CO_2 hydrogenation in benzene solution in the presence of tertiary amines [5a]. The systems showed a better performance when small amounts of water were added, but turnover numbers [9*] did not exceed 150 even under drastic conditions. Investigations by an industrial research group showed that higher yields could be obtained using an isopropanol/amine mixture containing up to 20 vol% water [5g]. Very recently we showed that water soluble rhodium catalysts may be employed in water/amine solutions allowing up to 3440 catalytic cycles within twelve hours under very mild conditions [6c]. Efficient catalytic synthesis of formic acid has also been described using supercritical CO_2 as a solvent and reactant [5h].

The first detailed, mechanistic study of the hydrogenation of CO_2 to formic acid was carried out by Nicholas *et al.* using THF as a solvent and $[(nbd)Rh(MePPh_2)_3][BF_4]$ (nbd = norbornadiene) as a catalyst [5c]. Small amounts of water were shown to be crucial for the formation of an active species which appeared to be a cationic dihydride complex of rhodium under these conditions and performed 64 turnovers in 24 h. Almost at the same time we reported that up to 1150 moles of formic acid per mole rhodium per day may be formed under even milder reaction conditions (40 atm total pressure, room temperature) when a DMSO/NEt_3 mixture is used as solvent and when the catalyst is formed *in situ* from $[\{Rh(cod)(\mu\text{-}Cl)\}_2]$ (**2**) (cod = 1,5-cyclooctadiene) and the bidentate phosphane ligand $Ph_2P\text{-}(CH_2)_4\text{-}PPh_2$ (**1**) [6a]. NMR spectroscopic investigations using the model complexes $[(Ph_2P\text{-}(CH_2)_n\text{-}PPh_2)_2Rh(H)]$ ($n = 2,3$) showed that neutral rhodium hydrides are most likely to be the catalytically active species in DMSO solutions [6b].

In the present paper we describe details of the further development and optimisation of all relevant reaction paramaters of this catalytic system (Scheme 1). Further evidence for the participation of neutral rhodium hydrides in the catalytic cycle is also given and a plausible mechanism is discussed in detail. A few of the results presented in this paper have been included in earlier communications [6a,b].

2. Results and discussion

The final concentration of formic acid and thus the turnover number of a potential catalyst is solely influenced by the equilibrium constant if the reaction is fully reversible. The yield of HCO_2H obtained from hydrogenation of CO_2 in DMSO/NEt_3 catalysed by

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* Reference number with asterisk indicates a note in the list of references.

2/1 follows the trends expected for an exothermic, but endergonic reaction of two gaseous molecules. It rises linearly with pressure in the investigated region from 10–80 atm resulting in a formic acid concentration of 3.54 mol/l at 80 atm and room temperature [6a]. On the other hand, there is a linear decrease of the equilibrium concentration of formic acid with increasing temperature in the investigated temperature range of 22–73°C and a final concentration of only 0.23 mol/l is observed at 73°C and 40 atm. It also becomes clear from eqn. (1) that the unfavourable thermodynamics of the hydrogenation of carbon dioxide are mainly due to entropic reasons. In order to shift the equilibrium to the right it is therefore necessary to decrease the entropic difference between the gaseous substrates and the liquid formic acid. This can be achieved by lowering the entropy of the substrates via solvatation and/or by rising the entropy of formic acid via cleavage of the strong hydrogen bonds.

The concentrations of formic acid in various solvents obtained by reacting CO_2 with H_2 in an approximate 1:1 ratio for 20 h using the *in situ* catalyst **2/1** at a total pressure of 40 atm at room temperature are summarised in Table 1. The formic acid concentration after a reaction time of 20 h correlates qualitatively with the polarity of the solvents. The exceptionally poor results with methanol are probably due to the protic nature of this solvent (*vide infra*). Dipolar aprotic solvents are best suited for CO_2 hydrogenation and formic acid concentrations up to 2.13 mol/l are achieved in DMSO. These solvents dissolve extremely large amounts of CO_2 under the reaction conditions. The solubility of CO_2 in DMSO/NEt_3 under the conditions of Table 1 corresponds to solution of *ca.* 750 ml gaseous CO_2 in 10 ml of the mixture or to approximately 13% CO_2 of the total mass of the liquid phase. The solution of such a large amount of gas leads to an appreciable increase in volume of the liquid phase as visually observed in the high pressure reactor described in the Experimental section. However, no correlation between solubility of CO_2 and final concentration of formic acid is observed, despite the resulting high CO_2 density in the reaction mixture. The solubility of H_2 under the reaction conditions is to small to be determined using the methodology described in the Experimental section, but is certainly higher in nonpolar solvents than in very polar systems [4]. The fact that equilibrium 1 is shifted to the right in polar aprotic solvents can therefore be attributed mainly to the interactions of the strongly polarised solvent molecules with HCO_2H disfavouring hydrogen bonding between formic acid molecules [10*].

In contrast to findings of other groups [5], small amounts of water do not improve the yield of formic acid when added to dipolar aprotic solvent systems under our reaction conditions (Table 2). Higher concentrations of H_2O may even exhibit a negative effect on the performance of the reaction system. The detrimental influence of water must be attributed to a deactivation of the hydrophobic catalyst, as H_2O has been shown to be an excellent solvent for CO_2 hydrogenation when water soluble catalysts are used [6c]. This emphasises the fact that the solvent system does not only determine the equilibrium constant for eqn. (1), but may also strongly affect the activity of the catalyst. Thus, the values in Table 1 do not necessarily correspond to the equilibrium concentrations in all cases, although the reaction time chosen was twice as long as required for equilibration in DMSO/NEt_3 under the given conditions. Despite these limitations, it becomes clear from Tables 1 and 2 that—in agreement with thermodynamic considerations—thoroughly dried

TABLE 1. Influence of solvent parameters [11] on the yield of formic acid obtained from rhodium-catalysed hydrogenation of CO_2

Solvent	μ [Debye]	ϵ	E_T	Solubility of CO_2 [mol/l] at equilibrium pressure [atm] [a]	c (formic acid) [b]
NEt_3	0.8	2.4	33.3	3.70 (22.23)	0.17
THF	1.7	7.4	37.4	5.47 (17.41)	0.37
MeOH	1.65	32.6	55.5	2.09 (21.43)	0.79
acetone	2.7	20.7	42.2	7.23 (16.44)	1.75
DMA [c]	3.8	37.8	43.7	5.99 (21.91)	1.84 [d]
DMSO	3.9	48.9	45	3.40 (17.07)	2.13
DMPU [e]	4.23	36.12	–	3.09 (20.50)	2.10

[a] Determined in a 5:1 mixture of volume of the solvent and NEt_3 under initial pressure of *ca.* 22 atm at room temperature; see Experimental section for details.

[b] Reaction conditions: catalyst = **2/1**, $c(Rh) = 10^{-2}$ mol/l, **1**:Rh = 1.2, T = r.t., $p^0 = 40$ atm, t = 20 h.

[c] DMA is N,N-dimethylacetamide.

[d] Reaction time 16 h.

[e] DMPU is N,N′-dimethylpropylene urea, solvent parameters from [12].

TABLE 2. Influences of addition of base and of water content on the yield of formic acid obtained from rhodium-catalysed hydrogenation of CO_2 in polar aprotic solvents

Solvent	Base	Additive	c (formic acid) [a]
DMSO	–	–	0.034 [b]
DMSO	NEt_3	molecular sieves 3Å	1.74
DMSO	NEt_3	–	1.39
DMSO	NEt_3	100 μl H_2O	1.56
DMSO	NEt_3	200 μl H_2O	0.65
DMSO	NBu_3	–	1.45
DMSO	$HNMe_2$	–	1.02
DMSO	DABCO [c]	–	1.15
DMA	$HNMe_2$	molecular sieves 3Å	1.25
DMA	$HNMe_2$	–	1.03

[a] Reaction conditions: solvent: 5 ml, c(base) = 1.20 mol/l, catalyst = 2/1, c(Rh) = 5×10^{-3} mol/l, 1:Rh = 1.2, T = r.t., p^0 = 40 atm, t = 6.5 h.

[b] c(Rh) = 6×10^{-3} mol/l.

[c] DABCO is 1,4-diazabicyclo[2.2.2]octane.

polar aprotic solvents should be employed for the hydrogenation of carbon dioxide using hydrophobic phosphane complexes of rhodium as catalysts.

The addition of amines is a necessary prerequisite for high yields of formic acid, as already noted in earlier communications [6a,c]. The results in Table 2 show that various amines can be used, but tertiary amines like triethylamine and tributylamine are most effective. These amines form heterogeneous mixtures with DMSO at ambient pressure with most of the catalyst formed from **2** and **1** being dissolved in the DMSO phase as judged from the colours of the two layers. Homogeneous solutions are obtained in the presence of formic acid and the DMSO/NEt_3 system also becomes homogeneous at higher CO_2 pressures. The CO_2 effect is reversible and two separate layers are obtained again when the pressure is released. Hydrogen pressure up to 20 atm has no visible influence on the DMSO/NEt_3 mixture. The homogeneity of the mixture can thus be attributed to CO_2 acting as a cosolvent owing to its high solubility under the given conditions (Table 1). Thus, the mixture consists of a single phase at any time under the reaction conditions as confirmed visually during experiments using the high pressure reactor described in the Experimental section. Homogeneous DMSO solutions are obtained under any conditions if the bicyclic amine DABCO is used, but the yield of formic acid per NR_3 group is lower in this case, as might be expected from the fact that the two basic centres are fixed in close proximity in the bicyclic structure.

It is important to note, that the role of the amine in the stabilisation of the formic acid is not the formation of a simple 1:1 formate salt. Wagner [13a] and Sekyia [13b] demonstrated that mixtures from HCO_2H and NR_3 form azeotropes in the molar ratio of 3:2 to 6:2. The azeotrope composition of HCO_2H/NEt_3 at 20 atm is almost exactly 5:2 [13b]. Figure 1 shows the calculated formic acid concentration in a DMSO/HCO_2H/NEt_3 mixture as function of the NEt_3 content together with experimental data obtained from CO_2 hydrogenation under standard reaction conditions (DMSO, room temperature, 40 atm total initial pressure). If no amine is added, only very small amounts of formic acid are formed. Up to 30 vol% amine, the ratio HCO_2H/NEt_3 lies quite constant at *ca.* 3:2 (solid line) between the 1:1 salt (dotted line) and the 5:2 azeotrope (dashed line). The presence of DMSO is necessary, however, as indicated by the poor formic acid yield in pure NEt_3 (Table 1).

The rhodium-catalysed formation of formic acid from carbon dioxide and dihydrogen is a very clean process under all conditions tested up to now. Other reduction products like CO, formaldehyde or methanol have never been observed by GC or NMR analysis of the gaseous or the liquid phase in the reaction vessel. In the presence of alcohols, alkylformates are possible products from hydrogenation of CO_2 [7], but methylformate was not detected by ^1H-NMR-spectroscopy when methanol was used as a solvent under the reaction conditions of Table 1. Furthermore, carbon dioxide, hydrogen and dimethylamine are known to react to N,N'-dimethylformamide (DMF) in nonpolar solvents in the presence of transition metal catalysts at rather forcing reaction conditions [8]. However, no DMF was detected by ^1H-NMR spectroscopy under our reaction conditions even if molecular sieves were added to remove any water eventually formed from condensa-

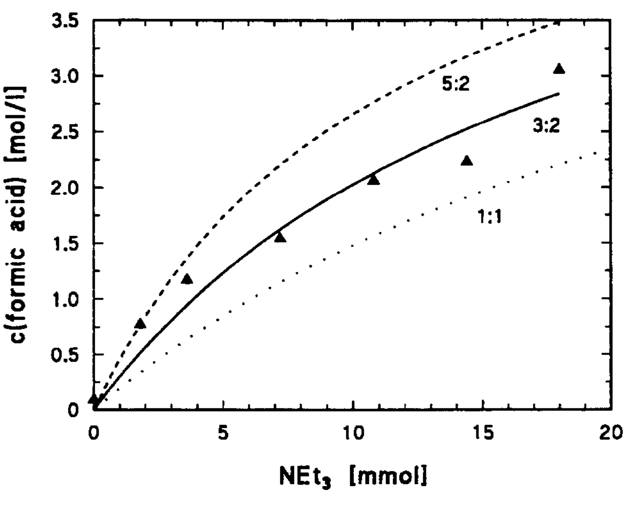


Fig. 1. Ratio HCO_2H/NEt_3 as obtained by hydrogenation of CO_2 in 5 ml of DMSO in the presence of different amounts of NEt_3. Catalyst = 2/1, c(Rh) = 5×10^{-3} mol/l, 1:Rh = 1.2, T = r.t., p^0 = 40 atm, t = 6.5 h.

tion of formic acid and dimethylamine (Table 2). This finding supports the proposal that DMF is formed directly at the metal centre and not via the intermediate formation of formic acid in the above mentioned reaction [8c]. The only side reaction observed during the present study was very slow formation of iso-propanol in some cases when acetone was used as a solvent, depending on the exact conditions and on the catalyst used.

After the reaction conditions have been optimised, several possibilities remain open regarding the activity of the catalyst. The effects of structural changes in the phosphane ligand have already been addressed briefly [6b] and will be the subject of subsequent publications. In the present paper, we wish to concentrate on the nature of the actual catalytically active rhodium species and how it can be produced most efficiently from the *in situ* catalysts.

Kinetic measurements yield valuable information for a better insight into reaction mechanisms and are necessary for quantification and optimisation of the activity of the catalyst. However, the commercial high pressure reactor with sampling device used in earlier investigations [6a] did not allow such experiments on a small scale with reasonable accuracy under reproducible conditions (*vide infra*). Therefore, a modified reactor was designed and used to obtain samples at given time intervals for the determination of the formic acid concentration by ^{1}H-NMR spectroscopy (see Experimental section for details).

Figure 2 shows a typical concentration/time profile as obtained using the acetone/NEt_3 solvent system in order to avoid any complications arising from the heterogeneity of the DMSO/NEt_3 system at ambient pressure. No formation of iso-propanol was observed over the whole course of reaction. The experiment was carried out at room temperature and at an initial total pressure of 40 atm of a 1:1 mixture of CO_2 and H_2 using the *in situ* catalyst **2**/**1**.

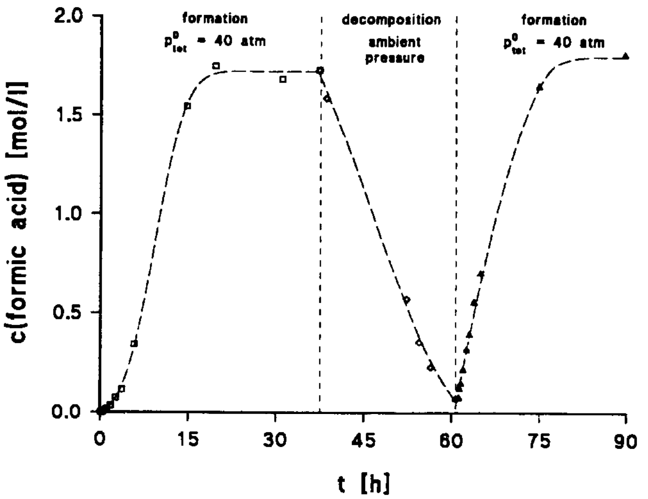


Fig. 2. Reversibility of the rhodium catalysed hydrogenation of CO_2 to formic acid in acetone/NEt_3 (5:1). Catalyst = **2**/**1**, *c*(Rh) = 2.48 $\times 10^{-3}$ mol/l, **1**:Rh = 1.2, T = r.t., $p^0 = 40$ atm. See text for experimental details.

The first set of data points in Figure 2 (□) shows the formation of formic acid using a freshly prepared catalyst solution. During the first four to five hours the reaction rate is continuously increasing. A similar induction period was also demonstrated in DMSO solution, where it was not detected in earlier experiments [8a] owing to technical limitations. The following nearly linear increase in formic acid concentration corresponds to a constant turnover frequency of approximately 54 h^{-1}. Finally, the reaction fades out as the concentration of formic acid reaches the equilibrium value under the given conditions and after 20 h the formic acid concentration remains constant at about 1.7 mol/l. After 40 h the pressure was reduced to 1 atm (◇). Decomposition of formic acid immediately started with a turnover frequency of 30 h^{-1}. The rate of decomposition is nearly constant over the whole observation period, indicating an overall rate law that is zero order or pseudo-zero order in HCO_2H. At a formic acid concentration of 0.07 mol/l the autoclave was re-pressurised with 40 atm of H_2/CO_2 (△). Now, the formation of HCO_2H took place without any initial period and with a turnover frequency of 65 h^{-1} comparable to the maximum rate of the first catalytic run. The final concentration of HCO_2H was identical within experimental error to the one achieved with the freshly prepared catalyst.

Autocatalysis by H^+ might serve as a possible explanation for the observed induction period, but can be ruled out as addition of various amounts of acetic acid prior to reaction has no significant effect on the reaction rate and the induction period. Furthermore, the induction period shows a remarkable dependence on the rhodium concentration, lower concentrations leading to longer induction periods. Finally, the absence of the induction period in the second formation period proves unambiguously that the catalytically active species is formed from the *in situ* catalyst slowly in the early stages of the first catalytic run, but remains active for a long time. In addition to this mechanistic information, the experiment summarised in Fig. 2 clearly demonstrates the full reversibility of the rhodium catalysed hydrogenation of CO_2 to formic acid, a fact that is of special interest in the context of H_2 storage [3].

Figure 3 shows the influence of the ratio **1**/Rh on the catalytic activity of the *in situ* systems **2**/**1** and [{Rh(cod)(μ-H)}$_4$] (**3**)/**1**. The turnover frequency has a

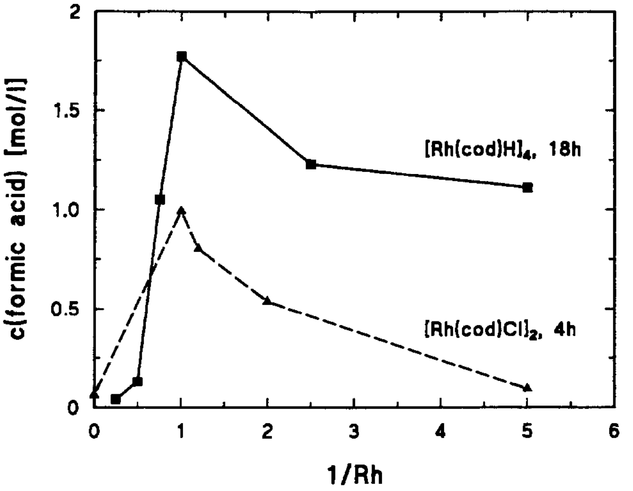


Fig. 3. Influence of the ratio **1**/Rh on the yield of formic acid obtained with the *in situ* catalyst **2**/**1** at $c(\mathrm{Rh}) = 5.0 \times 10^{-3}$ mol/l, after 4 h (▲) and **3**/**1** at 2.50×10^{-3} mol/l after 18 h (■). Reaction conditions: T = r.t., $p^0 = 40$ atm, DMSO/NEt_3 (5:1).

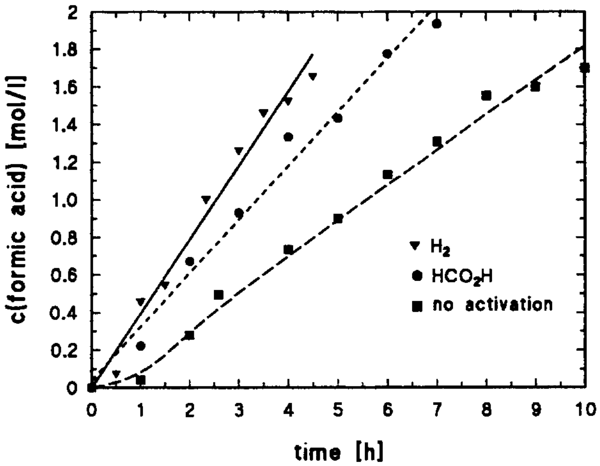


Fig. 4. Activation of the *in situ* catalyst **2**/**1** by treatment with H_2 or HCO_2H prior to reaction. Reaction conditions: $c(\mathrm{Rh}) = 10^{-2}$ mol/l, **1**/Rh = 1.2, T = r.t., $p^0 = 40$ atm, DMSO/NEt_3 (5:1). (■) = no activation; (●) = HCO_2H (0.43 mol/l), 30 min; (▼) = 20 atm H_2, 30 min.

rather narrow maximum at a **1**/Rh ratio of 1:1, indicating that exactly one chelating ligand is bound to rhodium in the catalytically active species. These results strongly support the proposal [6b] that a neutral rhodium hydride species $[(\mathbf{1})\mathrm{Rh(H)}]_x$ (**4**) is the active species in the hydrogenation of CO_2 using the **2**/**1** catalyst system. Intermediate **4** may exist either as monomer ($x = 1$) or as polynuclear hydride bridged cluster ($x = 2$–4) under the given reaction conditions [14].

Reactions of the *in situ* catalyst **2**/**1** with H_2 [15] or HCO_2H [16] in the presence of NEt_3 have been described as forming rhodium hydrides similar to **4**. We found that the induction period is indeed absent when catalyst solutions were treated with either 20 atm of H_2 or with excess HCO_2H for 30 min prior to reaction (Fig. 4). A similar activation of the catalyst precursor by hydrogenation was reported by Nicholas and attributed to the formation of a cationic dihydride species [5c]. The activation of the catalyst does not only result in the disappearance of the induction period, but also results in slightly higher turnover frequencies (21 h^{-1} for no activation, 29 h^{-1} for activation with HCO_2H

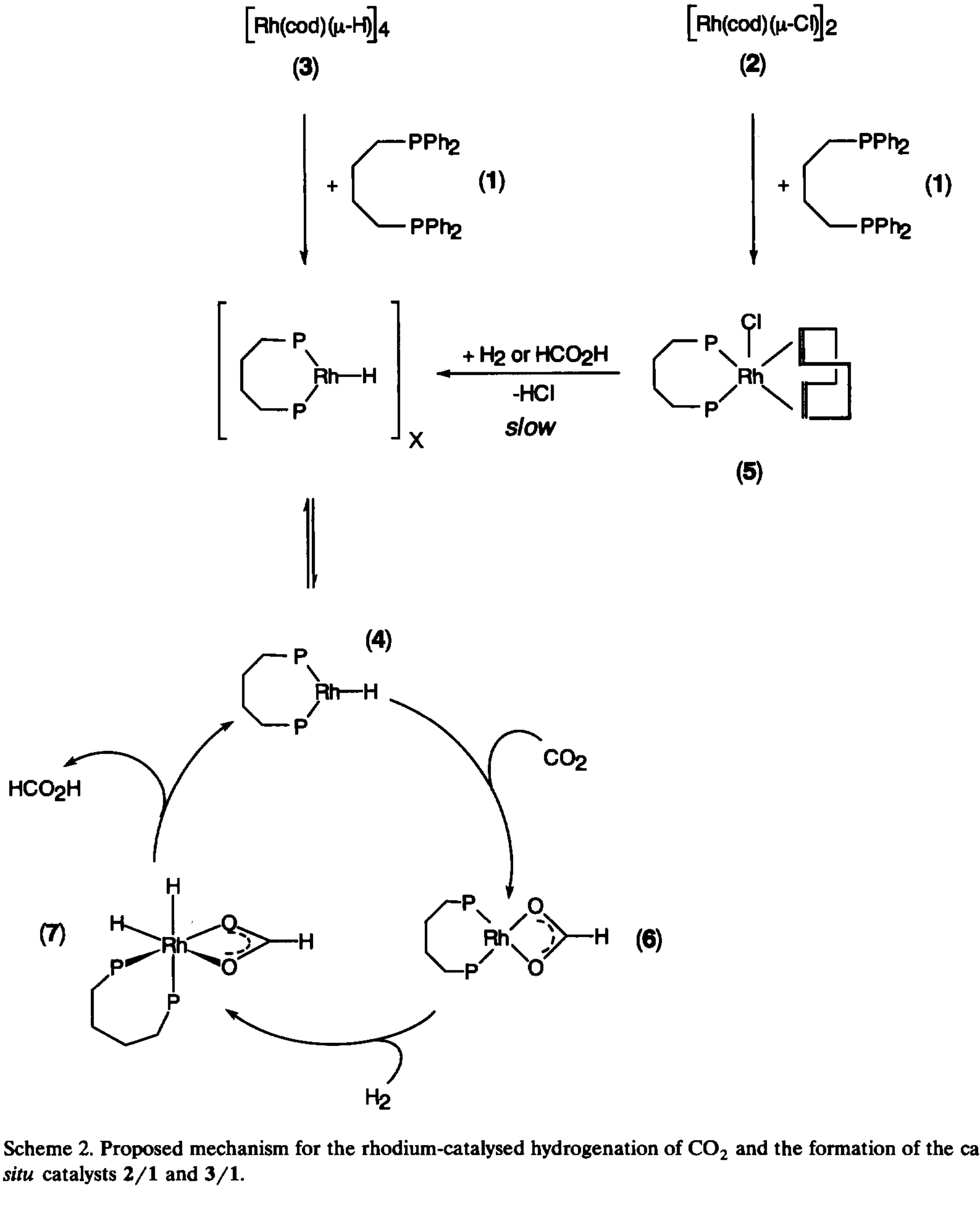
TABLE 3. Hydrogenation of CO_2 to formic acid with various rhodium catalyst systems

Catalyst	c(Rh) [mol/l]	Activation	t [h]	$c(HCO_2H)$ [a] [mol/l]	Turnover number
$[\{\mathrm{Rh(cod)}(\mu\text{-Cl})\}_2]$ (**2**)	5.17×10^{-3}	–	20	0.062	12
2 + **1** (**1**/Rh = 1.2)	5.11×10^{-3}	–	6	1.29	252
2 + **1** (**1**/Rh = 1.2)	1.02×10^{-2}	HCO_2H, 30 min	6	1.78	174
2 + **1** (**1**/Rh = 1.2)	5.01×10^{-2}	H_2, 20 atm, 30 min	6	2.03	405
$[\mathrm{Rh(nbd)}(\mathbf{1})][CF_3SO_3]$ [b]	1.04×10^{-2}	HCO_2H, 60 min	18	1.26	121
$[\mathrm{Rh(nbd)}(\mathbf{1})][CF_3SO_3]$ [b]	5.17×10^{-3}	H_2, 1 atm, 20 min	18	0.93	180
2 + PPh_3 (PPh_3/Rh = 2.4)	1.05×10^{-2}	HCO_2H, 20 min	18	1.21	115
$[\mathrm{HRh(PPh_3)_3}]$	1.02×10^{-2}	HCO_2H, 45 min	19	1.66	163
$[\{\mathrm{Rh(cod)}(\mu\text{-H})\}_4]$ (**3**)	8.87×10^{-3}	–	18	0.19	21
3 + **1** (**1**/Rh = 1.2)	7.87×10^{-4}	–	18	1.73	2198
3 + **1** (**1**/Rh = 1.2)	6.13×10^{-3}	–	0.8	1.91	312
$[\mathrm{Rh_2(OAc)_4}]$ + **1** (**1**/Rh = 0.62)	2.05×10^{-2}	HCO_2H, 20 min	18	2.16	105
$RhCl_3 \times nH_2O$ + **1** (**1**/Rh = 1.2)	1.03×10^{-2}	HCO_2H, 15 min	18	1.29	125
Rh/C, 5% [c]	–	–	18	n.d. [d]	0

[a] Reaction conditions: solvent = DMSO/NEt_3 (5:1), T = r.t., $p^0 = 40$ atm.
[b] nbd = norbornadiene.
[c] Solvent = acetone/NEt_3 (5:1).
[d] n.d. = not detected.

and 39 h^{-1} for activation with H_2), although the same catalytically active species **4** is most probably present in all cases. It can therefore be concluded that the concentration of the actual catalyst is different in all three experiments owing to different selectivities for the formation of **4** under the corresponding conditions. It is noteworthy, that CO_2 was introduced before hydrogen in all catalytic runs unless H_2 was used for activation. We found that the catalytic activity is extremely low and does not improve during the reaction when the catalyst solution formed from **2**/**1** in DMSO/NEt_3 is stirred under 20 atm of CO_2 for more than one hour instead of introducing H_2 immediately. After stirring a catalyst solution for thirty minutes under 20 atm of CO_2, a formic acid concentration of only 0.43 mol/l was observed after a reaction time of six hours under the conditions of Fig. 4. It can therefore be concluded that a side reaction involving CO_2 reduces the rhodium concentration available for the formation of **4**.

Table 3 summarises the results obtained with different rhodium compounds as catalysts or precursors, used either directly or in the presence of **1** under various conditions. The presence of a phosphane ligand is a necessary prerequisite for high activity and stability of the catalyst. Metallic rhodium is sometimes observed in the absence of a stabilising ligand, but like



Scheme 2. Proposed mechanism for the rhodium-catalysed hydrogenation of CO_2 and the formation of the catalytically active species from the *in situ* catalysts **2**/**1** and **3**/**1**.

Rh/C shows no catalytic activity. Rhodium compounds in oxidation state II or III can serve as catalyst precursor albeit with reduced activity. Most probably, they are reduced to Rh^I species under the given reaction conditions or during the activation process [16b]. Even after activation, the cationic rhodium complex $[Rh(nbd)(\mathbf{1})][CF_3SO_3]$ is far less active than the related *in situ* system **2/1**, strongly suggesting that neutral hydrides are the active species, rather than cationic dihydrides as under the conditions described by Nicholas *et al.* [5c]. This is further emphasised when triphenylphosphane is used as a ligand, as neutral monohydride and the *in situ* system may be compared directly in this case.

Stimulated by the good agreement of all experimental data and the mechanistic proposal, the hydride bridged cluster **3** was used as catalyst precursor in the presence of 4.8 equiv of **1**. It was hoped that replacement of cod by **1** would lead directly to the postulated intermediate **4** thus yielding a very active catalytic system without the need for any activation. The system showed a high efficiency under standard conditions and up to 2200 turnovers could be achieved at a rhodium concentration of 7.87×10^{-4} mol/l. A reaction using a rhodium concentration ten times higher was stopped after fifty minutes and ^1H-NMR spectroscopical analysis revealed a formic acid concentration of 1.91 mol/l corresponding to a turnover number of 312 and a turnover frequency of 375 h^{-1}. The latter value corresponds to the highest catalytic activity reported for CO_2 hydrogenation to formic acid in conventional solvent systems. We therefore conclude that species **4** is indeed the catalytically active intermediate and propose the mechanistic cycle shown in Scheme 2 based on our earlier model [6b].

The reaction sequence summarised in Scheme 2 readily explains the formation of **4** from **2/1** and **3/1**. The induction period and the activation can be rationalised by slow conversion of the chloride complex **5** to the desired hydride **4** upon reaction with H_2 [15] and HCO_2H [16c], respectively. Reaction of **5** with CO_2 to form carbonate or bicarbonate complexes may account for the less effective conversion of **2/1** to **4** in the presence of CO_2 [17]. Once **4** is formed, it inserts CO_2 to yield **6** by analogy with the reaction of the model complex $[(Ph_2P{-}(CH_2)_3{-}PPh_2)_2RhH]$ with CO_2 [6b]. Carboxylate complexes similar to **6** have been synthesised recently by Werner *et al.* via an independent route [18]. Scheme 2 also explains the decline of the catalytic activity in the presence of more than one equivalent of **1** per rhodium centre, as complex **4** is expected to react immediately with excess **1** to form $[(\mathbf{1})_2RhH]$, which is anticipated to be a rather poor catalyst owing to its 18e configurations [6b].

3. Conclusion

In conclusion, thermodynamical and mechanistic considerations have led to the development of a very efficient catalytic system for the rhodium-catalysed formation of formic acid from carbon dioxide and dihydrogen. Up to 2200 mole of HCO_2H per mole of rhodium with turnover frequencies as high as 375 h^{-1} can be achieved using the *in situ* catalyst **3/1**. All experimental results can be explained on the basis of the catalytic cycle outlined in Scheme 2 involving neutral rhodium monohydride complexes as key intermediates. The nature of the species formed from **3** and **1** and its reactivity towards H_2 and CO_2 is currently under investigation and more detailed kinetic studies are under way in order to verify our mechanistic proposal.

4. Experimental section

The rhodium complexes used as catalysts were prepared according to the following literature procedures or slight modifications thereof: **2** [19], **3** [20], $[Rh(nbd)(\mathbf{1})][CF_3SO_3]$ [21] $[Rh_2(OAc)_4]$ [22], $[HRh(PPh_3)_3]$ [23]. PPh_3 was purchased from Strem Chemicals and used as received. **1** was synthesised from 1,4-dibromobutane and $LiPPh_2$ in THF according to ref. 24.

4.1. Catalytic runs

In a typical catalytic run **2** (7.4 mg, 30.0 μmol Rh) and **1** (15.4 mg, 36.0 μmol) were dissolved in 5.0 ml of the appropriate dried and deoxygenated solvent under argon and NEt_3 (1.0 ml) was added. The mixture was transferred to a 100 ml stainless steel autoclave that had been evacuated and purged with argon three times. The reactor was pressurised first to 20 atm with CO_2 and then to a total of 40 atm with H_2. The pressure dropped to about 35 atm as soon as stirring was commenced due to solution of CO_2 in the solvent system. The reaction mixture was vigorously stirred for the desired reaction time at room temperature using a magnetic stirring bar. After venting, 30 μl of mesitylene was added as internal standard to 1 ml of the solution and the formic acid concentration was quickly determined directly in this mixture by ^1H-NMR spectroscopy at 60 MHz. The turnover numbers were calculated from the formic acid concentration and the initial rhodium concentration neglecting the change of volume due to HCO_2H formation. This simplification becomes relevant only at higher formic acid contents and a deviation of 7.5% is calculated for 2.0 M HCO_2H

under the assumption that there are no excess volumes in the $DMSO/NEt_3/HCO_2H$ system.

4.2. Kinetic measurements

The experiments summarised in Fig. 4 were carried out according to the above procedure in a 500 ml autoclave equipped with a dip tube to obtain liquid samples. This proved unsatisfactory for more detailed kinetic studies and therefore a special reactor was designed, based on a 250 ml stainless steel high pressure vessel with heavy glass windows designed for pressures up to 200 atm. An additional 500 ml reservoir for the gaseous reactants can be connected to ensure a nearly constant pressure throughout the reaction and a pressure transducer allows online recording of the pressure in the system with 0.1 atm accuracy. The whole apparatus can be evacuated to 5×10^{-3} atm using a rotary vane pump guaranteeing a reproducible oxygen free atmosphere after purging with CO_2 or argon and repeating the procedure three times. Reaction temperatures above room temperature can be achieved with an electric heater. The reaction vessel can be equipped with either a standard two blade stirrer or a gas entrainment impeller and the stirring rate is adjustable. Furthermore, an external pump permits the addition of liquids to the reaction system under reaction conditions. Gaseous and liquid samples can be taken from the reactor under working conditions. The use of a 1/16″ capillary and an HPLC valve (SSI) for the liquid sampling device ensures a very small dead volume of 0.05 ml resulting in a large number of samples even if the reactions are carried out on a small scale.

In the experiment described in Fig. 2, a solution of **2** (18.31 mg, 37.13 μmol) and **1** (38.00 mg, 89.10 μmol) in a mixture of 5 ml NEt_3 and 25 ml acetone was pumped within 3 min into the reaction vessel pressurised with 40 atm of an approximate 1:1 mixture of H_2 and CO_2. Stirring was started using a two blade stirrer operating at a constant speed of 750 rpm. Samples of 0.1 ml were taken at known time intervals and instantaneously frozen in liquid nitrogen. The frozen samples were diluted with 0.5 ml acetone/acetone-d_6 (10:1) and ^{1}H-NMR spectra recorded at 200 MHz immediately to determine the HCO_2H/NEt_3 ratio. This procedure ensures that no significant decomposition of formic acid takes place before the HCO_2H concentration is determined. The formic acid concentration was calculated from the HCO_2H/NEt_3 ratio and the initial concentration of NEt_3 (*vide supra*).

4.3. Solubility measurements

The equipment described above was used to determine the solubility of CO_2 in the solvent/NEt_3 mixtures under conditions as closely related to catalytic runs as possible. The reactor was pressurised to $p^\circ \approx 22$ atm with CO_2 and the number of moles n° was calculated from the known volume V° of the vessel using the van der Waals equation for CO_2 [4]. A known volume V^s of the solvent/NEt_3 mixture was pumped into the autoclave while the stirrer was running. The number of moles of CO_2 dissolved was obtained from the difference between n° and the remaining number of moles n' in the gas phase calculated from the pressure p' after introduction of the solvent and the corresponding volume $V' = V^\circ - V^s$. The solubility of H_2 could not be determined by this method as the pressure difference due to solution was too small.

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