

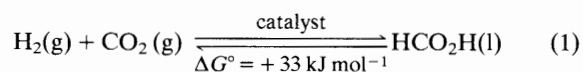
Direct Formation of Formic Acid from Carbon Dioxide and Dihydrogen using the $[\{\text{Rh}(\text{cod})\text{Cl}\}_2]-\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ Catalyst System†

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Formic acid, isolable as sodium formate from the reaction mixture, is produced directly from hydrogen and carbon dioxide with yields up to 1150 moles per mole of rhodium using a homogeneous catalyst formed *in situ* from $[\{\text{Rh}(\text{cod})\text{Cl}\}_2]$ and $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$; the precious metal is recovered during work-up in a catalytically active form.

There is an ongoing interest in the use of carbon dioxide as a C_1 building block in organic chemistry.¹⁻⁴ The hydrogenation of CO_2 to formic acid appears to be a straightforward approach to this goal and has attracted additional attention as a possible way of reversibly storing hydrogen.² Equilibrium (1) lies far to the left under standard conditions,⁵ but it can be shifted to the right by suitable choice of the reaction parameters (elevated pressure, base addition *etc.*). Owing to the relatively inert character of the CO_2 molecule a catalyst is required, however.¹⁻⁴



† cod = cycloocta-1,5-diene; dppb = 1,4-bis(diphenylphosphino)butane.

Rhodium(I) compounds, *e.g.* Wilkinson's catalyst $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$, have been reported to act as catalysts for the hydrogenation of carbon dioxide to yield formic acid⁶ or its derivatives,^{7,8} but turnover numbers were very low even under rather forcing conditions. We now wish to address *in situ* systems consisting of $[\{\text{Rh}(\text{cod})\text{Cl}\}_2]$ † and the bidentate phosphine ligand dppb† as very active catalysts for direct formation of formic acid from carbon dioxide and dihydrogen. Up to 1150 moles of formic acid per mole rhodium are formed at room temperature and an initial total pressure of 40 atm within less than 24 hours.

In a typical experiment $[\{\text{Rh}(\text{cod})\text{Cl}\}_2]$ (60 μmol Rh) and dppb (72 μmol) are dissolved in 5.0 cm^3 of dimethyl sulfoxide under a nitrogen atmosphere and NEt_3 (1.0 cm^3 , 7.21 mmol) is added. The heterogeneous mixture is stirred vigorously for twenty minutes and transferred to a stainless steel autoclave.

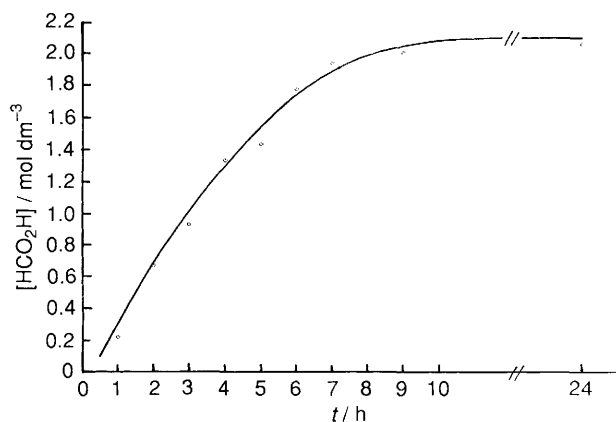


Fig. 1 Time dependence of the formation of formic acid from carbon dioxide and dihydrogen catalysed by $[\{\text{Rh}(\text{cod})\text{Cl}\}_2]$ ($60 \mu\text{mol Rh}$) in the presence of dppb ($72 \mu\text{mol}$) dissolved in a mixture of dimethyl sulfoxide (5.0 cm^3) and triethylamine (1.0 cm^3 , 7.21 mmol) at a total initial pressure of 40 atm

The autoclave is purged three times with carbon dioxide, and pressurised first to 20 atm with CO_2 and then to a total of 40 atm with H_2 . The concentration of formic acid in the homogeneous orange solution obtained after a standard reaction time of 18 hours is determined by ^1H NMR spectroscopy. Concentrations between 1.9 and 2.2 mol dm^{-3} are usually observed under these conditions, corresponding to formation of 190–220 moles of formic acid per mole of rhodium. Under the same initial pressure a formic acid concentration of 1.55 mol dm^{-3} was obtained after 22 hours using a rhodium concentration of $1.35 \times 10^{-3} \text{ mol dm}^{-3}$. The latter experiment corresponds to a yield of 1150 moles of formic acid per mole of rhodium.

No formation of formic acid is observed in the absence of a catalyst or if $[\{\text{Rh}(\text{cod})\text{Cl}\}_2]$ is used without the addition of a phosphine ligand. In the latter case, metallic rhodium is formed, which does not, however, catalyse the hydrogenation of carbon dioxide under the reaction conditions. The addition of a small amount of formic acid *prior* to reaction does not alter the final concentration of formic acid. The addition of base appears to be crucial for high formic acid yields, as the concentration of formic acid is two orders of magnitude smaller if the hydrogenation of carbon dioxide is carried out in the absence of triethylamine under otherwise identical reaction conditions. Nevertheless, under typical experimental conditions the final formic acid:triethylamine ratio is in the range of 1.6:1–1.8:1. It is noteworthy in this context that the system formic acid–triethylamine does not form a simple 1:1 salt, but yields an azeotrope of approximately 5:2 composition.⁹

Fig. 1 shows the time dependence of the concentration of formic acid during hydrogenation of carbon dioxide at a total initial pressure of 40 atm using the catalyst system $[\{\text{Rh}(\text{cod})\text{Cl}\}_2]$ -dppb at a rhodium concentration of $1.0 \times 10^{-2} \text{ mol dm}^{-3}$. The equilibrium concentration is reached within 10 hours. The nearly linear increase in formic acid concentration at the early stage of reaction corresponds to a turnover frequency of 30 moles of formic acid per mole of rhodium per hour. This value increases to 47 h^{-1} at a rhodium concentration of $5.0 \times 10^{-3} \text{ mol dm}^{-3}$.

The yield of formic acid depends linearly on the total initial pressure as shown in Fig. 2. According to eqn. (1), the formation of formic acid is fully reversible and decomposition to hydrogen and carbon dioxide occurs at ambient pressure at a rate comparable to the rate of formation. The decomposition of formic acid by rhodium phosphine complexes is well described in the literature¹⁰ and is utilised, for example, in transfer hydrogenation reactions.¹¹

Upon addition of 1 equiv. of sodium hydroxide per mole of formic acid in the form of 10% aqueous NaOH to the reaction

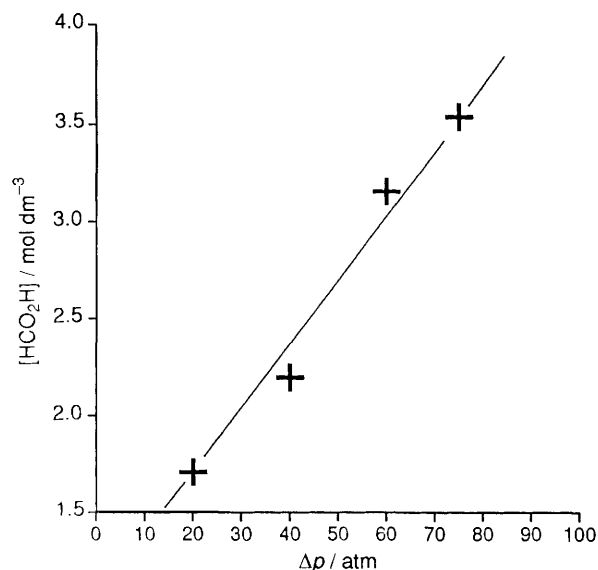


Fig. 2 Pressure dependence of the equilibrium concentration of formic acid formed by rhodium catalysed hydrogenation of carbon dioxide

mixture, an orange precipitate is formed which can be filtered off, washed with water, and dried to give a pale brown powder. This material may be re-used as a catalyst in the presence of excess of phosphine at least ten times with only slight loss of activity. As sodium formate is practically insoluble in dimethyl sulfoxide, it can be isolated in analytically pure form from the filtrate by removal of water and triethylamine under reduced pressure, filtration and washing with diethyl ether. The yield is 91% based on the amount of formic acid present in solution at the end of reaction.

In conclusion we have shown that the *in situ* system $[\{\text{Rh}(\text{cod})\text{Cl}\}_2]$ -dppb catalyses the reversible formation of formic acid from carbon dioxide and dihydrogen very efficiently, thus providing a possible way of activating carbon dioxide and/or storing hydrogen. The wide range of possible rhodium precursors and chelating phosphine ligands provides opportunity for further fine tuning of the catalyst.

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