

Hydrogenation of carbon dioxide to formic acid using a 6,6'-dichloro-2,2'-bipyridine complex of ruthenium, *cis*-[Ru(6,6'-Cl₂bpy)₂(H₂O)₂](CF₃SO₃)₂

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Received 2 November 1994; accepted 13 March 1995

Abstract

The 6,6'-dichloro-2,2'-bipyridine complex of ruthenium, *cis*-[Ru(6,6'-Cl₂bpy)₂(H₂O)₂](CF₃SO₃)₂ **1** in ethanol and in the presence of triethylamine, is a very effective catalyst for the hydrogenation of carbon dioxide to formic acid. The formic acid thus produced formed a salt or an adduct with the amine; yields up to 5000 moles per mole of ruthenium can be achieved. In the absence of triethyl amine, the product is ethyl formate and the turnover number is much lower.

Keywords: Carbon dioxide; Formic acid; Hydrogenation; Pyridine derivatives; Ruthenium; Triethylamine

1. Introduction

Carbon dioxide is a natural and most abundant carbon source and is considered a major atmosphere pollutant, responsible for the greenhouse effect. Therefore it comes as no surprise that there has been widespread and ongoing interest in the use of CO₂ as raw material for chemical synthesis [1]. Although hydrogenation of CO₂ to formic acid seems to be straightforward, there have been only a few reports in the open literature describing this conversion by homogeneous catalysts [2]. One of the major reasons for the scarcity of this reaction is that it is thermodynamically unfavorable [3].

It was reported that complexes of most group VIII transition-metals could be used as catalysts for the homogeneous hydrogenation of CO₂ to

formic acid. Among them, the more active being Pd(Ph₂PCH₂CH₂PPh₂)₂ and RuH₂(PPh₃)₄ [2] (a). But the turnover numbers were all very low even under rather forcing conditions. Cationic complex [Rh(NBD)(PMe₂Ph)₃]⁺ has been found to serve as a precatalyst for the CO₂ to formic acid reaction at moderate temperature in THF solution, with turnover numbers of 10–60/day. The study with this cationic complex has provided the first detailed insight into the mechanism of homogeneous catalytic hydrogenation of carbon dioxide to formic acid [2] (c). Leitner et al. have demonstrated that formic acid could be produced from carbon dioxide and hydrogen with yields up to 1150 moles per mole of rhodium, using homogeneous catalysts formed in situ from [{Rh(COD)Cl}₂] and bidentate phosphines [2] (d,e); and by use of [{Rh(COD)(μ-H)}₄] as precursor, up to 2200 moles of formic acid may

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be formed per mole of rhodium [2] (f). The same authors have also been able to achieve very high turnover numbers (up to 3439) for the same reaction using water-soluble rhodium–phosphine complexes in water–amine mixtures [2] (g). Noyori et al. has recently reported efficient production of formic acid in a supercritical mixture of carbon dioxide and hydrogen containing a catalytic ruthenium(II) phosphine complex. A very high initial rate of reaction –up to 1400 moles of formic acid per mole of catalyst per hour was obtained by use of the supercritical phase. The same reaction under identical conditions but in liquid organic solvent was much slower [2] (h). We now report that the 6,6'-dichloro-2,2'-bipyridine complex of ruthenium, *cis*-[Ru(6,6'-Cl₂bpy)₂(H₂O)₂](CF₃SO₃)₂ **1**, in the presence of triethyl amine, is a very efficient catalyst for the hydrogenation of carbon dioxide to formic acid.

2. Results and discussion

Complex **1** is a versatile catalyst or catalyst precursor for the hydrogenation of olefins and organic carbonyl compounds [4]. It has also been shown to be active for the reductive deoxygenation of aryl ketones [5]. Furthermore, it catalyses the transfer-hydrogenation of unsaturated organic compounds, using formic acid/formate as the hydrogen source [6]. It is this last catalytic property that prompted us to study the catalytic hydrogenation of CO₂ to formic acid with **1**.

The CO₂ reduction reactions were carried out in a 100 cm³ stainless steel autoclave. In a typical run, a 10 cm³ ethanol solution of **1** (concentrations: 2.71 × 10⁻⁴ to 33.9 × 10⁻⁴ mol dm⁻³) was loaded into the autoclave and 2.0 cm³ of NEt₃ was added to the solution. After flushing with CO₂ three times, the system was heated with stirring at 100°C or 150°C and under 60 atm of 1:1 mixture of CO₂ and H₂. At the end of the required length of time, the reactor was cooled rapidly and vented carefully. The amount of formic acid was determined by titration method [7].

Table 1
Hydrogenation of CO₂ to 'formic acid' catalyzed by **1**^a

	[1]/10 ⁻⁴ mol dm ⁻³	Temp/°C	Turnover number ^b
1	33.90	100	450
2	11.90	100	948
3	11.90	100	160 ^c
4	2.71	100	2630
5	16.90	150	800
6	5.64	150	2640
7	2.82	150	5000
8	2.82	150	4650 ^d

^a Reaction conditions: solvent = ethanol (10 cm³), 2 cm³ NEt₃ added, total pressure = 60 atm (CO₂:H₂ = 1:1), reaction time = 8 h.

^b mol of 'formic acid' / mole **1**.

^c No NEt₃ added, the product is ethyl formate.

^d Total pressure = 40 atm (CO₂:H₂ = 1:1).

Results of catalytic hydrogenation of CO₂ by **1** are summarized in Table 1. All reactions reported were carried out in ethanol. In the absence of NEt₃ (entry 3), the product was ethyl formate which was detected by GC. The turnover number in this reaction was determined both by GC and titration method. The results of these two analysis methods agreed quite well. For all other reactions in which NEt₃ was added, no ethyl formate could be detected by GC, apparently, the formic acid produced might have formed a salt or an adduct with the amine. Up to 5000 moles of 'formic acid' per mole ruthenium can be formed (entry 7), this is one of the highest turnover numbers reported so far. Comparison of entries 2 and 3 in Table 1 indicates that turnover number of the reaction with no NEt₃ is about one sixth that of the reaction in which the amine is added. Decreasing the concentrations results in very substantial increase of the yields of 'formic acid'. Similar concentration dependence of the turnover number has also been observed with the Rh catalytic systems reported by Leitner et al. [2] (d). It has been observed that addition of NEt₃ to a solution of **1** (of catalytic concentration) in ethanol led to instant color change from orange red to blue, and that **1** can be regenerated by acidification of the blue solution. We suspect that the blue color is due to a hydroxo complex or a mixture of hydroxo complexes of ruthenium. It is well known that hydroxo-ruthe-

nium complexes can easily form dimers and tetramers in which the ruthenium moieties are linked by hydroxo bridges [8]. Therefore it is not unreasonable to suggest that this dependency of turnover numbers on catalyst concentrations may be due to the formation of higher concentrations of catalytically inactive oligomeric hydroxo-ruthenium complexes in more concentrated solutions of **1**. On a preparative scale, the blue precipitate can be obtained by addition of NEt_3 to a more concentrated solution of **1** in ethanol. However, the limited solubility of this blue precipitate in common organic solvents including ethanol renders NMR study of this species very difficult. Although the blue precipitate is considerably soluble in acetonitrile to give a blue solution initially, this solution gradually turns red, indicating that it may have reacted with acetonitrile. Infrared spectroscopy study of the blue solid did not show the presence of hydroxo group unequivocally. Therefore, much work still has to be carried out for the characterization of this blue species.

The conversion $\text{CO}_{2(\text{g})} + \text{H}_{2(\text{g})} \rightleftharpoons \text{HCOOH}_{(\text{l})}$ occurs with $\Delta H^\circ_{298} = -31.6 \text{ kJ mol}^{-1}$ and $\Delta G^\circ_{298} = +32.9 \text{ kJ mol}^{-1}$, the positive ΔG° value is mainly due to entropic reasons. It is therefore expected that the equilibrium concentration of HCOOH should decrease with increased reaction temperature, and that is what Leitner et al. has found out with their Rh bidentate phosphine systems [2] (f). But in our case, we have learned that increasing the reaction temperature from 100°C to 150°C nearly doubles the turnover numbers (entries 4 and 7). The direct proportionality between turnover numbers and reaction temperature will have to be explained after detailed kinetic and mechanistic studies are performed. It should be noted that the NEt_3 may have shifted the equilibrium to the right by forming a salt or a stable adduct with the formic acid, thus providing a thermodynamic sink for the CO_2 to formic acid reaction. We have not studied the pressure dependence of the formation of 'formic acid', but it has been found that lowering the total pressure to 40 atm ($\text{CO}_2:\text{H}_2 = 1:1$) leads to a less than 10% decrease in the turnover numbers (entries 7 and 8).

There are no grounds at this stage to propose a detailed mechanism for the **1** catalyzed hydrogenation of CO_2 . But we can probably rule out the mechanism involving the intermediacy of metallo carboxylic acid formed by H_2O or OH^- addition to metal carbonyls, since we found no indication for simultaneous (reverse) water gas shift catalysis – free CO was not detected by GC in the gas phase of the CO_2 hydrogenation system. The formation of the blue solution when NEt_3 is added seems to indicate that the mechanism of the catalytic CO_2 reduction reaction in the presence of the amine may be different from that of the reaction which is carried out without the addition of NEt_3 .

Acknowledgements

We gratefully thank The Hong Kong Polytechnic University for financial support.

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