

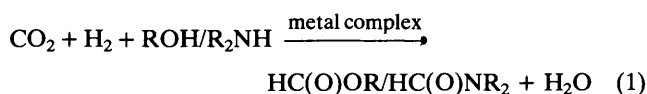
## Reversible Homogeneous Catalysis of Carbon Dioxide Hydrogenation/Reduction at Room Temperature and Low Pressures†

Serge Schreiner, James Y. Yu, and Lauri Vaska\*

Department of Chemistry, Clarkson University, Potsdam, New York 13676, U.S.A.

The reaction between CO<sub>2</sub>, H<sub>2</sub>, and Me<sub>2</sub>NH to yield HC(O)NMe<sub>2</sub> and H<sub>2</sub>O is catalysed by [Pt<sub>2</sub>(μ-dppm)<sub>3</sub>] (dppm = Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>) under unprecedented mild conditions in toluene solution, and the catalysis is readily reversible.

Thermal reduction of carbon dioxide by dihydrogen, mediated by transition metal complexes or supported metals, has routinely been effected under forced conditions. In homogeneous catalysis in solution, the reactions between CO<sub>2</sub>, H<sub>2</sub>, and alcohols (ROH) or amines (R<sub>2</sub>NH) lead to formates<sup>1,2</sup> or formamides<sup>1,3</sup> [equation (1)] and virtually all these conversions have been carried out at elevated temperatures and pressures.<sup>1–3</sup> In heterogeneous catalysis by supported metals, the hydrogenation usually proceeds to methane<sup>4</sup> or methanol<sup>5</sup> [equation (2)] and the processes invariably require high temperatures.<sup>4,5</sup> A notable exception is the reduction of bicarbonate to formate in aqueous solution by supported palladium catalysts under ambient conditions.<sup>6</sup>



Herein we report that a diplatinum complex, [Pt<sub>2</sub>(μ-dppm)<sub>3</sub>] (**1**) (dppm = Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>),<sup>7</sup> is an effective catalyst precursor for reaction (3) under mild conditions. The catalytic synthesis of dimethyl formamide (DMF) takes place in homogeneous solution at room temperature and is clearly observable even under a total pressure of 1 atm of the three reactant gases [equation (3)]. Furthermore, the reaction is readily reversible, unusual for homogeneous catalysis by metal complexes.



Some pertinent results are summarized in Table 1. Two sets of experiments were carried out: under a total pressure of ca. 1 atm (entries 1, 2), and at elevated and varying pressures (entries 3, 4). Under ca. 1 atm, the yield of DMF, obtained at 25 °C, decreased substantially when the reaction solution was

warmed to 50 °C (entries 1a,b). A separate experiment, commencing at 70 °C, gave no DMF or any other product for 5 days (entry 2). The reversibility of the catalysis is further demonstrated by reactions with pressure-temperature variations. Entries 3 and 4 in Table 1 refer to two runs with changing conditions in the sequences shown (a → b → c).

**Table 1.** Reversible catalytic formation of DMF from CO<sub>2</sub>, H<sub>2</sub>, and Me<sub>2</sub>NH in toluene solution (50 ml) mediated by [Pt<sub>2</sub>(μ-dppm)<sub>3</sub>] (3–9 × 10<sup>-5</sup> mol) [equation (3)].<sup>a</sup>

Entry <sup>b</sup>	Reaction temp./°C	Total pressure/atm <sup>c</sup>	Turnover <sup>d,e</sup> DMF/Pt <sub>2</sub> /day
1a	25	0.96	8.7
1b	50	0.83	-5.7
2	70	0.75	0
3a	25	92	240
3b	25	1.4	-180
4a	100	114	1375
4b	100	1.0	-409
4c	25	92	486

<sup>a</sup> Experiments were carried out for periods lasting from one to several days, using a gas burette-manometer system (entries 1, 2) or a Parr pressure vessel (entries 3, 4). Each entry represents a 24 h period. Samples were withdrawn from the reactors and analysed by i.r. and g.c. methods. DMF and Me<sub>2</sub>NH were quantitatively determined on a pre-calibrated carbowax 20 M + KOH g.c. column. Blank runs under the same conditions, *i.e.*, with all the reactants present except the catalyst precursor [equation (3)], gave no catalytic products. <sup>b</sup> Each number refers to a separate experiment, the letters (a, b, c) refer to sequential variation of conditions within that experiment. <sup>c</sup> At reaction temperature. Initial partial pressures of the reactants applied (at 25 °C): entries 1, 2: CO<sub>2</sub> 0.20–0.27; H<sub>2</sub> 0.33–0.51; Me<sub>2</sub>NH 0.14–0.17; entries 3, 4: CO<sub>2</sub> 13.9–87.4; H<sub>2</sub> 20.4–79.6; Me<sub>2</sub>NH 1.0 atm. <sup>d</sup> Yield of DMF: mol per mol [Pt<sub>2</sub>(μ-dppm)<sub>3</sub>] (introduced initially) per day (reaction period). The negative turnover numbers indicate the rates of the reverse reaction, *i.e.*, the disappearance of DMF produced during the preceding reaction period. <sup>e</sup> Since the rates (and equilibria, which were not established under all applied conditions) were found to be dependent on the partial pressures of the individual reactants, the yields of DMF under similar total pressures are not necessarily comparable.

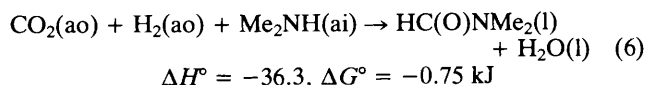
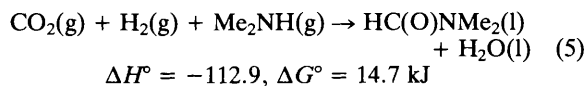
† No reprints available.

Experiment 3a,b indicates that the catalytic synthesis of DMF at 25 °C is reversed simply by lowering the initially applied total pressure. The combined effects of temperature and pressure on the catalytic reversibility of the system are demonstrated by entries 4a,b, and c.

The reverse reaction has been found to be accompanied by an increase in the concentration of dimethylamine, giving additional evidence for the reversibility of the catalysis [equation (3)]; the expected increases in  $p(\text{CO}_2)$  and  $p(\text{H}_2)$  could not be determined with our experimental set-up. A quantitative assessment of the overall material balance is complicated by the formation of dimethylcarbamate [equation (4)], a reversible side-reaction whose equilibrium is itself very sensitive to temperature–pressure variations. The non-catalytic, spontaneous formation of carbamate represents a common reaction between  $\text{CO}_2$  and amines or ammonia.<sup>8</sup>



Although thermochemical values for reaction (3) in toluene are not available, the data<sup>9</sup> in other environments [equations (5), (6)] indicate that there is a delicate balance between the reactants and products which explains the observed ready reversibility thermodynamically. Kinetically, the facile catalysis with an apparently low activation energy may derive from the structural features of the catalyst precursor  $[\text{Pt}_2(\mu\text{-dppm})_3]$ . The complex displays two terminal vacant co-ordination sites and a third one for the insertion into the Pt–Pt bond.<sup>7c</sup> Preliminary data indicate that (i) each of the reactants, when treated separately with  $[\text{Pt}_2(\mu\text{-dppm})_3]$ , displays a markedly different reactivity toward the catalyst precursor,  $\text{Me}_2\text{NH} \gg \text{CO}_2 > \text{H}_2$ , and (ii), it is the applied partial pressures of the three individual gases (and their consequent solubilities in toluene) which determine the rates and equilibria of the reversible reaction [equation (3)]. The selectivity of the DMF synthesis was found to be about 90–95%. The only other catalytic product was trimethylamine.



The mechanism of this complex catalytic system is under active investigation, including the characterization of reaction intermediates and attempts to study the reverse reaction by starting with DMF and  $\text{H}_2\text{O}$ .

This work was supported in part by the Office of Naval Research.

Received, 26th January 1987; Com. 8/00288F

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