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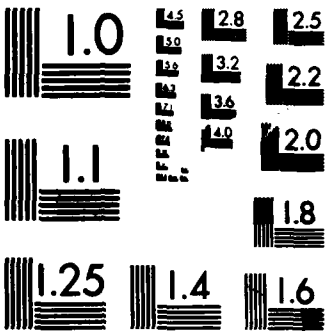

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Reversible Homogeneous Catalysis of Carbon Dioxide Hydrogenation/Reduction at Room Temperature and Low Pressures Mediated by a Platinum(0)-Diphosphine Cluster Complex in Solution

by

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A platinum complex, $[Pt_2(\mu\text{-}PCP)_3]$ (PCP = $(C_6H_5)_2PCH_2P(C_6H_5)_2$), catalyzes the synthesis of N,N-dimethylformamide (DMF) from CO_2, H_2 and $(CH_3)_2NH$ in toluene solution at 25-100°C and total pressures of 0.96-114 atm of the three reactant gases. The turnover numbers, DMF/complex/day, range from 9 at 25°C and 0.96 atm to 1375 at 100°C and 114 atm. The homogeneous synthesis of DMF is readily reversible by either increasing the temperature, lowering the pressure of the reactants, or both, during the catalytic reaction. The formation of DMF appears to be dependent on the partial pressures of the individual reactants. Separate reactions of the three reactants with $[Pt_2(\mu\text{-}PCP)_3]$ at ambient conditions (25°C, 700 torr) give adducts with $(CH_3)_2NH$, but not with CO_2 or H_2.

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Reversible Homogeneous Catalysis of Carbon Dioxide Hydrogenation/Reduction at Room Temperature and Low Pressures Mediated by a Platinum(0)-Diphosphine Cluster Complex in Solution

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Thermal reduction of carbon dioxide by dihydrogen catalyzed by transition metal complexes or supported metals has routinely been effected under forced conditions.[1] In homogeneous catalysis in solution, the reactions between CO_2, H_2 and alcohols (ROH) or amines (R_2NH) lead to formates[2,3] or formamides[2,4] (eq 1), and virtually all these conversions have been carried out at elevated

$$CO_2 + H_2 + ROH,\ R_2NH \xrightarrow{\text{Metal complex}} HC(O)OR,\ HC(O)NR_2 + H_2O \qquad (1)$$

temperatures and pressures.[2-4] In heterogeneous catalysis by supported metals, the hydrogenation usually proceeds to methane[5] or methanol[6] (eq 2), and the

$$CO_2 + 3,4H_2O \xrightarrow{\text{Metal}} CH_3OH,\ CH_4 + 1,2H_2O \qquad (2)$$

processes invariably require high temperatures.[5,6] A notable exception to forced conditions is the reduction of bicarbonate to formate in aqueous solution by supported palladium catalysts at ambient conditions.[7]

We wish to report that a diplatinum complex, $[Pt_2(\mu\text{-PCP})_3]$ (PCP = $(C_6H_5)_2PCH_2P(C_2H_5)_2$),[8] is an effective catalyst precursor for reaction (3) at

$$CO_2 + H_2 + (CH_3)_2NH \xrightleftharpoons{[Pt_2(\mu\text{-}PCP)_3]} HC(O)N(CH_3)_2\ (DMF) + H_2O \qquad (3)$$

mild conditions. The catalysis takes place in homogeneous toluene solution at room temperature and is clearly observable even under a total pressure of less than one atm of the three reactant gases (eq 3). Furthermore, the reaction is readily reversible, an unusual observation in homogeneous catalysis by metal complexes.

Some pertinent results are summarized in Table I. Two sets of experiments were carried out: (a) under total pressures of ca. 1 atm (entries 1,2), and (b) at elevated and varying pressures (entries 3,4). At 25°C and ca. 1 atm, the equilibrium (eq 3) was attained in about 24 h. When the same solution was subsequently warmed to 50°C, the yield of DMF *decreased* substantially (entry 1b), indicating that the reverse reaction (eq 3) had taken place. A separate experiment, commencing at 70°C, gave no DMF or any other product for 5 days (entry 2).

Further evidence for the reversibility of the catalysis is obtained from reactions at higher pressures. Entries 3 and 4 in Table I refer to two runs with pressure-temperature variations in the sequences shown (a→b). Experiment 3a,b demonstrates that the catalytic synthesis of DMF is reversed (eq 3) by simply lowering the initially applied total pressure[9] at room temperature. And the combined effects of temperature and pressure[9] on the catalytic reversibility of the system are shown by entry 4a,b,c.

Although thermochemical values for reaction (3) in toluene are not available, the data in other environments (eq 4,5) indicate that there is a

$$CO_2(g) + H_2(g) + (CH_3)_2NH(g) \rightarrow HC(O)N(CH_3)_2(\ell) + H_2O(\ell)$$

$$\Delta H^\circ = -112.9,\ \Delta G^\circ = 14.7\ kJ \qquad (4)^{10}$$

$$CO_2(ao) + H_2(ao) + (CH_3)_2NH(ai) \rightarrow HC(O)N(CH_3)_2(\ell) + H_2O(\ell)$$
$$\Delta H^\circ = -36.3,\ \Delta G^\circ = -0.75 \qquad (5)^{10}$$

delicate balance between the reactants and products which explains the observed ready reversibility thermodynamically. Kinetically, the facile catalysis with an apparently low activation energy seems to derive from the structural[8d] features of the catalyst precursor, $[Pt_2(\mu\text{-PCP})_3]$. The complex displays two terminal vacant coordination sites and a third one for insertion into the Pt-Pt bond. With CO, a fast reversible reaction gives a dicarbonyl complex, $[(CO)Pt(\mu\text{-PCP})_3Pt(CO)]$ (ν_{CO} = 1940 cm^{-1}), and with oxygen, a peroxo species is produced with this possible formulation, $[Pt(\eta^2\text{-}\mu\text{-}O_2)(\mu\text{-PCP})_3Pt]$ (ν_{O_2} = 827 cm^{-1}).[8b] Measurements of gas uptake of the three reactants (eq 3) individually by $[Pt_2(\mu\text{-PCP})_3]$ in toluene solutions at 25°C and 700 torr showed that dimethylamine forms adducts of indefinite compositions, but there is, perhaps surprisingly, no detectable reaction with carbon dioxide or hydrogen *under these conditions*.[8b] Yet, the activation of both CO_2 and H_2 by $[Pt_2(\mu\text{-PCP})_3]$ under low pressures is implicated by the catalytic results (entry 1, Table I).[11]

The selectivity of the DMF synthesis was found to be about 90-95%. The only other catalytic product was trimethylamine. It should also be noted that in all experiments, the final reaction mixture contained dimethylammonium carbamate, $[(CH_3)_2NH_2]^+[(CH_3)_2NC(O)O]^-$, which is spontaneously (non-catalytically) formed from CO_2 and $(CH_3)_2NH$.[13] Considering all these complications, including the different individual reactivities of the three catalytic reactants toward $[Pt_2(\mu\text{-PCP})_3]$,[9] it is premature to speculate about the mechanism of the overall catalysis (eq 3).[11]

Acknowledgment. This work was supported in part by the Office of Naval Research. We thank P.B. Kaufman and J.K. Hartikainen for helpful experimental assistance.

Table I. Reversible Catalytic Formation of N,N-dimethylformamide (DMF) from CO_2, H_2 and $(CH_3)_2NH$ in Toluene (50 mL) Solution Mediated by $[Pt_2(\mu\text{-PCP})_3]$ (3-9 x 10^{-5} mol) (eq 3)[a]

entry[b]	reaction temp, °C	total pressure, atm[c]	turnover,[d] DMF/Pt_2/day
1a	25	0.96	8.7
1b	50	0.83	-5.7
2	70	0.75	0
3a	25	101	9.3
3b	25	5.4	-8.2
4a	100	114	1375
4b	100	1.0	-409
4c	25	92	486

[a]Experiments were carried out for periods lasting from one to several days and by using a gas burette-manometer system (entries 1,2) or a Parr pressure vessel (entries 3,4). Each entry represents a 24-h reaction period. Samples were periodically withdrawn from the reactors and analyzed by IR and GC methods. DMF was quantitatively determined on a pre-calibrated Carbowax 20 M + KOH GC column. Blank runs under the same conditions, i.e., with all the reactants present except the catalyst precursor (eq 3), gave no products. [b]Each *number* refers to a separate experiment, the *letters* (a,b,c) refer to sequential variation of conditions within that experiment. [c]At reaction temperature. The *initial* pressures of the reactants applied at 25°C ranged as follows: entries 1,2: CO_2, 0.20-0.27; H_2, 0.33-0.51; $(CH_3)_2NH$, 0.14-0.17; entries 3,4: CO_2, 13.9-87.4; H_2, 20.4-79.6; $(CH_3)_2NH$, 1.02 atm. [d]The yield of DMF (mol)/$[Pt_2(\mu\text{-PCP})_3]$ (mol, introduced initially)/day (reaction period). The

Footnote d to Table I contd.

negative turnover numbers indicate the rates of the reverse reaction (eq 3), i.e., the disappearance of DMF produced during the preceding reaction period.

References and Notes

(1) Thermal catalysis of CO_2 reduction is to be distinguished from the systems which operate on supplied photochemical or electrochemical energy and usually at ambient temperatures and pressures. See, for example, these recent papers and the references quoted therein: (a) Kutal, C; Corbin, A.J.; Ferraudi, G. *Organometallics* 1987, *6*, 553-557. (b) Ishida, H.; Tanaka, K.; Tanaka, T. *Organometallics* 1987, *6*, 181-186. (c) DuBois, D.L.; Miedaner, A. *J. Am. Chem. Soc.* 1987, *109*, 113-117.

(2) For recent reviews on CO_2 activation by metal complexes and related reactions, see: (a) Inoue, S.; Yamasaki, N., Eds. *Organic and Bio-organic Chemistry of Carbon Dioxide*; John Wiley and Sons: New York, 1982. (b) Behr, A. In *Catalysis of C_1 Chemistry*; Keim, W., Ed.; D. Reidel: Dortrecht, Holland, 1983; pp. 169-217. (c) Darensbourg, D.J.; Kudaroski, R.A. *Adv. Organometal. Chem.* 1983, *22*, 129-168.

(3) Darensbourg, D.J.; Ovalles, C. *J. Am. Chem. Soc.* 1987, *109*, 3330-3336, and references therein.

(4) (a) Haynes, P.; Slaugh, L.H.; Kohnle, J.F. *Tetrahedron Lett.* 1970, 365-368. (b) Kudo, K.; Phala, H.; Sugita, N.; Takezaki, Y. *Chem. Lett.* 1977, 1495-1496. (c) Phala, H.; Kudo, K.; Sugita, N. *Bull. Inst. Chem. Res., Kyoto Univ.* 1981, *59*, 88-105.

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(6) (a) Denise, B.; Sneeden, R.P.A. *J. Mol. Catalysis* 1982, *17*, 359-366. (b) Iizuka, T.; Kojima, M.; Tanabe, K. *J. Chem. Soc., Chem. Commun.* 1983, 638-639. (c) He, M.-Y.; White, J.M. *J. Mol. Catalysis* 1985, *30*, 415-430. (d) Ref. 5a; and references quoted in the four papers cited above.

(7) Stalder, J.C.; Chao, S.; Summers, D.P.; Wrighton, M.S. *J. Am. Chem.*

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(9) It is actually the applied partial pressures of CO_2, H_2 and $(CH_3)_2NH$, and the consequent solubilities (concentrations) of the gases, which appear to determine the yield of DMF. The individual pressures were varied from experiment to experiment (footnote *c* to Table I). Thus, runs at similar *total* pressures (and temperatures) are not necessarily comparable. For example, it has been found that a relatively high CO_2 pressure lowers the yield due, probably, to suppressing the concentration of the active catalyst (cf. entries 3a and 4c, with P_{CO_2} = 87.4 and 13.9 atm, respectively).

(10) Calculated from the ΔH_f° and ΔG_f° values of the reactants and products: (a) *J. Chem. Phys. Ref. Data* 1982, *11*, Supplement No. 2. (b) Dean, J.A., Ed. *Lange's Handbook of Chemistry*, 13th Ed.; McGraw Hill: New York, 1985. (c) For notation of standard states, see ref. 12a.

(11) It is hoped that *in situ* catalytic studies under elevated pressures by using cylindrical internal reflectance coupled with an FTIR spectrometer[12] will shed some light on these and other mechanistic questions.

(12) Moser, W.R.; Chossen, J.E.; Wang, A.W.; Krouse, S.A. *J. Catalysis* 1985, *95*, 21-32.

(13) A common reaction between CO_2 and amines or ammonia; see, for example: Wright, H.B.; Moore, M.B. *J. Am. Chem. Soc.* 1948, *70*, 3865-3866, and references quoted.

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