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Carbon Dioxide Reduction via Homogeneous Catalytic Synthesis and Hydrogenation of *N,N*-Dimethylformamide

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Since the first announcement of carbon dioxide hydrogenation mediated by transition metal complexes in solution [1], a number of studies have been published describing the homogeneous catalytic conversion of CO_2 to formates [2, 3] or formamides [2, 4] (eqn. (1)). These products contain the carbonyl

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

carbon in 2+ formal oxidation state, and it appears that in all previously reported studies the reduction of carbon dioxide in solution catalysis has not proceeded beyond the formate/formamide level. These observations have posed the obvious question about the termination of the CO_2 reduction at bivalent carbon, and have led us to explore methods for reducing carbon dioxide to a lower-valent species (<2+) via homogeneous catalysis. Some results of these investigations, in part preliminary, are reported in this note.

Experimental

The reactants, products and reaction conditions are summarized in Table I. The catalytic solution to be tested was placed into a standard 300 ml pressure vessel, and air was removed by flushing with hydrogen and evacuation. Appropriate gases were added to desired pressures and the reactor was heated at reaction temperature, typically for 24 h. Gas and liquid samples were taken for analysis from the closed reactor initially, prior to heating, and at the conclusion of the experiment at room temperature. The gas phase was analyzed by IR and gas chromatography (GC) using a CTR-1 column (Alltech). Analyses of

TABLE I. Homogeneous Catalytic Synthesis (eqn. (2)) and Hydrogenation (eqn. (3)) of *N,N*-Dimethylformamide (DMF) Mediated by Metal Complexes (0.3–2.6 × 10^{-4} mol) in Solution (50 ml) under Total Pressures of 96–139 atm[a]

Entry	Metal complex[e]	Turnover (product/complex/day[b]) for reactions:		
		Eqn. (2), 125 °C[c]		Eqn. (3), 150 °C[d]
		(i) DMF[f]	(ii) $(CH_3)_3N$	(iii) $(CH_3)_3N$
1	$[Ru(H)(Cl)(CO)(Ph_3P)_3]$	97	15	32
2	$[Ru(H)(Br)(CO)(Ph_3P)_3]$	121	1.0	14
3	$[Ru(Cl)_2(Ph_3P)_3]$	201	1.3	13
4	$[Os(H)(Cl)(CO)(Ph_3P)_3]$	285	52	1.7
5	$[Os(H)_2(CO)(Ph_3P)_3]$	258	6.3	1.8
6	$[Ir(Cl)(CO)(Ph_3P)_2]$	14	1.0	0.6
7	$[Pt_2(\mu\text{-dppm})_3]$	1460[g]	7.4	0.03
8	$\{Pt(Ph_3P)(Ph_3PO)\}$	38	1.0	29
9	$[Rh(Cl)(Ph_3P)_3]$	16	0.4	
10	$[Ir(H)(CO)(Ph_3P)_3]$	47	5.4	
11	$Ru_3(CO)_{12}$[h,i]	74	1.8	
12	$Rh_6(CO)_{16}$[i]	26	0.15	
13	$[Ru(Br)_2(Ph_3P)_3]$			4.0
14	$[Ir(OH)(CO)(Ph_3P)_2]$			0.7
15	$[Pt_2(H)_2(\mu\text{-H})(\mu\text{-dppm})_2]Cl$			19

[a] At reaction temperature. [b] The turnover number represents the yield of the product (DMF or $(CH_3)_3N$) (mol)/metal complex (mol, introduced initially)/day (24 h reaction period). [c] In toluene solution. The initial pressures of the reactants applied at 25 °C ranged as follows: CO_2, 10–12; H_2, 67–94; $(CH_3)_2NH$, 1.0 atm; the total reaction pressures at 125 °C: 96–133 atm. [d] In neat DMF. P_{H_2} at 150 °C: 102–115 atm. In addition to $(CH_3)_3N$, this reaction yielded two, as yet unidentified products. [e] The catalyst precursors are commonly available metal complexes, except **8** (exact nature not established) [7]; **7** [6] and **15** [8], dppm = $Ph_2PCH_2PPh_2$. [f] The use of the following complexes in DMF synthesis has been reported previously: **3**, **6** [1] and **9** [1, 4(c)]. [g] At 75 °C. [h] At 100 °C. [i] The final reaction mixtures contained metal deposits; both experiments produced also methane, *ca.* 1.7 mmol.

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liquid samples were carried out by GC using Super Q (Alltech) and Carbowax 20 M + KOH columns. The latter was used for quantitative determination of amides and amines reported in this note.

The final product solutions were clear, transparent and homogeneous with respect to the metal complex used, except in experiments **11** and **12**, see Table I. In DMF synthesis (eqn. (2)), dimethylammonium dimethylcarbamate was produced as a by-product. The non-catalytic formation of carbamate represents a common reaction between CO_2 and amines or ammonia [5]. Blank runs under the catalytic conditions (Table I), *i.e.* with all of the reactants present except the catalytic precursor, gave no catalytic products. Extensive and thorough cleaning of the reactors was necessary to assure the absence of impurities remaining from the preceding experiments.

Results and Discussion

We have tested a number of transition metal complexes for the catalytic reaction between carbon dioxide, hydrogen and dimethylamine (DMA) (eqn. (2)), with the objective of reducing CO_2 beyond the

$$CO_2 + H_2 + (CH_3)_2NH \xrightarrow[\text{toluene}]{\text{metal complex}} HC(O)N(CH_3)_2 + H_2O/ + (CH_3)_3N \quad (2)$$

C^{2+} state in formamide. All of the complexes employed showed catalytic activity for the previously reported synthesis of *N,N*-dimethylformamide (DMF) [1] (Table I, column (i)). In addition to DMF, however, our experiments yielded trimethylamine (TMA) as a minor product with these selectivities: DMF, 85–99.5; TMA, 0.5–15 mol% (Table I, columns (i) and (ii)). The formation of TMA in the homogeneous catalytic synthesis of DMF by reaction (2) does not seem to have been reported previously.

These results suggested that trimethylamine may represent a secondary product, obtained from the catalytic hydrogenation of DMF produced initially (eqn. (2)). To test this hypothesis, we proceeded to carry out experiments by using neat DMF and hydrogen as starting materials (eqn. (3)). As shown in

$$HC(O)N(CH_3)_2 + 2H_2 \xrightarrow{\text{metal complex}} (CH_3)_3N + H_2O \quad (3)$$

Table I, column (iii), several complexes were apparently indeed active in catalyzing the hydrogenation of DMF to trimethylamine, while others displayed only marginal activity, and some – notably $[Os(H)(Cl)(CO)(Ph_3P)_3]$ (**4**) – gave considerably less TMA than in reaction (2) (*cf.* columns (ii) and (iii)). The latter observations seem to suggest that DMF may act as a catalytic inhibitor under these conditions.

By assuming the interpretation given in eqn. (3), and adding eqns. (2) (excluding the minor product TMA) and (3), we obtain eqn. (4) as the overall

$$CO_2 + 3H_2 + (CH_3)_2NH \xrightarrow{\text{metal complex}} (CH_3)_3N + 2H_2O \quad (4)$$

process which postulates the hydrogenation/reduction of carbon dioxide to the methyl group ($-CH_3$, C^{2-}) incorporated in the tertiary amine (TMA).

In order to ascertain this plausible interpretation, possible non-reductive routes to trimethylamine will also have to be considered. It has recently been reported that tertiary amines undergo scrambling of alkyl groups catalyzed by metallic surfaces [9] or cluster complexes in solution [10], and that secondary and primary amines are also involved in such exchange reactions via heterogeneous [11] or 'melt' catalysis [12]. It is thus conceivable that analogous catalytic reactions are taking place in our reaction systems as well. In the synthesis of DMF (eqn. (2)), the reactant dimethylamine (DMA, used in excess) may react with the emerging DMF (eqn. (5)) and/or

$$(CH_3)_2NH + HC(O)N(CH_3)_2 \xrightarrow{\text{metal complex}} (CH_3)_3N + HC(O)NH(CH_3) \quad (5)$$

undergo disproportionation (eqn. (6)). Both of these reactions yield trimethylamine, and *N*-methyl-

$$(CH_3)_2NH + (CH_3)_2NH \xrightarrow{\text{metal complex}} (CH_3)_3N + CH_3NH_2 \quad (6)$$

formamide (MF) and methylamine (MA), respectively. The latter two species may react further in various ways, e.g.: MA + DMA → TMA + NH_3; MA + DMF → MF + DMA; MA + MF → DMA + FA (formamide, $HC(O)NH_2$), etc. Throughout our studies of DMF synthesis we have not, however, detected CH_3NH_2, NH_3 or $HC(O)NH_2$ as products of reaction (2), and all but a few runs (**3**, **5** and **8**, Table I) did not yield *N*-methylformamide (eqn. (5)) either. These observations, including the relatively small yields of TMA, would tend to discount the disproportionation of DMA (eqn. (6)), but a participation of reaction (5) in the formation of TMA is possible with some of the complexes (**3**, **5** and **8** gave small amounts of MF). For the rest of the experiments in this series, eqn. (2) (where MF was definitely absent), the presently available data appear to suggest that trimethylamine results solely from the hydrogenation/reduction of DMF (eqn. (3)), especially in the runs yielding unequivocal catalytic amounts of TMA (Table I, column (ii), entries **1**, **4**, **5**, **7**, **10**).

In the second series of experiments where neat DMF and hydrogen were the sole starting materials (eqn. (3)), the type of methyl exchanges considered above (eqns. (5) and (6) etc.) cannot take place initially. But it is possible that DMA is formed via the DMF decomposition (eqn. (7)) and will sub-

$$HC(O)N(CH_3)_2 \rightleftarrows (CH_3)_2NH + CO \qquad (7)$$

sequently undergo reactions such as in eqn. (5). We have studied the thermal behaviour of DMF in separate experiments under various conditions and found that at 150 °C and lower pressures (e.g. *ca.* 1 atm H_2) some dissociation into DMA and CO (eqn. (7)) is indeed detectable, but that in blank runs under the conditions comparable to those given in Table I (column (iii)) no decomposition has been observed. Similarly, most of the catalytic experiments, DMF + H_2 (Table I, eqn. (3)), did not yield dimethylamine or carbon monoxide. The latter two species were, however, produced by complexes **1** and **15** (Table I, column (iii)), but a possible role of reaction (7) in the formation of TMA in these runs is not evident. As in the studies of DMF synthesis (eqn. (2)), none of the experiments in this series (eqn. (3)) gave methylamine, ammonia or formamide, and *N*-methylformamide was obtained in some of the cases (**1**, **3**, **4**, **5**, **14**) as a minor product, TMA/MF $\cong$ 3–35. All these findings tend to favor the reductive route to trimethylamine (eqn. (3)) over the non-reductive reaction paths (eqns. (7), (5) etc.), but the available limited data do not allow a definite conclusion at this time. It should be noted in this conjunction that in a previously reported related study the homogeneous catalytic hydrogenation of various amides was carried out with initially added CO (3.4 atm) in the presence of $Ru_3(CO)_{12}$ at 220 °C; with DMF, the turnover for TMA was 2 (*cf.* Table I, column (iii)) [13].

Our studies are continuing with the emphasis on mechanistic investigations.

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