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LETTER

Homogeneous Catalytic Production of Hydrogen and Other Molecules from Water–DMF Solutions

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We wish to report the non-photochemical, non-electrochemical catalysis of hydrogen evolution from aqueous *N,N*-dimethylformamide (DMF) solutions under relatively mild conditions. The recent indirect observations that the catalytic synthesis of DMF mediated by a platinum cluster complex, $[Pt_2(\mu\text{-dppm})_3]$ (dppm = $Ph_2PCH_2PPh_2$), is reversible (eqn. (1)) [1], has led us to investigate the reverse

$$CO_2 + H_2 + Me_2NH \underset{}{\overset{[Pt_2(\mu\text{-dppm})_3]}{\rightleftharpoons}} HC(O)NMe_2 + H_2O \qquad (1)$$

reaction by starting with water and DMF as the initial reactants. (For thermodynamic data for reaction (1), see ref. 1.) While the study of the 'reverse reaction' of a synthetic process has long been practiced in heterogeneous catalysis [2], it appears that in homogeneous systems such reactions have rarely been observed [3] or even attempted, i.e. by using the 'products' as starting materials [4].

Experimental

Reactions were carried out in 250-ml round-bottom flasks fitted with a side arm, thermometer and condenser and connected to a vacuum system. The metal complex, DMF (Baker Analyzed reagent) and distilled water were placed into the reactor, air was removed by evacuation and nitrogen gas was introduced to 500–670 Torr (N_2: Linde high purity dry grade, 99.99%). The reaction mixture was heated to 100 °C (or 120 °C in some experiments, not detailed in this note), and a transparent, homogeneous solution of the metal complex in DMF–H_2O resulted. Vigorous (magnetic) stirring was maintained throughout the experiment, and the total pressure of the system was monitored by a manometer in the closed, constant volume apparatus. Typically, after a 24-h period, the solution was cooled to room temperature, the pressure change recorded, and gas and liquid samples were taken for analysis. Gaseous samples were withdrawn via the vacuum system into an evacuated IR cell and analyzed by IR spectroscopy (qualitatively and semiquantitatively, CO_2, CO, Me_2NH (if detectable)), and then quantitatively by GC by using a hot wire detector and a stainless steel CTR 1 column packed with an activated molecular sieve (outer column) and a Porapak mixture (inner column). The yields of the gaseous products (Table 1) represent those found in the gas phase (major fraction) plus small amounts dissolved in solution [5]; since no data are available for DMF–H_2O solutions, the solubilities in DMF and H_2O were used separately and combined according to the individual volumes of H_2O and DMF employed (Table 1). Liquid samples were withdrawn through a serum cap covering the side arm and analyzed by a GC flame-ionization detector and using a Carbowax 20 M + KOH column. Subsequently, new N_2 was added to the system (to compensate for the pressure decrease due to the gas sample withdrawn), and the solution was re-heated for another 24-h period, etc. The time interval at 25 °C, between two reaction periods, was 1–4 h.

Results and Discussion

The results of the catalytic reaction between H_2O and DMF are summarized in eqns. (2)–(4) and Table 1. The following observations should be noted. (i) No gaseous or liquid products other than those indicated (Table 1) were detected; in particular, formic acid (cf. eqn. (7)) was not found. (ii) Entries 1–3 refer to blank runs in which one or more of the catalytic reactants were absent. (iii) The remainder of the data (entries 4–14) shows evidence for the catalysis (eqns. (2)–(4)). The majority of the experiments involved $[Pt_2(\mu\text{-dppm})_3]$ as the catalyst precursor, as this species was found to be the most active complex tested. (iv) According to eqn. (2), the yields of the three products, H_2, CO_2 and Me_2NH, are expected to show ratios of 1:1:1. Instead, we note throughout Table 1 that the observed yields consistently behave as a 1 H_2:~0.5 CO_2: ~0 Me_2NH.

$$H_2O(l) + HC(O)NMe_2(l) \xrightarrow[N_2,\,100\,°C]{\text{metal complex}} H_2(g) + CO_2(g) + Me_2NH(g) \qquad (2)$$

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TABLE 1. The reaction between water and DMF under nitrogen (500–900 Torr)[a] at 100 °C catalyzed by metal complexes ($0.8-1.0 \times 10^{-4}$ mol) in homogeneous H_2O–DMF solutions[b]

Entry[d]	Reactants (ml)		Metal complex	Time (days)[e]	Product yield per complex[c]			
	H_2O	DMF			H_2	CO_2	Me_2NH	CO
1		50		5	0	0	0	0
2a		50	$[Pt_2(\mu\text{-dppm})_3]$	1	0	1.8	(0)	0.50
2b				2	0	2.8	0.10	1.3
2c				6	0	4.1	0.8	2.5
3	10	40		7	0	0	0	0
4a	10	40	$[Pt_2(\mu\text{-dppm})_3]$	1	12	6.2	(0)	1.5
4b				2	12	5.9	0.48	1.7
4c				4	13	5.8	(0)	(0)
4d				6	16	5.2	(0)	1.3
5a[f]	10	40	$[Pt_2(\mu\text{-dppm})_3]$	1	(0)	2.2	(0)	f
5b				3	4.4	2.2	(0)	f
5c				4	9.4	4.6	(0)	f
5d				6	13	6.4	(0)	f
6a	2	48	$[Pt_2(\mu\text{-dppm})_3]$	1	7.2	3.8	(0)	1.3
6b				2	8.9	4.6	(0)	0.6
7a	15	35	$[Pt_2(\mu\text{-dppm})_3]$	1	15	6.8	(0)	0.68
7b				2	15	5.6	(0)	0.64
8a	25	25	$[Pt_2(\mu\text{-dppm})_3]$	1	40	21	(0)	1.4
8b				2	52	26	0.27	2.5
9a	30	20	$[Pt_2(\mu\text{-dppm})_3]$	1	15	6.6	0.24	0.56
9b				2	15	6.9	0.12	0.65
10	10	40	$[Ru(Cl)_2(Ph_3P)_3]$	3	7.5	3.1	(0)	0
11	10	40	$[Ru(H)(Cl)(CO)(Ph_3P)_3]$	3	8.5	5.2	(0)	0
12	10	40	$[Os(H)(Cl)(CO)(Ph_3P)_3]$	2	5.0	3.0	0.24	0
13	10	40	$[Rh(Cl)(CO)(Ph_3P)_2]$	1	3.0	1.4	(0)	0
14	10	40	$[Ir(Cl)(CO)(Ph_3P)_2]$	1	9.2	4.6	(0)	0

[a] The pressures in different experiments ranged as follows: (i) initial (N_2) at 25 °C, 500–670 Torr; (ii) at the conclusion of the first 24-h reaction period at 100 °C, 615–900 Torr (increase due to product gases and temperature increase); (iii) + ΔP after the first 24-h reaction period at 25 °C, 5–180 Torr (due to gaseous products); the latter range reflects the variation of yields as well as the different total volumes of the closed systems used (522–718 ml). [b] For procedures and analytical methods, see 'Experimental'. [c] Yield of product (mol) per metal complex (mol, introduced initially), ±10–15%. (0) = trace amounts detected, quantification not meaningful. [d] Each number refers to a separate experiment, the letters (a, b, c...) refer to sequential data obtained within that experiment. [e] 24-h reaction period at 100 °C. [f] Reaction carried out under CO, 550 Torr (initially at 25 °C).

$$Me_2NH(g) + 0.5CO_2(g) \underset{100\ °C}{\overset{25\ °C}{\rightleftarrows}} 0.5[Me_2NH_2]^+[Me_2NC(O)O]^-(cr) \qquad (3)$$

Eqns. (2) + (3):

$$H_2O(l) + HC(O)NMe_2(l) \xrightarrow[N_2,\ 100\ °C \rightarrow 25\ °C]{\text{metal complex}} H_2(g) + 0.5CO_2(g) + 0.5[Me_2NH_2]^+[Me_2NC(O)O]^-(cr) \qquad (4)$$

The interpretation of this apparent discrepancy is given in eqns. (2)–(4). The non-catalytic, spontaneous and rapid formation of carbamate (eqn. (3)) represents a common reaction between CO_2 and amines or ammonia [6], but the equilibrium of reaction (3) is very sensitive to temperature–pressure variations. In the present case, CO_2 and Me_2NH are catalytically produced in the hot solution where they remain dissociated, then enter the gas phase (their solubilities are minimal at 100 °C), and travel to the colder regions of the reactor where the reaction occurs (eqn. (3)), as evidenced by the appearance of white crystals of carbamate (identified by IR) on the surface of the condenser. Note that the gaseous and liquid samples were taken for analysis at 25 °C, so that the carbamate formation was apparently quantitative at this temperature. However, it was impossible to determine the amount of carbamate formed since most of the crystals simply disappeared upon opening the reactor. Separate experiments confirmed this property of $[Me_2NH_2]^+$-$[Me_2NC(O)O]^-$: the compound (identified by IR) is stable only in the presence of its components,

CO_2 and Me_2NH; i.e. in air, the crystals decompose into their gaseous precursors (identified by IR). It should be emphasized that the stoichiometry of the reaction between carbon dioxide and dimethylamine is always as shown in eqn. (3), that is, $2Me_2NH{:}1CO_2$. (v) With most of the metal complexes used, the catalytic rates have been found to decline with time within the periods of observation (usually 6 days), attributable to catalyst deactivation. For the Pt compound (entries 4–9), a likely candidate for this process is the reaction of $[Pt_2(\mu\text{-dppm})_3]$ with carbon monoxide (eqn. (5)) which has been established in separate experiments. Carbon monoxide is an inhibitor for reaction (2) as demonstrated by the comparison of runs 4 and 5, and some CO is always found in the reaction mixtures involving the platinum catalyst (Table 1). (vi) A number of experiments were carried out in which the ratio of the reactants, H_2O:DMF, was varied (entries 4, 6–9). It is seen that the yields are dependent on the initial concentrations of H_2O and DMF, and that the rate becomes maximum for the ratio 1:1 (entry 8), in agreement with the stoichiometry given in eqn. (2).

$$[Pt_2(\mu\text{-dppm})_3] + 2CO \rightleftharpoons [Pt_2(CO)_2(\mu\text{-dppm})_3] \quad (5)$$

For the overall reaction between H_2O and DMF (eqn. (2)), there are several possible routes from the reactants to products, e.g. eqns. (6)–(8) or some combinations thereof. Note that the routes considered here do not refer to mechanisms, which would require the inclusion of elementary steps of reactant–catalyst–intermediate interactions within each type of reaction path. Some mechanistic studies of the catalytic DMF synthesis (eqn. (1), but with other complexes) have been reported before [7, 8], including a detailed kinetic investigation using $[Rh(Cl)(Ph_3P)_3]$ as the catalyst precursor [8], but no definite conclusions as to the reaction course were reached.

A. Carbon monoxide route:

$$HC(O)NMe_2 \rightleftharpoons CO + Me_2NH \quad (6a)$$

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \quad (6b)$$

B. Formic acid route:

$$HC(O)NMe_2 + H_2O \rightleftharpoons HC(O)OH + Me_2NH \quad (7a)$$

$$HC(O)OH \rightleftharpoons H_2 + CO_2 \quad (7b)$$

C. Carbamic acid route:

$$HC(O)NMe_2 + H_2O \rightleftharpoons H_2 + Me_2NC(O)OH \quad (8a)$$

$$Me_2NC(O)OH \rightleftharpoons CO_2 + Me_2NH \quad (8b)$$

Except for eqn. (8a), all of the individual processes indicated have precedents in previously observed reactions involving the respective species. At present, there appears to be no definite evidence for the support of any of the possible routes shown (A, B, C). With regard to the question of the source of hydrogen atoms in the product H_2 (eqn. (2)), mechanistic considerations suggest that if route B or C is operative, one atom would originate from DMF (H-$C(O)NMe_2$) and the other from water, while in the case of route A, water is obviously the source for both hydrogens. Discrimination between the different routes by the use of deuterated species (D_2O, $DC(O)NMe_2$) would be difficult due to the known H–D exchange reactions involving N–H and O–H bonds and catalyzed by the same or similar complexes as employed in the present study [7, 9]. Further work is in progress and detailed results, together with a discussion of mechanisms for both the forward (eqn. (1)) and reverse (eqns. (2)–(4)) reactions, will be reported in a subsequent communication.

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