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

by

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) The reaction between water and N,N-dimethylformamide (DMF) at 100°C under nitrogen (<1 atm) mediated by several metal complexes in homogeneous H ₂ O-DMF solutions proceeds as follows: H ₂ O + HC(O)NMe ₂ → H ₂ + CO ₂ Me ₂ NH (in some cases, CO is also obtained as a minor product). One half of the CO ₂ produced reacts rapidly <i>in situ</i> with essentially all of the Me ₂ NH to give [Me ₂ NH ₂] ⁺ [Me ₂ NC(O)O] ⁻ , so that the observed yields behave as 1 H ₂ :~0.5 CO ₂ :~0 Me ₂ NH. The metal complexes used include [Ru(Cl) ₂ L ₃], [Ru(H)(Cl)(CO)L ₃], [Os(H)(Cl)(CO)L ₃], [Rh(Cl)(CO)L ₂], [Ir(Cl)(CO)L ₂] (L = Ph ₃ P), and [Pt ₂ (μ-dppm) ₃] (dppm = Ph ₂ PCH ₂ PPh ₂). The latter is the most active catalyst with turnover numbers up to 40 (H ₂ /complex/day). Variation of the starting H ₂ O-DMF ratio (1:24 to 1:0.67) shows that maximum yields result when H ₂ O:DMF = 1:1. Initial addition of CO retards the reaction significantly. The various possible routes of this complex catalytic system are briefly examined.			
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Homogeneous Catalytic Production of Hydrogen and Other Molecules from
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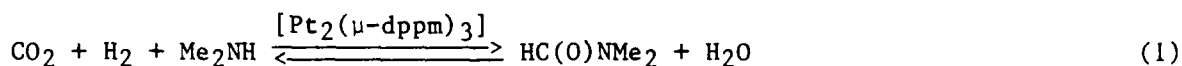
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Summary: The reaction between water and DMF at 100°C under nitrogen (<1 atm) mediated by platinum, ruthenium, osmium, rhodium or iridium complexes leads to the evolution of H₂, CO₂, and CO as a minor product; Me₂NH is also obtained, but it reacts *in situ* with one half of the CO₂ produced to yield [Me₂NH₂]⁺[Me₂NC(O)O]⁻. The various possible steps in this complex catalytic system are briefly examined.

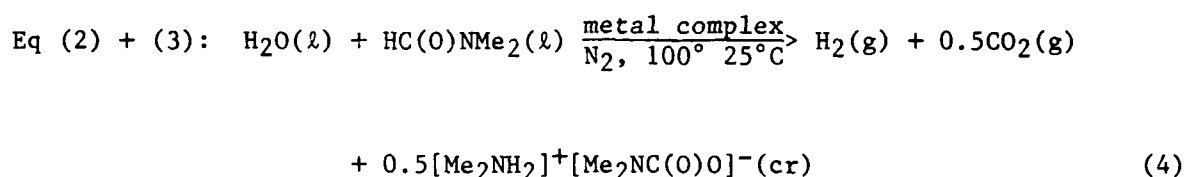
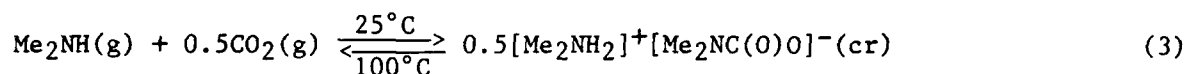
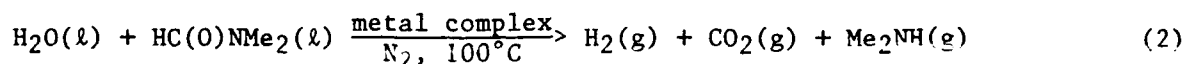
We wish to report a non-photochemical, non-electrochemical catalysis of hydrogen evolution from aqueous solutions at mild conditions. The recent indirect observations that the catalytic synthesis of N,N-dimethylformamide (DMF) mediated by a platinum cluster complex, [Pt₂(μ-dppm)₃] (dppm = Ph₂PCH₂PPh₂), is reversible (eq 1),¹ has led us to investigate the



reverse reaction by starting with water and DMF as the initial reactants. While the study of the "reverse reaction" of a synthetic process has long been practiced in heterogeneous catalysis,² it appears that in homogeneous

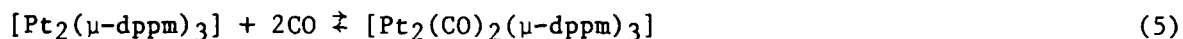
systems such reactions have rarely been observed³ or even attempted, i.e., by using the "products" as starting materials.⁴

The results of the catalytic reaction between H₂O and DMF are summarized in eq (2-4) and Table I.⁵ (i) Entries 1-3 refer to blank runs in



which one or more of the catalytic reactants were absent. (ii) The remainder of the data (entries 4-14) shows evidence for the catalysis, eq (4). The majority of the experiments has involved [Pt₂(μ-dppm)₃] as the catalyst precursor, as this species was found to be the most active complex tested. (iii) According to eq (2), the yields of the three products, H₂, CO₂ and Me₂NH, are expected to show these ratios: 1:1:1. Instead, we note throughout Table I that the observed yields consistently behave as 1 H₂:~0.5 CO₂:~0 Me₂NH. The interpretation of this apparent discrepancy is given in eq (2-4). The non-catalytic, spontaneous, and rapid formation of carbamate (eq 3) represents a common reaction between CO₂ and amines or ammonia,⁷ but the equilibrium of reaction (3) is very sensitive to temperature-pressure variations. In the present case, CO₂ and Me₂NH 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 (eq 3), as evidenced by the appearance of white crystals of carbamate on the condenser's surface. (iv) 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, 6-9), a likely candidate for this process is the reaction of $[\text{Pt}_2(\mu\text{-dppm})_3]$ with carbon monoxide (eq 5) which has



been established in separate experiments.⁸ Carbon monoxide is a definite 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 I). (v) A number of experiments was carried out in which the ratio of the reactants, $\text{H}_2\text{O}:\text{DMF}$, 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 eq (2).

For the overall reaction between H_2O and DMF (eq 2), there are several possible routes from the reactants to products, e.g., eq (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* (eq 1, but with other complexes) have been reported before,^{9,10} including a detailed kinetic investigation using $[\text{Rh}(\text{Cl})(\text{Ph}_3\text{P})_3]$ as the catalyst precursor,¹⁰ but no definite conclusions as to the reaction course were reached.

A. Carbon monoxide route:



B. Formic acid route:



C. Carbamic acid route:¹¹



Except for eq (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), but the results, together with some auxiliary data (not included here) and associated arguments, tend to disfavor A and B. In regard to the question of the source of hydrogen atoms in the product H₂ (eq 2), mechanistic considerations suggest that if route B or C is operative, one atom would originate from DMF (H-C(O)NMe₂) and the other from water, while in the case of route A, H₂O is obviously the source for both hydrogens. Discrimination between the different routes by the use of deuterated species (D₂O, DC(O)NMe₂) 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.^{9,14} Further work is in progress, and detailed results, together with a discussion of mechanisms for both the forward (eq 1) and reverse (eq 2-4) reactions, will be reported in a subsequent communication.

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

Table I. The reaction Between Water and DMF under
 Nitrogen (500-900 torr)^a at 100°C Catalyzed by Metal Complexes
 (0.8-1.0 x 10⁻⁴ mol) in Homogeneous H₂O-DMF Solutions (eq 4)^b

entry ^d	reactants, mL			time, days ^e	products, turnover number ^c			
	H ₂ O	DMF	metal complex		H ₂	CO ₂	DMA ^f	CO
1	-	50	-	5	0	0	0	0
2a	-	50	[Pt ₂ (μ-dppm) ₃]	1	0	1.8	(0)	0.50
2b				2	0	1.4	0.05	0.67
2c				6	0	0.69	0.14	0.41
3	10	40	-	7	0	0	0	0
4a	10	40	[Pt ₂ (μ-dppm) ₃]	1	12	6.2	(0)	1.5
4b				2	5.8	3.0	0.24	0.42
4c				4	3.2	1.5	(0)	(0)
4d				6	2.6	0.87	(0)	0.21
5a ^g	10	40	[Pt ₂ (μ-dppm) ₃]	1	(0)	2.2	(0)	^g
5b				3	1.5	0.75	(0)	^g
5c				4	2.4	1.2	(0)	^g
5d				6	2.2	1.1	(0)	^g
6a	2	48	[Pt ₂ (μ-dppm) ₃]	1	7.2	3.8	(0)	1.3
6b				2	4.5	2.3	(0)	0.29
7a	15	35	[Pt ₂ (μ-dppm) ₃]	1	15	6.8	(0)	0.68
7b				2	7.3	2.8	(0)	0.32
8a	25	25	[Pt ₂ (μ-dppm) ₃]	1	40	21	(0)	1.43
8b				1	26	13	0.14	1.25

Table I continued

9a	30	20	[Pt ₂ (μ-dppm) ₃]	1	15	6.6	0.24	0.56
9b				2	7.4	3.4	0.06	0.33
10	10	40	[Ru(Cl) ₂ (Ph ₃ P) ₃]	3	2.5	1.0	(0)	0
11	10	40	[Ru(H)(Cl)(CO)(Ph ₃ P) ₃]	3	2.8	1.7	(0)	0
12	10	40	[Os(H)(Cl)(CO)(Ph ₃ P) ₃]	2	2.5	1.5	0.12	0
13	10	40	[Rh(Cl)(CO)(Ph ₃ P) ₂]	1	3.0	1.4	(0)	0
14	10	40	[Ir(Cl)(CO)(Ph ₃ P) ₂]	1	9.2	4.6	(0)	0

^aThe pressures in different experiments ranged as follows: (i) initial (N₂) at 25°C, 500-670; (ii) at the conclusion of the first 24-h reaction period at 100°C, 615-900 (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). ^bFor experimental procedures and analytical methods, see ref. 5. ^cYield of product (mol) per metal complex (mol, introduced initially) per day (24-h reaction period). Where data are given for several reaction periods of the same experiment, the turnover number (TN) represents the total cumulative yield divided by the number of days indicated. TN, ±10-15%. (0) = trace amounts detected, quantification not meaningful. ^dEach number refers to a separate experiment, the letters (a,b,c,...) refer to sequential data obtained within that experiment. ^e24-h reaction period at 100°C, see ref. 5. ^fDMA = Me₂NH, see eq 4. ^gReaction carried out under CO, 550 torr (initially at 25°C).

References and Notes

- (1) Schreiner, S.; Yu, J.Y.; Vaska, L. *J. Chem. Soc., Chem. Commun.* 1988, 602.
- (2) See, for example, (a) Bond, G.C. *Catalysis by Metals*; Academic Press: New York, 1962, Chapters 16 and 18. (b) Klier, K. *Adv. Catal.* 1982, 31, 243, and references quoted therein.
- (3) Yoshida, T.; Okano, T.; Otsuka, S. *J. Chem. Soc., Chem. Commun.* 1979, 870.
- (4) For some pertinent reviews, see: (a) Collman, J.P.; Hegedus L.S.; Norton, J.R.; Finke, R.G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, California, 1987, Part II. (b) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley: New York, 1986, Chapters 7 and 8. (c) Masters, C. *Homogeneous Transition-Metal Catalysis*; Chapman and Hall: New York, 1981. (d) Parshall, G.W. *Homogeneous Catalysis*; Wiley-Interscience: New York, 1980. (e) Nakamura, A.; Tsutsui, M. *Principles and Applications of Homogeneous Catalysis*; Wiley-Interscience: New York, 1980.
- (5) Procedure and analyses: Experiments 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 (N₂: Linde "High purity dry grade, 99.99%"; our analysis: 0.35% O₂). 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-H₂O 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 (qualitatively and semiquantitatively, CO₂, CO, Me₂NH (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); a Porapak Q column was used as reference. The yields of the gaseous products (Table I) represent those found in the gas phase (major fraction) plus small amounts dissolved in solution;⁶ since no data are available for DMF-H₂O solutions, the solubilities in DMF and H₂O were used separately and combined according to the individual volumes of H₂O and DMF employed (Table I). 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 N₂ 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.

(6) Gas solubility data from Landolt-Börnstein *Zahlenwerte und Funktionen*, 6th ed.; Springer: Berlin, 1962; Part IIb, Chapter 22261.

(7) E.g., Wright, H.B.; Moore, M.B. *J. Am. Chem. Soc.* 1948, 70, 3865, and references therein.

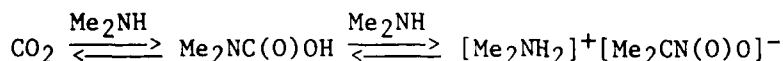
(8) (a) Eq (5) is based on CO uptake measurements in toluene solution, CO:Pt₂ = 2. The resulting dicarbonyl complex shows a $\nu_{\text{CO}} = 1940 \text{ cm}^{-1}$, suggesting that the CO's occupy the two terminal coordination sites,^{8b} in accordance with the molecular structure of [Pt₂(μ -dppm)₃].^{8c} The

carbonylation is reversible and accompanied by striking color changes:
 red + 2CO $\rightleftharpoons$ yellow-(CO)₂.^{8b} (b) Chin, C.-S.; Wier, P.J.; Sennett, M.S.;
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(11) Carbamic acids, including the dimethyl derivative, Me₂NC(O)OH, do
 not seem to exist in the free state, but they represent intermediates in the
 formation of carbamates (cf. eq 3):¹²



Metal-carbamato complexes, M(O₂CNR₂)_n, are, of course, well known,¹³ and
 they may be invoked as catalytic intermediates in these reactions (eq 8).
 In fact, a "carbamate route" has been proposed for the DMF synthesis
 reaction, although the assumed intermediate was formulated as containing
 carbamic acid, H₂Rh(Me₂NC(O)OH)L_n, rather than carbamato ligand.¹⁰

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