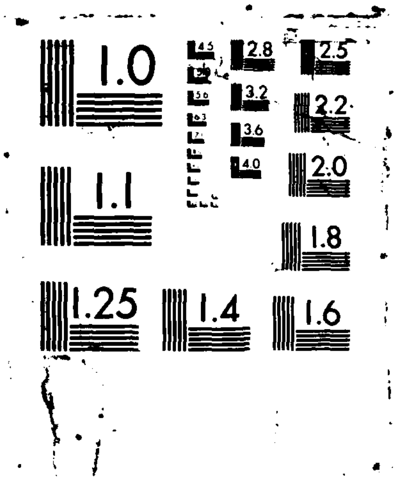
AD-A192 690 CARBON DIOXIDE REDUCTION VIA HOMOGENEOUS CATALYTIC 1/1
SYNTHESIS AND HYDROGEN..(U) CLARKSON UNIV POTSDAM NY
DEPT OF CHEMISTRY S SCHREINER ET AL. 25 FEB 88 TR-2
UNCLASSIFIED N00014-84-K-0658 F/G 7/3 NL


1.0
2.8
2.5
3.2
2.2
3.6
4.0
2.0
1.1
1.8
1.25
1.4
1.6

(4)

OFFICE OF NAVAL RESEARCH

Contract N00014-84-K-0658

R&T Code 413g003--02

Technical Report No. 2

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

by

Serge Schreiner, James Y. Yu, and L. Vaska*

Prepared for Publication

in the

Inorganica Chimica Acta

Clarkson University
Department of Chemistry
Potsdam, NY 13676

February 25, 1988

Reproduction in whole or in part is permitted for
any purpose of the United States Government

This document has been approved for public release
and sale; its distribution is unlimited.

REPRODUCED AT GOVERNMENT EXPENSE

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
Unclassified

1b RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

3. DISTRIBUTION / AVAILABILITY OF REPORT
Approved for public release and sale; its distribution is unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
No. 2

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
Clarkson University

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
Office of Naval Research

6c. ADDRESS *(City, State, and ZIP Code)*
Department of Chemistry (L. Vaska)
Clarkson University
Potsdam, NY 13676

7b. ADDRESS *(City, State, and ZIP Code)*
800 North Quincy Street
Arlington, VA 22217

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
ONR

8b. OFFICE SYMBOL *(If applicable)*
413

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
N00014-84-K-0658

8c. ADDRESS *(City, State, and ZIP Code)*
See 7b

10 SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO

11. TITLE *(Include Security Classification)*
Carbon Dioxide Reduction via Homogeneous Catalytic Synthesis and Hydrogenation of N,N-dimethylformamide

12. PERSONAL AUTHOR(S)
S. Schreiner, James Y. Yu, L. Vaska

13a. TYPE OF REPORT
Technical

13b. TIME COVERED
FROM ________ TO ________

14. DATE OF REPORT *(Year, Month, Day)*
1988/2/25

15. PAGE COUNT

16. SUPPLEMENTARY NOTATION
Submitted for publication in Inorganica Chimica Acta

17 COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
Carbon Dioxide, Hydrogenation, Homogeneous Catalysis, N,N-dimethylformamide, ethyl radical ←

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

The previously reported catalytic reaction between CO_2, H_2 and $(CH_3)_2NH$ to yield N,N-dimethylformamide (DMF) has been found to produce also trimethylamine (TMA) in the presence of several Ru, Os, Rh, Ir and Pt complexes. In separate experiments, the hydrogenation of DMF, catalyzed by the same or other complexes, also gave TMA. Thus, evidence is presented for the overall catalytic reduction of CO_2 to the methyl group ($-CH_3$, incorporated in TMA). Keywords [illegible]

20 DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS

21 ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a NAME OF RESPONSIBLE INDIVIDUAL
L. Vaska

22b TELEPHONE *(Include Area Code)*
315-268-2393/2389

22c OFFICE SYMBOL

DD FORM 1473, 84 MAR
83 APR edition may be used until exhausted.
All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

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

SERGE SCHREINER, JAMES Y. YU and L. VASKA*

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

(Received

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

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

carbonyl 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.

---

*Address all correspondence to this author

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 hr. 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 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 C^{2+} state in

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

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).

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

As shown in 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

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

overall 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)

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

and/or undergo disproportionation (eqn. 6). Both of these reactions yield

$$(CH_3)_2NH + (CH_3)_2NH \xrightarrow{\text{Metal complex}} (CH_3)_3N + CH_3NH_2 \qquad (6)$$

trimethylamine, and N-methylformamide (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

$$HC(O)N(CH_3)_2 \rightleftharpoons (CH_3)_2NH + CO \tag{7}$$

subsequently undergo reactions such as in eqn. (5). We have studied the thermal behavior 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 ≅ 3-35. All these findings tend to favor the reductive route to trimethylamine (eqn. 3) over the non-reductive reduction 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.

Acknowledgements

This work was supported in part by the Office of Naval Research. We thank Phillip B. Kaufman for experimental assistance.

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

		Turnover: product/complex/day[b]		
	Reactions:	Eqn. (2), 125°C[c]		Eqn. (3), 150°C[d]
Entry	Metal Complex[e]	(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

Footnotes to Table I

[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 hr 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.

References

1 P. Haynes, L.H. Slaugh and J.F. Kohnle, *Tetrahedron Letters*, 365 (1970).

2 Recent reviews: (a) S. Inoue and N. Yamazaki (eds.), 'Organic and Bio-organic Chemistry of Carbon Dioxide', Wiley, New York, 1982; (b) A. Behr, in W. Keim (ed.), 'Catalysis of C_1 Chemistry', D. Reidel, Dortrecht, Holland, 1983, p. 169; (c) D.J. Darensbourg and R.A. Kudaroski, *Adv. Organometal. Chem.*, *22*, 129 (1983); (d) A.L. Lapidus and Y.Y. Ping, *Russian Chem. Rev.*, *50*, 63 (1981); (e) D. Walther and E. Dinjus, *Z. Chem.*, *23*, 237 (1983).

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

4 (a) Y. Kiso and K. Saeki, *Japan. Kokai*, *77*, *36,617* (1977); (b) K. Kudo, H. Phala, N. Sugita and Y. Takezaki, *Chem. Lett.*, 1495 (1977); (c) H. Phala, K. Kudo and N. Sugita, *Bull. Inst. Chem. Res.*, *Kyoto Univ.*, *59*, 88 (1981).

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

6 (a) C.-S. Chin, M.S. Sennett, P.J. Wier and L. Vaska, *Inorg. Chim. Acta*, *31*, L443 (1978), and unpublished results; (b) L. Manojlovič-Muir, K.W. Muir, M.C. Grossel, M.P. Brown, C.D. Nelson, A. Yavari, E. Kallas, R.P. Moulding and K.R. Seddon, *J. Chem. Soc.*, *Dalton Trans.*, 1955 (1986).

7 (a) L. Vaska and M.E. Tadros, *J. Am. Chem. Soc.*, *93*, 7099 (1971); (b) M.E. Tadros and L. Vaska, *J. Colloid Interface Sci.*, *85*, 389 (1982).

8 M.P. Brown, R.J. Puddephatt, M. Rashidi and K.R. Seddon, *J. Chem. Soc., Dalton Trans.*, 516 (1978).

9 S.-I. Murahashi, T. Hirano and T. Yano, *J. Am. Chem. Soc.*, *100*, 348 (1978).

10 R.B. Wilson, Jr. and R.M. Laine, *J. Am. Chem. Soc.*, *107*, 361 (1985).

11 G.A. Vedage, R.G. Herman and K. Klier, *J. Catalysis*, *95*, 423 (1985).

12 J.F. Knifton, *J. Chem. Soc., Chem. Commun.*, 412 (1985).

13 R.M. Laine, B.R. Cho and R.B. Wilson, Jr., C_1 *Mol. Chem.*, *1*, 1 (1984).

DL/1113/87/2

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2
Dr. Bernard Douda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code L52 Port Hueneme, California 93401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1

	No. Copies
Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1

END
DATE
FILMED
6-1988
DTIC