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Technical Report No. 5

Catalytic Reduction of Carbon Dioxide to Methane and Other Species via
Formamide Intermediation: Synthesis and Hydrogenation of HC(O)NH_2
in the Presence of $[\text{Ir}(\text{Cl})(\text{CO})(\text{Ph}_3\text{P})_2]$

by

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Prepared for Publication

in

Journal of Molecular Catalysis

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Potsdam, NY 13676

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

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2b. DECLASSIFICATION / DOWNGRADING SCHEDULE				
4. PERFORMING ORGANIZATION REPORT NUMBER(S) No. 5			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
11. TITLE (Include Security Classification) Catalytic Reduction of Carbon Dioxide to Methane and Other Species via Formamide Intermediation: Synthesis and Hydrogenation of HC(O)NH_2 in the Presence of $[\text{Ir}(\text{Cl})(\text{CO})(\text{Ph}_3\text{P})_2]$				
12. PERSONAL AUTHOR(S) L. Vaska, Serge Schreiner, Robert A. Felty and James Y. Yu				
13a. TYPE OF REPORT Technical		13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) 1988/10/13	
15. PAGE COUNT				
16. SUPPLEMENTARY NOTATION Submitted for publication in Journal of Molecular Catalysis				
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Carbon Dioxide, Hydrogenation, Catalysis, Formamide, Methane	
FIELD	GROUP	SUB-GROUP		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) -Formamide, HC(O)NH_2 , is catalytically synthesized from CO_2 , H_2 and NH_3 in homogeneous toluene or alcohol solutions mediated by $[\text{Ir}(\text{Cl})(\text{CO})(\text{Ph}_3\text{P})_2]$. The same iridium compound is used in the catalytic hydrogenation of neat formamide which leads to methane and N-methylformamides. The latter overall reaction is complicated due to the concurrent thermal decomposition of formamide yielding carbon black, NH_3 , CO , CO_2 and H_2O . The various possible steps in this complex catalytic system are briefly examined.				
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

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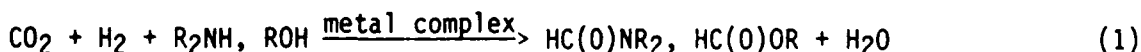
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(Received

Introduction

In search of homogeneous catalytic systems for the hydrogenation/
reduction of carbon dioxide, we have discovered a process that utilizes
ammonia as a co-catalyst and leads to methane as the final reaction
product. Previous studies of CO₂ hydrogenation mediated by metal complexes
in solution have been carried out in the presence of secondary amines or
alcohols, and these reactions have usually led to alkyl-formamides or
formates (eqn. 1) [1-7], that is to say that the CO₂ reduction has



terminated at bivalent carbon, C²⁺ (a notable exception is reported in
ref. [7]). These observations raised the possibility that the bulky alkyl
groups (R) in HC(O)NR₂ or HC(O)OR (eqn. 1) might be responsible for
preventing or suppressing a further reduction - via catalytic hydrogenolysis

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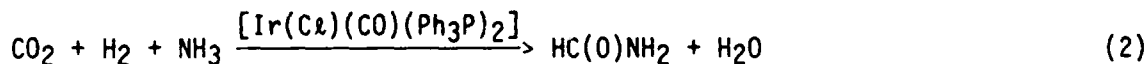
of the C-N or C-O bond - for steric reasons. It occurred to us, therefore, that the use of ammonia instead of amines (eqn. 1) could possibly circumvent this presumed hindrance. Accordingly, a study was undertaken with the objective of catalytically reducing carbon dioxide beyond the 2+ formal oxidation state of carbon via *unsubstituted formamide* intermediation. This goal has indeed been achieved, but the work has also produced some complex and unexpected results. In this note we report some observations on the reactions mediated by *trans*-chlorocarbonylbis(triphenylphosphine)iridium(I).

Experimental

The reactions were carried out in standard 50 (Parr) and 300 ml (Parr and Autoclave Engineers, Inc.) pressure vessels. For typical procedures and analyses of the products, see those of analogous experiments reported in ref. [7].

Results and discussion

We first established that the iridium complex is an effective catalyst precursor for the synthesis of formamide (eqn. 2) [8]. The reactions were

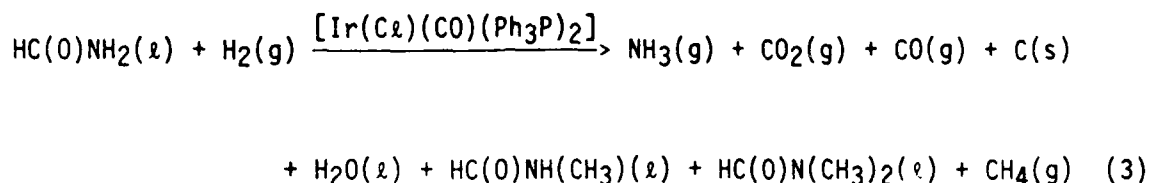


carried out in homogeneous toluene or methanol solutions. Some results are summarized in Table 1 (entries 2, 3; 1 is a blank run). The best yields were obtained in methanol where the products included methylformate and methylformamides (entry 3, see eqns. 11, 9, 10 discussed below).

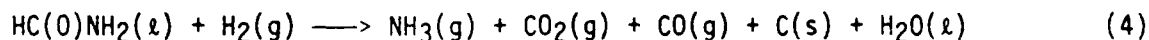
We then proceeded to catalytically hydrogenate neat formamide in the presence of $[\text{Ir}(\text{Cl})(\text{CO})(\text{Ph}_3\text{P})_2]$ under conditions similar to those applied

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for the catalytic preparation of the amide (eqn. 2). The principal results are given in eqn. 3. Separate experiments at analogous conditions, but



without the iridium complex gave the products shown in eqn. 4, i.e., the



blank runs produced five species which were also found among the products of the catalytic experiments (eqn. 3) (there was at least one additional species produced in both sets of experiments).

These surprising results raised the possibility of a catalytic role of the stainless steel components in the pressure reactors used. Thus, additional blank runs were carried out with and without a glass liner (containing the reaction mixture) in the pressure vessel, with and without stainless steel fittings in contact with liquid formamide, and with fittings made of titanium. The results of all these blank experiments were qualitatively identical, i.e., the same products were obtained as given in eqn. 4, and no methane or methylformamides (eqn. 3) were detected. Subsequent studies in all-glass apparatus confirmed that the species produced (eqn. 4) result from a non-catalytic, thermal decomposition of neat formamide [9] (these results will be detailed in another communication.)

In summary, then, the *catalytic* hydrogenation of formamide mediated by $[\text{Ir}(\text{Cl})(\text{CO})(\text{Ph}_3\text{P})_2]$ yielded methane, N-methylformamide (MMF), and, as a

minor product, N,N-dimethylformamide (DMF), eqn. 5 (eqn. 3 minus eqn. 4),

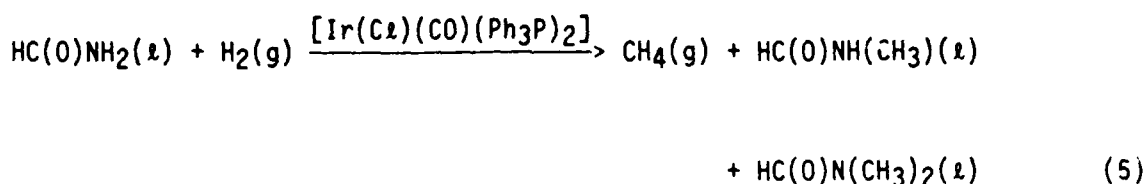


Table 1 entries 5, 6; 4 is a blank run.

The most conspicuous result of all of the experiments, catalytic (eqn. 3) and thermal (eqn. 4), was that the reactions produced copious amounts of black material, found in the reactor at the conclusion of the runs. The black solid, present in powdery and colloidal form, was separated from a faint-yellow solution (containing the Ir complex) and was then heated in oxygen atmosphere, eqn. 6. The product of combustion was carbon dioxide,



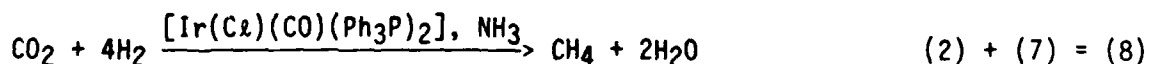
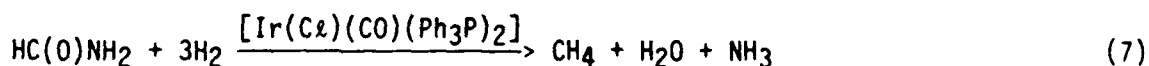
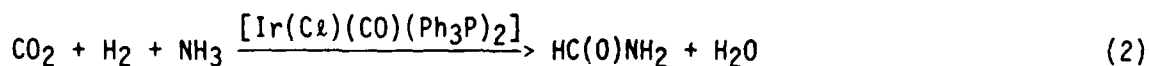
indicating that the black precipitate was elemental carbon; collected yields of C(s) (eqns. 3, 4) were in the 20-50 mmol range.

More importantly, and pertinent to the catalytic studies reported in this note, the heat treatment of the black product in oxygen (eqn. 6) left no solid residue, giving negative evidence for a possible presence of metallic iridium or other Ir-containing species, e.g., IrO₂ (derived from the catalyst precursor, [Ir(Cl)(CO)(Ph₃P)₂]), in our catalytic system (eqn. 3).

There are a number of possible routes for the synthesis of the catalytic products from formamide and hydrogen (eqn. 5), and, ultimately, from CO₂, H₂ and NH₃ (eqn. 2). For the latter reaction, the path is likely

to be analogous with that of the catalytic formation of DMF (eqn. 1, $R = CH_3$), i.e., when, instead of ammonia, dimethylamine is used as a co-reactant [1,2,3,5]. Herein we briefly consider only the second overall phase of the catalytic reduction of carbon dioxide, the hydrogenation of formamide (eqn. 5).

An inquiry into the reaction course leading to methane (eqns. 3, 5) is obviously a complex problem. The thermal decomposition of formamide yields several carbon-containing species (eqn. 4), and these are necessarily produced also in the hydrogenation experiments (eqn. 3). Any one of these products - CO_2 , CO and $C(s)$ - could, in principle, serve as a precursor to CH_4 . Additionally, the catalytic methanation may proceed through (experimentally undetectable) intermediates such as $HC(O)H$, $HC(O)OH$, CH_3OH and/or CH_3NH_2 . Separate experiments are under way to test all these possibilities. At present, one can only summarize the overall stoichiometry of carbon dioxide methanation, formulated in eqns. 2, 7 and 8. It is seen



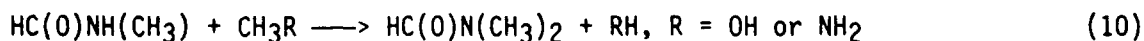
that ammonia emerges as a co-catalyst for this particular process.

Regarding the formation of methylformamides (eqn. 5), we first note that the yield of DMF is only a few percent of that of MMF (Table 1, entries 5, 6). Limited and fragmentary data also indicate that in extended

runs (not detailed here) the formation of MMF occurs initially and then ceases, while a moderate build-up of DMF continues. These observations suggest that DMF is a secondary product and a successor of MMF. We thus propose that N-methylformamide results by the reaction of formamide with a methyl-containing intermediate, CH_3R (eqn. 9), produced by the catalytic

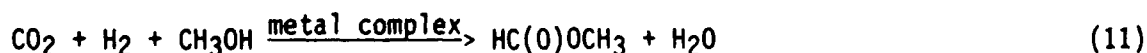


hydrogenation of HC(O)NH_2 or one or more of its decomposition products (eqn. 3), and that DMF is formed subsequently from MMF by reaction with probably the same intermediary species, eqn. 10. Although neither methanol



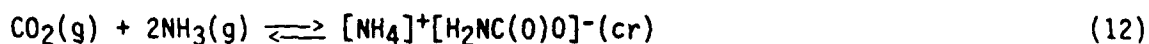
nor methylamine (eqns. 9, 10) were detected in our reaction mixtures, both alcohols [10] and amines [11] are known to react with formamide thermally to yield alkylformamides, and both have been implicated as intermediates in the catalytic synthesis of substituted formamides from $\text{CO}/\text{H}_2/\text{NH}_3$ [12].

Circumstantial evidence for the possibility of CH_3OH intermediation (eqns. 9, 10, $\text{R} = \text{OH}$) in our system is found in the catalytic *synthesis* of formamide (eqn. 2): in methanol solvent the products included methylformate (MF) and methylformamides (Table 1, entry 3), but these species were absent in toluene (entry 2). While the formation of MF represents a well-known catalysis, eqn. 11 [4,5,6], the production of MMF and DMF under these



conditions implies that they result by reactions 9 and 10, respectively (R = OH).

It should be finally noted that all experiments involving carbon dioxide and ammonia as reactants (eqn. 2) or products (eqns. 3, 4) yield ammonium carbamate, eqn. 12 [13]. The equilibrium of this reaction is very



sensitive to temperature-pressure variations, and a possible intermediary role of the carbamate in reactions 2, 3 and 4 is unknown.

Acknowledgements

We thank P. Baltusis, J. Hartikainen and P.B. Kaufman for experimental assistance. This work was supported in part by the Office of Naval Research and the Petroleum Research Fund, administered by the American Chemical Society.

TABLE 1

Catalytic synthesis (eqn. 2) and hydrogenation (eqn. 5) of formamide mediated by $[\text{Ir}(\text{C}_2)(\text{CO})(\text{Ph}_3\text{P})_2]$ ($0.94\text{--}1.93 \times 10^{-4}$ mol) in solution (50-100 ml)^a

Entry ^b	Cat	Reactants	p ^c atm	Solvent	Temp °C	Time days ^d	Product yield per $[\text{Ir}]_{\text{e,f}}$				
							FA	CH ₄	MMF	DMF	MF
1	-	CO ₂ + H ₂ + NH ₃	91	tol	125	1	0	0	0	0	0
2	[Ir]	CO ₂ + H ₂ + NH ₃	86	tol	125	1	14	0	0	0	0
3a	[Ir]	CO ₂ + H ₂ + NH ₃	122	MeOH	125	2	594	0	9	0.2	7
3b						10	1145	0	123	3	33
4	-	H ₂ + FA	109	FA	150	1		0	0.4	0	0
5a	[Ir]	H ₂ + FA	151	FA	100	1		0			
5b			147		125	2		0			
5c			167		150	3		10	93	0	0
5d			164		150	4		37	108	4	0
5	[Ir]	H ₂ + FA	109	FA	150	1		9	36	0.6	0

Footnotes to TABLE 1

^aAbbreviations: Cat = catalyst precursor; [Ir] = $[\text{Ir}(\text{Cl})(\text{CO})(\text{Ph}_3\text{P})_2]$;

tol = toluene; FA = $\text{HC}(\text{O})\text{NH}_2$; MMF = $\text{HC}(\text{O})\text{NH}(\text{CH}_3)$; DMF = $\text{HC}(\text{O})\text{N}(\text{CH}_3)_2$;

MF = $\text{HC}(\text{O})\text{OCH}_3$.

^bEach number refers to a separate experiment, the letters (a,b,c,...) refer to sequential data obtained within that experiment.

^cp = total pressure at reaction temperature (125-150°C). Initial partial pressures of the reactants applied at 25°C: entries 1-3: CO_2 , 13-17; H_2 , 50-68; NH_3 , 1-4; entries 4-6: H_2 , 79-124 atm.

^d24-h reaction period at reaction temperature.

^eTotal cumulative yield of product (mol) per $[\text{Ir}(\text{Cl})(\text{CO})(\text{Ph}_3\text{P})_2]$ (mol, introduced initially), ± 10 -15%.

^fOnly the catalytic products (eqns. 2, 5 and text) are shown, i.e., carbamate (eqn. 12) and other thermally produced species (eqns. 3, 4) are not included.

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