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FORMAMIDES FROM CARBON DIOXIDE, AMINES AND HYDROGEN IN THE PRESENCE OF METAL COMPLEXES

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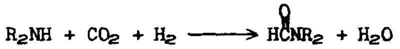
We have discovered what is believed to be a new reaction promoted by certain transition metal complexes. Formamides are formed from carbon dioxide, selected amines and hydrogen (Eq. 1).



$$R_2NH + CO_2 + H_2 \longrightarrow H\overset{O}{\overset{\|}{C}}NR_2 + H_2O \qquad (1)$$

Typically, the catalyst, amine and benzene solvent were placed in an 80-ml autoclave and hydrogen introduced at 400 psi; subsequently, the total pressure was increased to a steady-state 800 psi with carbon dioxide. The vessel was then heated and the contents stirred overnight.

As shown by the data in Table I for the formation of dimethylformamide (DMF), complexes of several metals catalyze the topic reaction under relatively mild conditions. Although the reaction is not fast at 100-125°, it is clearly catalytic and by re-using a portion of the product solution from one experiment as catalyst for the next experiment, a thousand or more moles of DMF per mole of catalyst have been realized (expts. 2 and 7). Of course, in the absence of any catalyst no DMF is produced.

Other secondary amines, such as di-n-propylamine, pyrrolidine and piperidine, also are readily converted to the corresponding formamides in the presence of, e.g., $(Ph_3P)_3RhCl$. Results with primary amines varied. In some instances quaternary ammonium carbamates were formed while in other cases the anticipated N-alkylformamides were produced. N-Ethylformamide was obtained from ethylamine at 125° in the presence of $(Ph_3P)_2(CO_3)Pt$.

Attempts were made to extend the reaction to the preparation of N,N-dimethylthioformamide from carbon oxysulfide or carbon disulfide. However, with $(Ph_3P)_3CuCl$ as catalyst, the reaction of COS, $(CH_3)_2NH$ and H_2 at 100° produced mainly tetramethylurea and a trace of DMF. With CS_2 a black residue resulted from which dimethylammonium dimethylthiocarbamate was isolated.

In view of the diversity of metal complexes that promote formamide formation, it is difficult to propose a single mechanism that would account for all cases. Data have been obtained for a limited number of complexes which exclude certain possibilities but do not prove a specific mechanism.

Tetramethylurea must be considered as a possible intermediate to DMF (Eq. 2) since it

Table I. N,N-Dimethylamide Formation from Carbon Dioxide[a]

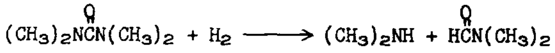
Expt. No.	Catalyst[b]	Amount of Catalyst, mmoles	$(CH_3)_2NH$, mmoles	Temperature, °C	Mmoles DMF/mmole of Catalyst
1	$(Ph_2PCH_2CH_2PPh_2)_2CoH$ (1)	1.08	138	100	5
2	$(Ph_2PCH_2CH_2PPh_2)_2CoH$	0.05[c]	131	125	1,000
3	$(Ph_3P)_3RhCl$ (2)	0.30	122	100	43
4	$(Ph_3P)_3RhCl$	0.02[c]	138	125	>170
5	$(Ph_3P)_2(CO)RhCl$ (3)	0.38	144	100	1
6	$(Ph_3P)_2(CO)IrCl$ (4)	0.35	133	100	28
7	$(Ph_3P)_2(CO)IrCl$	0.2[c]	138	125	1,200
8	$(Ph_3P)_2(CO_3)Pd$ (5)	0.79	159	100	120
9	$(Ph_3P)_2(CO_3)Pt$ (5)	0.70	155	125	104
10	$(Ph_3P)_3Pt$ (6)	0.56	155	125	19
11	$(Ph_3P)_3RuCl_2$ (7)	0.39	132	125	8
12	$(Ph_3P)_3CuCl$ (8)	0.63	133	100	8
13	$(Ph_3P)_3CuCl$	0.03[c]	142	125	>900
14	$H_2PtCl_4 \cdot 6H_2O$	0.56	124	125	11

[a] The conditions for all expts. except 9 and 10 were: benzene solvent, 15 ml; CO_2, 400 psi at room temp.; H_2, 400 psi at room temp. (total pressure, 800 psi); time ~17 hrs. For expts. 9 and 10 the conditions were: benzene solvent, 30 ml; CO_2, 800 psi; H_2, 400 psi; reaction time, ~17 hrs.

[b] References to the literature description of these complexes are given in parentheses.

[c] Approximately one ml. of the product solution from the previous expt. was used as catalyst for this expt.

can be formed from carbon dioxide and dimethylamine (9). However, tetramethylurea is not converted to DMF under the present conditions.



$$(CH_3)_2N\overset{O}{\overset{\|}{C}}N(CH_3)_2 + H_2 \longrightarrow (CH_3)_2NH + H\overset{O}{\overset{\|}{C}}N(CH_3)_2 \qquad (2)$$

To gain mechanistic information, D_2 was employed with $(Ph_3P)_2(CO)IrCl$ as catalyst under the same conditions as expt. 6. The product consisted of 44.5% DMF-d_1 and 55.5% DMF-d_0 and the recovered gas was 20% D_2, 47% HD and 33% H_2 (deuterium contents were determined by mass spectrometric analyses). Obviously, exchange reactions had occurred. Independently, it was shown that dimethylamine in the presence of $(Ph_3P)_2(CO)IrCl$ exchanges with gaseous D_2; however, under the same conditions, DMF is stable to exchange with either dimethylamine, D_2 or D_2O. Any deuteration of DMF must have taken place during its formation and not subsequently.

To minimize exchange complications, the above experiment was repeated and the reaction time limited to 10-15 minutes rather than the usual 17 hrs. The resultant DMF consisted of 90% DMF-d_0 and only 10% DMF-d_1: the recovered gas contained 67% D_2 and 33% of mixed HD and H_2. Similar results were obtained with $(Ph_3P)_3CuCl$ as catalyst.

In the experiment just described, approximately equal molar amounts of D_2 and dimethylamine were present. When the amount of dimethylamine was reduced eight-fold, the isolated DMF consisted of 71% DMF-d_1 and 29% DMF-d_0.

The deuterium content of the product DMF appears to parallel the deuterium content of the amine and not that of the gaseous hydrogen. Indicative of this, with short reaction times the product was mainly DMF-d_0 and the recovered gas mainly D_2, whereas with longer reaction times the relative amount of DMF-d_1 increased as exchange between D_2 and dimethylamine became more extensive. Also, as the amount of dimethylamine was reduced, relative to D_2, its deuterium content from the exchange reaction should increase and more DMF-d_1 would result, as was observed.

These results preclude any mechanism, at least for the iridium system, which involves the formation of the formyl moiety by direct hydrogen cleavage of intermediates such as those shown in eqs. 3-5, since high DMF-d_1 contents should have resulted when the gas was rich in D_2.* Assuming a metal hydride intermediate that has a deuterium content similar to that of the amine,**

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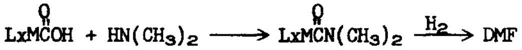
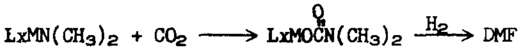
* To account for the deuterium content of the DMF on the basis of discrimination in the cleavage reaction due to the lower reactivity of D_2 relative to H_2, an unusually large isotope effect of ~25 to 35 would have to be invoked.

** Deuterium contents would be similar if the rate of exchange of the metal hydride with the amine were fast compared to the rate of exchange of the metal hydride with gaseous hydrogen.

$$\mathrm{LxMH + CO_2 \longrightarrow LxM\overset{O}{C}OH \xrightarrow{H_2} \left[H\overset{O}{C}OH\right] \xrightarrow{(CH_3)_2NH} DMF} \qquad (3)$$

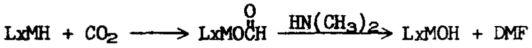


$$\mathrm{LxM\overset{O}{C}OH + HN(CH_3)_2 \longrightarrow LxM\overset{O}{C}N(CH_3)_2 \xrightarrow{H_2} DMF} \qquad (4)$$



$$\mathrm{LxMN(CH_3)_2 + CO_2 \longrightarrow LxMO\overset{O}{C}N(CH_3)_2 \xrightarrow{H_2} DMF} \qquad (5)$$

the following is a possible mechanism for the iridium system which is consistent with the above results:



$$\mathrm{LxMH + CO_2 \longrightarrow LxMO\overset{O}{C}H \xrightarrow{HN(CH_3)_2} LxMOH + DMF} \qquad (6)$$

$$\mathrm{LxMOH + H_2 \longrightarrow LxMH + H_2O} \qquad (7)$$

It is considered pertinent that a cobalt hydride has been shown to react with carbon dioxide to give an intermediate which is converted to methylformate by methyl iodide (10). Presumably the intermediate is a metal formate similar to the one shown in eq. 6.

Undoubtedly, other mechanisms are consistent with the data but only one other possibility will be mentioned at this time. Carbon dioxide may have been reduced to carbon monoxide which in turn reacted with the amines to form formamides. This route cannot be excluded, but it is not favored. With $(Ph_3P)_3RhCl$ as catalyst, no $(Ph_3P)_2(CO)RhCl$ or other metal carbonyl could be detected in the product by I.R. techniques. A metal carbonyl would be expected if free carbon monoxide were formed since $(Ph_3P)_3RhCl$ reacts rapidly with carbon monoxide to form $(Ph_3P)_2(CO)RhCl$ (11) and the latter, we find, does not release its CO, under the present conditions, to form DMF from dimethylamine.

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