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SYNTHESIS OF DIMETHYL FORMAMIDE FROM CARBON DIOXIDE, HYDROGEN AND DIMETHYL AMINE CATALYZED BY PALLADIUM(II) CHLORIDE

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Dimethyl formamide was catalytically synthesized from dimethyl amine, carbon dioxide and hydrogen in the presence of palladium(II) chloride and bases in the methyl cellosolve.

There are some known reactions of the fixation of CO_2 into organic compounds catalyzed by transition metal complexes.$^{1-5)}$ Dimethyl formamide(DMF) has been synthesized from dimethyl amine(DMA), CO_2 and H_2 in benzene in the presence of transition metal complexes,$^{2)}$however , the reaction rates was slow with a low yield.

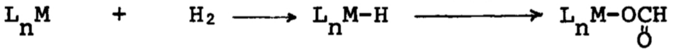
In the course of our studies on the synthesis of alkali metal formates from CO_2, H_2 and aqueous alkali metal hydroxides with palladium(II) chloride($PdCl_2$),$^{6)}$we have found that DMF can be prepared by the reaction of DMA with CO_2 and H_2 in good yield when the reaction is carried out in methyl cellosolve(MC) in the presence of $PdCl_2$ and alkali metal carbonates.

$$HN(CH_3)_2 \quad + \quad CO_2 \quad + \quad H_2 \xrightarrow{PdCl_2/KHCO_3/\text{in MC}} (CH_3)_2NCHO \qquad (1)$$

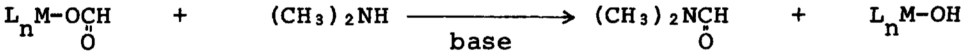
Typically, $PdCl_2$(0.29 mmol), $KHCO_3$(4.5 mmol) and MC solution of DMA(10 mmol/10 ml) were placed in a 30ml stainless steel autoclave and CO_2 was introduced until the pressure reaches to 40atm, subsequently, the total pressure was increased to 120atm with H_2. The vessel was then heated and rocked constantly at 170°C. After reacting for 1.5hr, the yield of DMF was determined by gas chromatography (PEG 20M, 160°C).

Table 1 shows the results of the reactions carried out under various conditions. The data of Runs 1 through 9 show that the MC is effective as solvent, and $PdCl_2$, CO_2 and H_2 are necessary for this reaction. The reaction was enhanced very much by the presence of a base (Run 4,5,11-14); $KHCO_3$, K_2CO_3 and cyclic tertiary amine being the most effective. In the absence of a base, the yield of DMF becomes remarkably lower (Run 9). Such effect of bases has been observed in the synthesis of formates from alcohols, CO_2 and H_2 catalyzed by transition metal complexes.$^{3)}$ In the course of the reaction, $PdCl_2$ is reduced to metallic palladium, however palladium metal itself can also act as an effective catalyst (Run 10).

Although the mechanism of the reaction is not clear at present, the following is suggested as one of the possible courses.$^{2.7)}$



$$L_nM \quad + \quad H_2 \longrightarrow L_nM\text{-}H \xrightarrow{CO_2} L_nM\text{-}O\underset{\overset{\|}{O}}{C}H \qquad (2)$$



$$L_nM\text{-}O\underset{\overset{\|}{O}}{C}H \quad + \quad (CH_3)_2NH \xrightarrow[\text{base}]{} (CH_3)_2N\underset{\overset{\|}{O}}{C}H \quad + \quad L_nM\text{-}OH \qquad (3)$$

Table 1 Formation of DMF from DMA, CO_2 and H_2[a)]

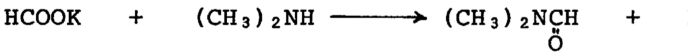
Run	DMA (mmol)	$PdCl_2$ (mmol)	Base (mmol)		Solvent	Temp. (°C)	DMF Yield (mol %)[b)]
1	10.7	0.80	$KHCO_3$	10.0	H_2O	150	15
2	10.2	0.53	"	"	MeOH	"	0
3	11.2	0.52	"	"	Ethylene glycol	"	64
4	10.8	0.13	"	5.7	MC[g)]	"	87
5	10.0	0.29	"	4.5	"	170	99
6	11.6	0	"	9.9	"	150	0
7[c)]	12.3	0.50	"	10.3	"	"	9
8[d)]	10.5	0.51	"	10.2	"	"	0
9	10.2	0.50		0	"	"	12
10[e)]	10.4	0.44	$KHCO_3$	5.6	"	170	62
11	11.2	0.55	K_2CO_3	6.5	"	150	99
12	10.3	0.50	$NaHCO_3$	10.0	"	"	18
13	10.6	0.66	Et_3N	14.4	"	170	18
14	11.1	0.36	DBO[f)]	11.7	"	"	94

a) Reaction condition: Solvent 10 ml, CO_2 40 atm, H_2 80 atm at room temp., Reaction time 5 hr except Run 5(1.5 hr). b) Based on charged DMA. c) Without CO_2. d) Without H_2. e) Pd metal as catalyst. f) DBO: 1,4-Diazabicyclo[2.2.2]-octane. g) MC: Methyl cellosolve.

$$L_nM\text{-}OH + H_2 \longrightarrow L_nM\text{-}H + H_2O \qquad (4)$$

In the $KHCO_3$ system, however, potassium formate was detected in the reaction products after the treatment with excess water. DMF was obtained in some extent even in the absence of CO_2 (Run 7). Therefore, the following route is conceivable for the reaction in the alkali metal carbonates.

$$L_nM\text{-}H + KHCO_3 \longrightarrow HCOOK + L_nM\text{-}OH \qquad (5)$$

 (6)

$$HCOOK + (CH_3)_2NH \longrightarrow (CH_3)_2N\underset{\overset{\|}{O}}{C}H + KOH \qquad (6)$$

$$KOH + CO_2 \longrightarrow KHCO_3 \qquad (7)$$

Further investigations are in progress to elucidate the reaction mechanism, to apply this reaction for other transition metal complexes.

References

1) I.S.Kolomnikov, T.S.Lobekva, and M.E.Vol'pin, Izv. Akad. Nauk SSSR, Ser Khim., 2329 (1970).
2) P.Haynes, L.H.Slaugh, and J.F.Kohnle, Tetrahedron Lett., 365 (1970).
3) Y.Inoue, Y.Sasaki, and H.Hashimoto, J.C.S.Chem.Comm., 718 (1975).
4) Y.Inoue, H.Izumida, Y.Sasaki, and H.Hashimoto, Chem. Lett., 863 (1976).
5) H.Koinuma, H.Kato, and H.Hirai, Chem. Lett., 517 (1977).
6) K.Kudo, N.Sugita, Y.Takezaki, Nippon Kagaku Kaishi, 302 (1977).
7) M.E.Vol'pin and I.S.Kolomnikov, Organometallic Reaction, <u>5</u> 341 (1974).

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