JOURNAL OF CATALYSIS 95, 423–434 (1985)

Chemical Trapping of Surface Intermediates in Methanol Synthesis by Amines

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Received April 4, 1985

The rates of methylisopropylamine synthesis from mixtures of CO/H_2/isopropylamine and CH_3OH/H_2/isopropylamine were studied under methanol synthesis conditions using a Cu/ZnO catalyst. Comparison of the rates of methylation of isopropylamine with carbon monoxide/hydrogen and with methanol demonstrated that the major pathway for isopropylamine methylation was by the reaction of isopropylamine with a methanol precursor and not with the product methanol. In a similar methylation reaction, diethylamine reacted with CO/H_2 and produced methyldiethylamine. In order to determine whether the added diethylamine reacted more rapidly with surface C_1 aldehydic residue, surface formate, or adsorbed CO, the hydrogenation of *N,N*-diethylformamide, a potential intermediate of the reaction of adsorbed CO and surface formate with diethylamine, was studied. The hydrogenation of *N,N*-diethylformamide gave methyldiethylamine as one of the primary products, but the rate of hydrogenation of *N,N*-diethylformamide did not account for the rate of the overall synthesis of methyldiethylamine from CO/H_2/diethylamine. Further, the diethylamine methylation reaction did not interfere with the water-gas shift (WGS) reaction, and the yields of CO_2 and H_2O were exactly those predicted from the WGS reaction rates in the absence of diethylamine but in the presence of an equivalent amount of water. The C_1 methanol precursor undergoing amination was deduced to be an aldehydic type intermediate.

INTRODUCTION

The intermediates involved in the synthesis of methanol from carbon monoxide and hydrogen are not only of fundamental interest because carbon–hydrogen bonds are formed in this reaction without the rupture of the carbon–oxygen bond in the carbon monoxide reactant, but are also of practical interest because these intermediates can be utilized as building blocks in organic syntheses of compounds with carbon–carbon, carbon–nitrogen, and additional carbon–oxygen bonds. Although surface formate and methoxide have been identified by spectroscopic, chemical trapping, and isotopic labeling methods on both Cu/ZnO and related catalysts, it has also been proposed that a formyl, hydroxycarbene, or formaldehyde type intermediate plays a key role in the synthesis (*1–3*). A number of homogeneous catalyzed transformations of synthesis gas (H_2/CO) to oxygen-containing organic compounds have been indicated to occur via metal formyl intermediates (*4–11*). A variety of formyl complexes has been synthesized (*12–22*), and at least some of them could be reduced to yield formaldehyde and methanol (*21, 22*). Infrared spectroscopic evidence for the formation of the formyl from coadsorbed CO and H_2 on the heterogeneous Cu/ZnO catalyst at near-ambient conditions has been reported (*23*).

In this paper, we present evidence that a reactive intermediate involved in the formation of methanol from carbon monoxide and hydrogen over Cu/ZnO catalyst is trapped by amines via a highly efficient formation of a carbon–nitrogen bond that results in the selective synthesis of methylated amines. This intermediate has chemical characteristics of a surface aldehydic residue.

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0021-9517/85 $3.00

EXPERIMENTAL

The Cu/ZnO = 30/70 mol% catalysts were coprecipitated from a nitrate solution by Na_2CO_3, calcined, pelletized, and reduced with 2% hydrogen in nitrogen, according to a procedure previously described in detail (*2*, *24*). A schematic of the catalytic reactor system has been presented (*2*), but a Gilson Model 302 high-pressure unit for pumping liquids into the synthesis gas stream at the reactor pressure of 75 atm has been added at the top of the reactor preheater section. The exit gas was reduced to atmospheric pressure and was sampled by an on-line Hewlett–Packard 5730A gas chromatograph, coupled with a Model 3388A integrator/controller. All products were identified by GC/MS analysis of collected liquid samples by using the Finnigan 4021 GC/MS/Nova system. Quantitative GC analysis of the reactants and products was carried out using a 6-ft. × $\frac{1}{8}$-in. Chromosorb-101 column and a thermal conductivity detector. The relative molar concentrations of all components in the exit stream were determined from the integrated peak areas using response factors of 45 for methanol, 33 for water, 72 for ethanol, 100 for methylethylamine, 125 for diethylamine, 200 for diethylmethylamine, and 215 for triethylamine, determined by using calibration mixtures of these compounds and taking the methanol response factor from earlier work (*2*). Hydrogen was excluded from the composition analysis. The GC data were corrected for the sensitivities of each component by dividing the integrated areas by the respective response factors and then normalizing to obtain the percentage molar concentration. The amount of material leaving the reactor, in millimoles per hour, was calculated assuming a nitrogen balance, and this procedure gave carbon and oxygen balances within 0.5 and 1.6%, respectively.

RESULTS

The methylation of amines with the carbon monoxide/hydrogen mixture was carried out over Cu/ZnO (30/70) catalyst under the methanol synthesis conditions at 75 atm and a gas hourly space velocity (GHSV) of 6120 liters/kg cat./hr. A 2.45-g portion of the catalyst was centered in the reactor and was reduced in a manner described in Ref. (*2*). After completion of the reduction, the reactor was cooled to room temperature and pressurized to 75 atm with a H_2/CO = 70/30 vol% synthesis gas. Maintaining a gas flow of 6120 liters/kg cat./hr, the reactor was heated to the reaction temperature and an amine was injected continuously into the gas stream at the reactor inlet. The amine was vaporized in the preheater section of the reactor and entered the catalyst bed as a gas in the mixture with carbon monoxide and hydrogen. When the reaction was carried out at 190°C with an injection rate of 42.3 mmol of isopropylamine/2.45 g cat./hr, about 10% of the amine reacted with the synthesis gas to produce methylisopropylamine (Table 1). No disproportionation of isopropylamine was observed at this temperature. To determine whether methanol or its precursor was the reactant in methylisopropylamine synthesis, the rates of isopropylamine reaction with CO/H_2 (Experiment (A)) and with methanol (Experiment (B)) were measured and compared. The amount of methanol injected in Experiment (B) was equivalent to the total amount of methyl groups synthesized in Experiment (A) from CO/H_2. The results are shown in Table 1 and they demonstrate that the rate of methylation of the amine was higher with CO/H_2 than with methanol.

The reduction of amides over the Cu/ZnO (30/70) catalyst is of particular interest because formamide is a potential intermediate to be considered during the synthesis of methylamines from synthesis gas and amines. *N,N*-Diethylformamide was taken as a representative amide, and it was hydrogenated at 215°C and 75 atm. As shown in Table 2, when the flow rate of *N,N*-diethylformamide was 10.8 mmol/2.45 g cat./hr, 62% of it was converted to diethyl-

TABLE 1

Results of the Catalytic Synthesis of Methylamines at 190°C, GHSV = 6120 liters/kg cat./hr, and at 75 atm over 2.45 g of Cu/ZnO (30/70) Catalyst

	Isopropyl-amine	CO	H_2	CO_2	H_2O	CH_3OH	Isopropyl-methylamine	Isopropyl-dimethylamine
Expt (A)								
(mmol/hr) In	42.3	184.0	429.0	—	—	—	—	—
(mmol/hr) Out	38.3	169.9	n.d.[b]	4.0	0.3	5.6	4.0	0.0
Expt (B)								
(mmol/hr) In	41.3[a]	—	429.0	—	—	9.9	—	—
(mmol/hr) Out	39.5	0.0	n.d.	0.0	1.7	8.2	1.7	0.1

[a] Plus 184.0 mmol/hr nitrogen.
[b] Not determined.

methylamine and the remaining 38% of the product was distributed among methanol, ethanol, methylethylamine, diethylamine, and triethylamine. When the flow rate of *N,N*-diethylformamide and hydrogen was doubled and tripled at 215°C and 75 atm, the yields of diethylamine and methanol increased while the yield of all other products decreased (Table 2, Experiments (B) and (C)). Under all conditions studied, the conversion of *N,N*-diethylformamide was 100% with no observable amounts of CO, CO_2, and *N,N*-diethylformamide within the analytical detection limit of 0.02 mmol/hr. The exit gas composition is plotted in Fig. 1 as a function of the reciprocal flow rate of hydrogen. Because the feed rate of *N,N*-diethylformamide was kept proportional to that of hydrogen, the ordinate axis in Fig. 1 is proportional to the contact time of both components.

DISCUSSION

The results presented in Table 1 show that isopropylamine reacts with the synthesis gas CO/H_2 [Eq. (1) and (2)] at rates that are comparable to the methanol synthesis [Eq. (3)] rate.

TABLE 2

Hydrogenation of *N,N*-Diethylformamide (NNDEF) at 215°C, 75 atm over 2.45 g of Cu/ZnO (30/70) Catalyst

Flow rate of substrate	Flow rate of hydrogen		H_2O	CH_3OH	C_2H_5OH	MEA	DEA	DEMA	TEA	NNDEF	CO	CO_2
Expt (A)												
(20 μl/min of	10.5 liters	(mmol/hr) In	—	—	—	—	—	—	—	10.8	—	—
(NNDEF)	(STP)/hr	(mmol/hr) Out	7.6	2.9	0.5	1.4	1.9	6.7	0.9	<0.02	<0.02	<0.02
		Exit gas composition[a] (mol%)	34.70	13.24	2.28	6.39	8.68	30.59	4.11	<0.01	<0.01	<0.01
Expt (B)												
(40 μl/min of	21.0 liters	(mmol/hr) In	—	—	—	—	—	—	—	21.6	—	—
(NNDEF)	(STP)/hr	(mmol/hr) Out	13.0	7.6	0.7	1.7	6.2	12.6	1.0	<0.02	<0.02	<0.02
		Exit gas composition[a] (mol%)	30.37	17.76	1.64	3.97	14.49	29.44	2.34	<0.01	<0.01	<0.01
Expt (C)												
(60 μl/min of	31.5 liters	(mmol/hr) In	—	—	—	—	—	—	—	32.4	—	—
(NNDEF)	(STP)/hr	(mmol/hr) Out	19.1	13.0	0.8	2.0	11.0	18.3	1.1	<0.02	<0.02	<0.02
		Exit gas composition[a] (mol%)	29.25	19.91	1.23	3.06	16.85	28.02	1.68	<0.01	<0.01	<0.01

Note. MEA, methylethylamine; DEMA, diethylmethylamine; DEA, diethylamine; TEA, triethylamine.
[a] Exit gas composition excluding hydrogen.

$$RNH_2 + CO + 2H_2 \rightarrow RNHCH_3 + H_2O \quad (1)$$

$$RNH_2 + 2CO + H_2 \rightarrow RNHCH_3 + CO_2 \quad (2)$$

(R = isopropyl)

$$CO + 2H_2 \rightarrow CH_3OH \quad (3)$$

Reaction (2) may or may not occur through the sequence of reaction (1) and the water-gas shift (WGS) reaction

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (4)$$

Clearly the carbon source for the CH_3 group of the amine product is CO in the synthesis gas but the key mechanistic problem to be resolved is which carbon species, gaseous or adsorbed, reacts with the injected amine. We shall consider the following paths to the methylated amine:

A. Direct reaction of the amine with the methanol product

$$RNH_2 + CH_3OH \rightarrow RNHCH_3 + H_2O \quad (5)$$

B. Routes via formamide intermediate

$$RNH_2 + CO \rightarrow H(CO)NHR \quad (6)$$

$$RNH_2 + HCOO^{\ominus}_{(s)} + H^{\oplus}_{(s)} \rightarrow HCOO^{\ominus}\,\overset{\oplus}{H_3N}R \quad (7)$$

$$HCOO^{\ominus}\,\overset{\oplus}{H_3N}R \rightarrow H(CO)NHR + H_2O \quad (8)$$

$$H(CO)NHR + 2H_2 \rightarrow RNHCH_3 + H_2O \quad (9)$$

C. Route via carbamic acid and carbamates

$$RNH_2 + CO_2 \rightleftharpoons RNHCOOH \quad (10)$$

$$RNHCOOH + RNH_2 \rightleftharpoons RNHCOO^{\ominus}\,\overset{\oplus}{H_3N}R \quad (11)$$

$$RNHCOOH + 3H_2 \rightarrow RNHCH_3 + 2H_2O \quad (12)$$

D. Routes via aldehydic intermediates

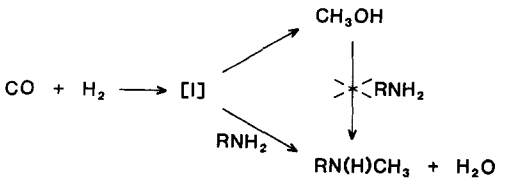
$$H_2CO \text{ (or HCOH, HCO)} + RHN_2 \rightarrow H_2C(OH)NHR \quad (13)$$

$$H_2C(OH)NHR + H_2 \rightarrow RNHCH_3 + H_2O \quad (14)$$

Based on the comparison of the rates of the methyl group synthesis on the amine, of methanol synthesis, and of formamide hydrogenation, Routes A–C are ruled out as major pathways under the present conditions using the Cu/ZnO catalyst. On the other hand, the amine trapping of aldehydic intermediate (Route D) is consistent with the observed product composition and formation rate. In this route, formaldehyde H_2CO, adsorbed formyl HCO, and surface-bonded hydroxycarbene HCOH are expected to undergo similar reactions. A detailed analysis underlying the above conclusions is given in the subsequent paragraphs.

A. Direct Coupling of Isopropylamine with Methanol or Adsorbed Methoxide

As noted under Results, data in Table 1 established that the rate of methylation of isopropylamine with methanol was lower than that with the synthesis gas CO/H_2. The faster rate of methylation with CO/H_2 demonstrates that the major path for isopropylamine methylation is by reaction of the amine with an *intermediate* in methanol synthesis or with CO and not with the product methanol. This observation is schematically represented by the scheme



(15)

in which the direct coupling reaction (5) can be at the most a minor pathway. Furthermore, adsorbed methoxide is not expected to qualify as intermediate **I**. There are no known reactions of methoxide reacting

with an amine to give methylamine, and it is generally accepted that bases such as alkoxides would not react with amines. Hence, we conclude that the *minor* pathway role of the direct coupling reaction (5) can be extended to the reaction between the amine and the surface methoxide.

B. Routes via Formamide Intermediate

Several pathways involving known reactions of amines could lead to a formamide intermediate. These involve the direct insertion of CO into the N–H bond of the amine (*25*) [Eq. (6)], reaction of surface carboxylate, protons, and the amine (*26*) [Eqs. (7)–(8)], as well as the reduction of carbamic acid formed by Route C. In order to obtain methylamine as a product, the formamide intermediate would have to be hydrogenated as shown in Eq. (9) (*27*). However, the formamide hydrogenation products are quite complex as shown in Table 2, and for this reason it was deemed necessary to determine which are the primary products, what are the rates of their formation, and then to compare these rates with that of the synthesis of methylamines wherein the methyl group is formed from CO/H_2.

The formamide hydrogenation study was conducted with *N,N*-diethylformamide under the conditions at which diethylamine was used to trap the C_1 intermediates in our earlier work (*3*), i.e., at 215°C, 75 atm, and hydrogen gas hourly space velocity of 4290 liters (STP)/kg cat./hr over identical Cu/ZnO catalyst. These conditions and the results of amine trapping are close enough to those when isopropylamine was the trapping agent, so that the conclusions derived from the comparison of *N,N*-diethylformamide hydrogenation and the diethylamine reaction with CO/H_2 are expected to be generally valid for all formamides and the corresponding amines produced by their hydrogenation. As indicated in Table 2, the *N,N*-diethylformamide (NNDEF) was completely converted to diethylmethylamine (DEMA) [Eq. (16)], methanol [Eq. (17)], diethylamine (DEA) [Eq. (17)], ethylmethylamine (EMA) [Eq. (18)], triethylamine (TEA) [Eq. (18)], and ethanol [Eq. (19)], with no traces of CO or CO_2 in the exit gas stream within the analytical detection limit of 0.01%.

$$(C_2H_5)_2N-\overset{\overset{O}{\|}}{C}-H + 2H_2 \rightarrow (C_2H_5)_2NCH_3 + H_2O \quad (16)$$

$$(C_2H_5)_2N-\overset{\overset{O}{\|}}{C}-H + 2H_2 \rightarrow (C_2H_5)_2NH + CH_3OH \quad (17)$$

$$(C_2H_5)_2NCH_3 + (C_2H_5)_2NH \rightarrow C_2H_5NHCH_3 + (C_2H_5)_3N \quad (18)$$

$$(C_2H_5)_3N + H_2O \rightarrow (C_2H_5)_2NH + C_2H_5OH \quad (19)$$

The products of NNDEF hydrogenation are plotted in Fig. 1 as a function of the reciprocal flow rate of hydrogen. As the flow rate increased, the yields of EMA, TEA, and ethanol decreased; extrapolated to infinite flow rate or zero contact time, their yield approached zero. This shows that EMA, TEA, and ethanol were secondary products of the hydrogenation of NNDEF. The reactions given by Eqs. (16)–(19) were formulated from balancing the CH_3 and C_2H_5 groups and water, and the method is briefly described below. Since Eqs. (16) and (17) are the primary reactions, the amount of methanol produced has to be equal to the amount of DEA produced from NNDEF by reaction (17). Because the amount of methanol was found equal to the sum of DEA and TEA in the exit gas stream, however, TEA has to be produced by a secondary reaction of DEA. Further, ethylamine was not observed in the exit gas stream within the analytical detection limit of 0.01%. Therefore, TEA and EMA would originate by the reaction given by Eq. (18). The amount of EMA was equal to the sum of TEA and ethanol. This stoichiometric relationship indicates that the

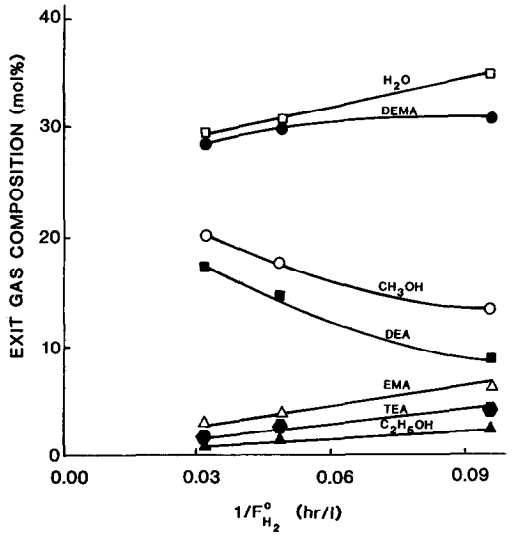


FIG. 1. The products of the hydrogenation of *N,N*-diethylformamide as a function of the reciprocal flow rate of hydrogen at 215°C, 75 atm, and over 2.45 g Cu/ZnO (30/70) catalyst. The molar feed rate of *N,N*-diethylformamide was kept at 0.025 × flow rate of hydrogen in mol/hr. DEMA = diethylmethylamine, DEA = diethylamine, EMA = ethylmethylamine, TEA = triethylamine.

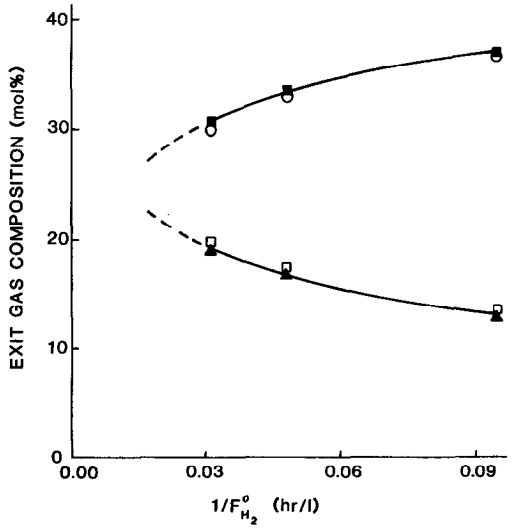
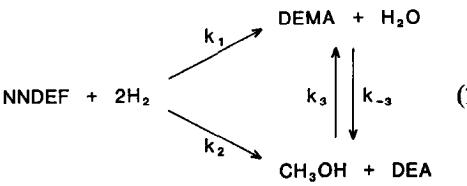


FIG. 2. Diethylmethylamine, diethylamine, methanol, and water produced by reactions (16) and (17) as a function of the reciprocal flow rate of hydrogen at 215°C, 75 atm over 2.45 g Cu/ZnO catalyst. The molar feed rate of *N,N*-diethylformamide was kept at 0.025 × flow rate of hydrogen in mol/hr. (■) Diethylmethylamine, (○) water, (□) methanol, (▲) diethylamine.

ethanol was produced by reaction (19). Hence, a part of DEA, DEMA, and H_2O produced by reactions (16) and (17) is consumed by reactions (18) and (19) to produce EMA, TEA, and ethanol. Therefore, the amount of DEA produced by reaction (17) is given by the sum of DEA and TEA in the exit gas stream. The amount of DEMA produced by reaction (16) is the sum of DEMA and EMA in the exit gas stream. Similarly, the amount of water produced by reaction (15) is given by the sum of water and ethanol in the exit gas stream.

The calculated amounts of DEMA and water produced by reaction (16), DEA produced by reaction (17), and methanol are plotted as a function of the reciprocal flow rate of hydrogen in Fig. 2. The amounts of DEMA and water calculated as due to reaction (16), as well as those of DEA and methanol due to reaction (17) are seen to be in stoichiometric equivalence over the whole range of flow rates which confirms the validity of the reaction scheme (15)–(18). The contact time dependence of the product yields in Fig. 2 leads to the following scheme of the primary reactions:



(20)

The kinetic constant k_{-3} is negligible compared to k_3 because the equilibrium constant of the conversion of methanol and diethylamine to water and diethylmethylamine is of the order of 10^6 at 215°C. Taking into account $k_3 \gg k_{-3}$ and denoting the concentration of NNDEF as z, of methanol and DEA as x, of DEMA and water as y, the above scheme translates into the following set of kinetic equations:

$$-\frac{dz}{dt} = (k_1 + k_2)zF(H_2) \qquad (21)$$

$$\frac{dx}{dt} = k_2zF(H_2) - k_3x^2 \qquad (22)$$

$$\frac{dy}{dt} = k_1 z F(H_2) + k_3 x^2. \qquad (23)$$

With the great excess of hydrogen present in the system, $F(H_2)$ is constant and will generate only a parametric dependence of the rate constants k_1 and k_2 on hydrogen pressure. The above system of kinetic equations does not have a closed analytical solution but can be solved numerically by the usual methods. Due to special experimental conditions employed here, however, a simplified treatment offers a straightforward interpretation of the observed dependence of the product yields on contact time. Since 100% of the NNDEF feed has been converted at all contact times studied, we shall assume its instant conversion to CH_3OH + DEA and DEMA + H_2O such that the concentration of CH_3OH and DEA is x_0 and that of DEMA and H_2O is y_0 at $t = 0$. The kinetic equations then simplify to the second-order decay for CH_3OH and DEA

$$\frac{dx}{dt} = -k_3 x^2 \qquad (24)$$

or

$$\frac{1}{x} - \frac{1}{x_0} = k_3 t \qquad (25)$$

and

$$y = z_0 - x, \qquad (26)$$

where z_0 is the concentration of NNDEF that has been instantly converted to the primary products, $z_0 = x_0 + y_0$. For a steady-state integral reactor employed here it holds that

$$m = F^0_{CH3OH} \int_0^{\alpha_L} \frac{d\alpha}{v_m(\alpha)}, \qquad (27)$$

where m is the total mass of the catalyst in the reactor, $F^0_{CH_3OH}$ is the initial flow rate of methanol fed into the reactor by instant reaction (17), α is the conversion of methanol by the reaction governed by k_3 in scheme (20), $\alpha = 1 - \frac{x}{x_0}$, and v_m is the reaction rate per unit catalyst mass, equal to $-k_3x^2$. Equation (27) integrates to

$$\frac{1}{x_L} - \frac{1}{x_0} = \left[k_3 m \frac{(p^0_{NNDEF})^2}{50}\right] \cdot \frac{1}{F^0_{NNDEF}}, \qquad (28)$$

where x_0 and x_L are percentage fraction of methanol at the beginning and the end of the reactor and F^0_{NNDEF} and p^0_{NNDEF} are the feed rate and partial pressure of NNDEF in the feed. Equation (28) is merely the second-order integral equation (25) transcribed for the steady-state flow reactor. In the above treatment, volume contraction due to hydrogen consumption and NNDEF as well as the product adsorption has been neglected. Both of these assumptions are plausible because of the high hydrogen-to-NNDEF ratio employed. The data for methanol from Fig. 2 are recast in the coordinates $(1/x_L)$ vs $(1/F^0_{H_2})$ in Fig. 3. The values of $x_0 = 27\%$ and $k_3 = 24.8$ mol-hr^{-1}-atm^{-2} per kg of catalyst are obtained from the intercept and the slope, respectively. Because of stoichiometric equivalence of methanol and DEA generated by the pri-

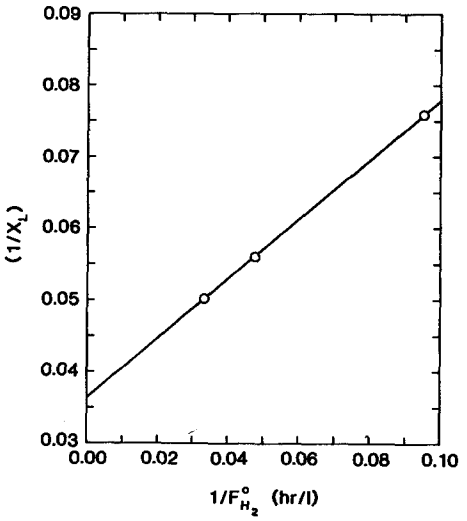
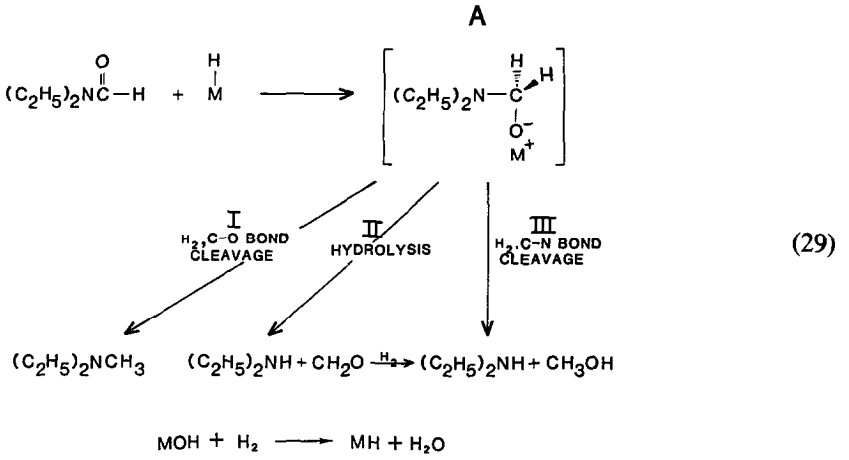


FIG. 3. Second-order kinetics of methanol concentration during *N,N*-diethylformamide hydrogenation. Data of Fig. 2 for methanol are used herein. x_L is the percentage concentration of methanol at the reactor exit and $F^0_{H_2}$ the flow rate of hydrogen. The molar feed rate of *N,N*-diethylformamide was kept at 0.025 × flow rate of hydrogen in mol/hr.

mary reaction (17), $2x_0 = 54\%$ represents the percentage of NNDEF converted to methanol and DEA by reaction (17) and $100 - 2x_0 = 46\%$ the percentage of NNDEF converted to DEMA and water in the primary reaction (16). These initial rates of formamide hydrogenation have mechanistic implications as discussed below.

The mechanism for the hydrogenation of *N,N*-diethylformamide over the Cu/ZnO catalyst may be similar to that suggested by Brown and Heim (*28*) for the reduction of amides by $LiAlH_4$. The following reaction scheme



(29)

is proposed for the hydrogenation of *N,N*-diethylformamide over the Cu/ZnO catalyst based, in part, on Ref. (*28*).

In this reaction sequence, the amide is first attacked by a hydride (MH), probably CuH, to form a tetrahedral intermediate (A). This intermediate can undergo:

Path I: Hydrogenolytic C–O bond cleavage to produce the direct hydrogenation product DEMA without the hydrogenolysis of the C–N bond.

Path II: Hydrolysis to produce DEA and formaldehyde. Formaldehyde can then undergo hydrogenation to produce methanol or couple with DEA to produce DEMA.

Path III: Hydrogenolytic C–N bond cleavage to produce methanol and DEA. Subsequently, these could undergo coupling to produce DEMA via dehydrogenation of methanol to formaldehyde and aminealdehyde coupling.

Here Path I corresponds to the primary reaction (16) and Path III to reaction (17). Formaldehyde generated by the hydrolytic Path II can be either rapidly hydrogenated to methanol over the Cu/ZnO catalyst as expected from the earlier found hydrogenation rates of aldehydes (*29*), or can couple with the amine via reaction scheme (32). Thus, Path II can contribute to both reactions (16) and (17). The kinetic analysis above results in 46% probability for reaction (16) and 54% for reaction (17). These numbers indicate that the rates of hydrogenolysis of the C–N bond by combined Paths III and II and of the C–O bond by combined Paths I and II are comparable. The point of significance for the mechanism of the amine-trapping reactions investigated here is that direct hydrogenation of the formamide to DEMA does not dominate the overall NNDEF hydrogenation rates. It is noteworthy that the C–N bonds involving ethyl groups of NNDEF are not severed by hydrogenolysis or by ethylene elimination because neither ethane nor ethylene are among the products. Only hydrolytic cleavage of this C–N bond (19) and alkyl transfer (18) occur as minor secondary reactions as is seen from the contact

time dependence of the product composition in Fig. 1.

In order to determine whether formamide is a possible intermediate in the methylation of an amine by CO/H_2, the rate of NNDEF hydrogenation to DEMA will now be compared with that of the reaction of DEA with CO/H_2 to produce DEMA. In the previous work (*3*), a 14.5 mmol/hr of DEA reacted with CO/H_2 to produce 11.2 mmol/hr of DEMA at 215°C, 75 atm, and 2.45 g of Cu/ZnO catalyst.

In the present experiments (cf. Table 2) 10.8 mmol/hr NNDEF, approximately equivalent to the 11.2 mmol/hr of DEMA in the previous DEA methylation experiment, was injected into the stream of hydrogen under identical conditions, and only 6.7 mmol/hr or 62% of NNDEF was hydrogenated to DEMA. Using the treatment that led to the reaction scheme (16)–(19), this amount corresponds to 5.0 mmol/hr or 46% of NNDEF being converted to DEMA by the primary reaction (16). A comparison of these two experiments indicates that the rate of hydrogenation of NNDEF to DEMA was significantly lower than the rate of production of DEMA from CO/H_2 and DEA. Hence, the reaction of CO/H_2 with DEA could not proceed exclusively via the NNDEF intermediate. However, the participation of this intermediate to a lesser extent cannot be ruled out, with two possible routes analogous to reactions (6) and (7). Another route via the reduction of carbamic acid is unlikely because of the instability of this compound at high temperatures.

Even though the intermediacy of the formamide cannot be completely excluded on the basis of the measured rates, the following arguments make the formamide pathways unlikely even as minor routes:

(i) Secondary alcohols which cannot generate formamides were found to couple with amines more rapidly than primary alcohols over the same Cu/ZnO catalyst (*30, 31*). The simplest explanation of this result is that the alcohols are partially dehydrogenated to their aldehydes and ketones which react with the amines according to Route II. Since the equilibrium of the dehydrogenation of secondary alcohols is shifted more in favor of ketones than that of primary alcohols to aldehydes, the secondary alcohols will react faster if the reaction rate is controlled by the dehydrogenation equilibria.

(ii) It has been shown earlier that the water-gas shift reaction is unaffected by the reaction of CO/H_2 with an amine (*3*). If formate is the common intermediate in the WGS reaction and methanol synthesis as suggested in Ref. (*3*) and literature cited therein, then the unchanged rates of the WGS reaction in the presence of amine indicate that neither the surface formate nor its precursor CO are the trapped C_1 intermediate. Since there is no pathway from amines and surface aldehydes or alkoxides to amides, the formamide cannot be an intermediate if the surface formate is common to the WGS reaction and methanol synthesis.

C. Route via Carbamic Acid and Carbamates

The formation of carbamic acid and particularly carbamates by reactions (10) and (11) can occur in the presence of CO_2 and amines. However, these reactions are not expected to be of importance at elevated temperatures because the equilibria are shifted to CO_2 and the amine. For example, the equilibrium constant K for ammonium carbamate formation by the reaction

$$2NH_3 + CO_2 \overset{K}{\rightleftharpoons} H_2NCOONH_{4(s)} \quad (30)$$

has the values 2.08×10^5 at 25°C, 1.11×10^{-5} at 190°C, and 1.14×10^{-6} at 215°C. These figures demonstrate that although at low temperatures carbamates will be formed (to the point of nuisance by clogging cold lines in the apparatus), they are unstable at the reaction temperatures. A further confirmation that carbamates are not intermediates under our conditions rests in the

observation that the overall rates of generation of CO_2 are equal in the presence of amine and in the absence of amine with equivalent amount of water injected into the system (*3*).

D. Routes via Aldehydic Intermediates

As of this time, spectroscopic evidence for aldehydic or hydroxycarbenoic intermediates in heterogeneously catalyzed methanol synthesis is lacking. Yet the reaction behaves in several ways as if aldehydic species were kinetically significant intermediates. By kinetic significance we mean that the intermediate is formed and destroyed at rates comparable to the overall steady-state synthesis rate. The chemical manifestations of aldehydic or hydroxycarbenoic surface species can be summarized as follows:

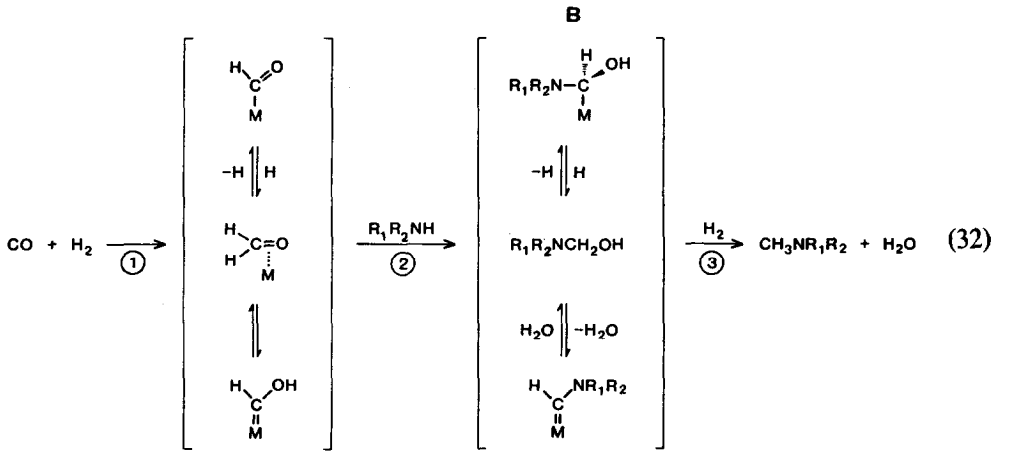
(i) Injection of *n*-propanol and propanaldehyde into the CO/H_2 synthesis gas gives rise to the branched product 2-methyl-1-propanol while the injection of 2-propanol gives rise to 2-butanol (*32*). These reactions are typical of aldol synthesis in which C_1 aldehyde condenses with the β-carbon of propanaldehyde or acetone and the product is hydrogenated (*32*).

(ii) Injection of methyl iodide gives rise to acetaldehyde (*33*) which is indicative of chemical trapping of surface formyl by the reaction

$$CH_3I + \underset{|}{HCO} \rightarrow CH_3CHO + \underset{|}{I} \quad (31)$$

(iii) The presently reported reactions of amine with the C_1 intermediates occur at high rates such that the above discussed Routes A–C do not account for the observed rates. Excluding the CO insertion, formamide, and carbamate routes, the only remaining C_1 intermediates that can react rapidly with amines are aldehydic and hydroxycarbenoic species.

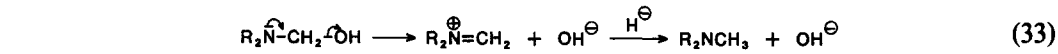
In this paragraph we shall summarize evidence that shows that all three "aldehydic" residues, formyl, adsorbed formaldehyde, and its isomer hydroxycarbene, will interact with amines in a similar fashion. Therefore, those surface aldehydic residues cannot be distinguished from each other by amine trapping but will rather behave as one and the same intermediate possessing the ability to couple directly with amines by an uncatalyzed reaction. The corresponding reaction sequence is represented by scheme (32).



There are many examples of reactions of free aldehydes with amines that result in the formation of derivatives of hydroxymethylamine (*34*). Although analogous reactions of adsorbed or π-bonded formaldehyde or of formyl bonded in organometallic complexes have not been reported, it is likely that these bonded aldehydic species

will react similarly as the free formaldehyde in step 2 of scheme (32). The isomer of formaldehyde, hydroxycarbene HC̈OH, is unstable by 79–84 kcal/mol with respect to formaldehyde (*35*) as a free molecule, but may be significantly stabilized by binding to the catalyst surface. In fact, metal complexes of hydroxycarbene derivatives are well known and their coupling with amines has been extensively studied by Fischer (*36*), and products analogous to those generated by step 2 of the bottom path scheme (32) have been described. The whole bottom path of scheme (32) involving the hydroxycarbene intermediate is also similar to the mechanistic proposal of Kölbel *et al.* (*37*) for the synthesis of methylamines from CO/H_2 and amines over iron catalysts.

To account for the observed rates of DEMA formation, the intermediates B in the surface aldehyde trapping scheme (32) must be different from the intermediate A in the formamide hydrogenation scheme (29) in that the hydrogenolysis of the C–O bond is much more effective in B than in A. The basic difference between these two types of intermediates is that A is bound to the surface oxygen-down while B moieties are either carbon-down species or a free hydroxymethylamine. The facile cleavage of the C–O bond in scheme (32) is thus seen to occur as an *SN*2 reaction involving the attack of surface hydroxycarbene by amine with the elimination of OH^- group or a hydride attack of the two top hydroxylated intermediates B with the elimination of OH^-. Both the amine and the hydride attacks are nucleophilic, and they are expected to be more facile in reaction scheme (32) than the corresponding hydride attack of the anionic intermediate A in the formamide hydrogenation (29). The OH^- elimination may also occur by the direct conversion of the hydroxymethylamine to a Schiff base, which is subsequently hydrogenated by a surface hydride,



(33)

The acceptors for the leaving OH^- group are likely to be metal cations such as $Zn^{\gamma+}$ or $Cu^{\delta+}$ in the oxide lattice of the catalyst and are expected to act as Lewis acids for this particular reaction.

CONCLUSION

Aside from the synthetic value of the C–N bond forming reaction between the injected amine and surface C_1 intermediate, the quantitative rate measurements of the amine reactions with CO/H_2 and with methanol, of formamide hydrogenation, and of the water-gas shift reaction over the same Cu/ZnO catalyst permit the conclusion that surface *formyl, π-bonded formaldehyde, or hydroxycarbene* has been trapped. Direct reactions of the amine with CO and CO_2 do not play a role and the trapping of surface formate is at most a minor reaction. It must be noted that formaldehyde was never observed in the gas phase under the presently employed methanol synthesis conditions. Therefore, the amine-trapping reactions are indicative of the *surface* aldehydic residues.

ACKNOWLEDGMENT

This work was supported in part by the U.S. Department of Energy Grants DE-FG22-83PC60786, DE-AC22-84PC70021, and XX-2-02173-01.

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