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A General Homogeneous Catalytic Method for the Homologation of Methanol to Ethanol

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The direct conversion of synthesis gas to ethanol[1] and the indirect reaction of synthesis gas with methanol to yield ethanol (homologation)[2] have been studied as possible alternative processes for the production of ethanol from coal. We have discovered an unusually general catalytic method for methanol homologation occurring in methanol solutions of amines at synthesis gas pressures near 300 atm and temperatures near 200 °C. Significantly, methanol is homologated while ethanol is essentially unaffected. In each case, carbon dioxide is the oxygenated byproduct, and ethanol is formed according to the following stoichiometry:[3]

$$\mathrm{CH_3OH + 2CO + H_2 = CH_3CH_2OH + CO_2} \qquad (1)$$

Since our first observation of this type of reaction using $Fe(CO)_5$ catalyst,[4] we have become aware of the method's generality extending to several diverse metal centers. Table I lists reactivity characteristics of complexes that we have found to be active in amine–methanol solution. At present, we have accumulated a reasonably detailed knowledge of the mechanism for the iron carbonyl system. More important, however, a clear picture of a common pathway for all of the complexes in Table I has emerged. In general, all of the catalytic reactions use methylammonium ions as methyl carriers, transition-metal complex anions as nucleophilic methyl acceptors, and catalytic decomposition of formic acid to remove protons generated in hydrogen activation steps.

In contrast to the well-known $HCo(CO)_4$-catalyzed reaction,[2] in which methyl groups are activated by protonation of methanol, the new systems activate methyl groups via equilibria[5] of eq 2 and 3, which are established rapidly in methanol solutions of amine

$$\mathrm{CH_3OH + CO \overset{B}{\rightleftharpoons} HCO_2CH_3} \qquad (2)$$

$$\mathrm{HCO_2CH_3 + B \rightleftharpoons CH_3B^+ + HCO_2^-} \qquad (3)$$

(B).[6] The method's characteristic selectivity for methanol vs. ethanol homologation arises in step 3, which generates the active methyl transfer reagent.[7] Attack (S_N2) on methyl formate by trimethylamine is preferred for steric reasons over attack on ethyl formate. In S_N2 reactions involving poor leaving groups, methyl transfers have been reported to be as much as 150 times faster than ethyl transfers.[8]

Table I. Reactivity Patterns for Catalysis of Methanol Homologation in Amine–Methanol Solution[a]

expt no.	complex (mmol)	reaction time, h	C_2H_5OH,[b] mmol	CH_4, mmol	turnover freq,[c] h^{-1}
1	$Fe(CO)_5$ (16.0)	6.0	34	73	1.1
2[d,e]	RhI_3 (5.0)	2.0	42	19	6.1
3[e,f]	$Ru_3(CO)_{12}$ (5.33)	3.4	26	26	0.96
4	$Mn_2(CO)_{10}$ (11.5)	6.0	102	22	0.90
5[g]	$Mn_2(CO)_{10}$ (11.5)/ $Fe(CO)_5$ (16.0)	6.0	330	67	2.9
6[e,g,h]	$Mn_2(CO)_{10}$ (6.3)/ $Fe(CO)_5$ (60.5)	2.0	199	79	11.0

[a] In methanol solution (160 mL) containing 1-methylpiperidine (2.0 M); reaction at 200 °C and at 300 atm of 3:1 CO/H_2 with continuous gas purge of 600 mL/min. The volumes and concentrations are measurements at ambient conditions. The head gas was analyzed on a 3.5-ft spherocarb column isothermally at 80 °C, and the product solution on a 6-ft porapak Q column programmed from 50 to 220 °C at 10 °C/min. [b] Includes a small amount of $HCO_2C_2H_5$. [c] Turnover frequency = mmol of $(C_2H_5OH + CH_4)$/[(mmol of mononuclear metal)(reaction time, h)]. [d] Trimethylamine replaced 1-methylpiperidine; volume of solution = 50 mL. [e] Gas purging was not used. [f] Trimethylamine (3.2 M) replaced 1-methylpiperidine. [g] The amount of $Fe(CO)_5$ was not included in the calculation of turnover frequency. [h] Initial volume = 84 mL, temperature = 220 °C, and 1,3-bis(1-methyl-4-piperidyl)propane (1.65 M) replaced 1-methylpiperidine.

At the pressure and temperature conditions given in Table I, metal carbonyl anions[9-11] are formed according to eq 4–6. At

$$\mathrm{Fe(CO)_5 + H_2 + B \rightleftharpoons HFe(CO)_4^- + CO + BH^+} \qquad (4)$$

$$\mathrm{Ru_3(CO)_{12} + H_2 + B \rightleftharpoons HRu_3(CO)_{11}^- + CO + BH^+} \qquad (5)$$

$$\mathrm{Mn_2(CO)_{10} + H_2 + 2B \rightleftharpoons 2Mn(CO)_5^- + 2BH^+} \qquad (6)$$

least early in the reaction using RhI_3 as catalyst the major rhodium species was also an anion, $Rh(CO)_2I_2^-$.[12] Formate ion generated in (3) is not inert. We have observed that methanol solutions of $[N(CH_3)_3H][HCO_2]$ rapidly react according to eq 7 in the

$$\mathrm{BH^+ + HCO_2^- \rightarrow H_2 + CO_2 + B} \qquad (7)$$

presence of $Fe(CO)_5$ under our reaction conditions. Reaction 7, which amounts to a catalytic decomposition of formic acid in basic solution, is probably initiated by the reduction of $Fe(CO)_5$ by HCO_2^- to form $HFe(CO)_4^-$. The ability to catalyze this reaction is a common property of metal carbonyls.[13-15] The effect of reaction 7 is to drive the equilibria 4–6 to the right by the removal of protons. Without formic acid decomposition the catalytic reactions in Table I would be stoichiometric in amine. Reaction 7 is the source of carbon dioxide produced in the net catalytic reaction in eq 1.

The net result of eq 2–7 is that methylammonium ions and metal carbonyl anions are both present when methanol solutions of appropriate metal carbonyl and amine are heated under CO

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(6) When methanol solutions of trimethylamine, 1-methylpiperidine, or 1,3-bis(1-methyl-4-piperidyl)propane are heated to 200 °C at 300 atm of $3CO/H_2$ pressure, (2) and (3) both reach equilibrium within 20 min and greater than 80% of each amine is converted to its methylammonium ion.

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and H_2 pressure. In cases where the anion is sufficiently nucleophilic, methyl transfer occurs. The highly nucleophilic anion $HFe(CO)_4^-$ appears to react as in eq 8–12. It is necessary to

$$CH_3B^+ + HFe(CO)_4^- \rightarrow CH_3HFe(CO)_4 + B \tag{8}$$

$$CH_3HFe(CO)_4 + CO \rightarrow CH_3C(O)HFe(CO)_4 \tag{9}$$

$$CH_3HFe(CO)_4 + CO \rightarrow CH_4 + Fe(CO)_5 \tag{10}$$

$$CH_3C(O)HFe(CO)_4 + CO \rightarrow CH_3C(O)H + Fe(CO)_5 \tag{11}$$

$$CH_3C(O)H + H_2 \xrightarrow{HFe(CO)_4^-} CH_3CH_2OH \tag{12}$$

note, at this point, that eq 2–4, 7–9, 11, and 12 add up to give the measured overall stoichiometry, eq 1. As mentioned earlier, formation rates of the ions, $N(CH_3)_4^+$ and $HFe(CO)_4^-$, are high, and reactions 3 and 4 are at or near equilibrium. The methyl-transfer step in reaction 8 is apparently rate limiting.[16] Consistent with this interpretation, the second-order rate constant thus calculated for reaction 8 is comparable to that obtained in the stoichiometric reaction between $N(CH_3)_4^+$ and $HFe(CO)_4^-$ in 1-methyl-2-pyrrolidinone solutions.[17,18] Similar agreement between the results of catalytic and of stoichiometric reactions has also been established for the Mn-catalyst systems. Although kinetic measurements do not give information on the course of the reaction after rate-limiting methyl transfer, step 8, the following arguments for steps 9–12 are valid. Cooke[19] has shown that protonation of the ions $RFe(CO)_4^-$ and $RC(O)Fe(CO)_4^-$ (R = nonyl, amyl), in the presence of CO, yields RH and RC(O)H, respectively, consistent with steps 9–11. Acetaldehyde, postulated as an intermediate in steps 11 and 12, was detected when the solution of $[N(CH_3)_4][HFe(CO)_4]$ in 1-methyl-2-pyrrolidinone solvent was heated under CO and H_2. Consistent with earlier reports,[20] we have shown that reaction 12 is rapid under our reaction conditions. In a recent study, Dombek[21] has shown that $CH_3Mn(CO)_5$ is readily reduced to CH_3CHO and C_2H_5OH under CO/H_2.

Although $Mn(CO)_5^-$ reacts significantly faster than $HFe(CO)_4^-$ with $N(CH_3)_4^+$ (by a factor of 5),[17] this is not reflected in the rates of the catalytic reaction in Table I; experiments 1 and 4 show that $Mn_2(CO)_{10}$ is less reactive than $Fe(CO)_5$. Under the reaction conditions, the manganese system is quickly driven to a lower pH than observed in the iron system. At the lower pH, formation of methyl formate and methylammonium ion is inhibited, and the catalytic reaction is slower. The lower pH in the manganese system suggests that the system is less effective for formic acid decomposition in reaction 7. Consistent with this view, addition of $Fe(CO)_5$, a known catalyst for reaction 7,[22] to the $Mn_2(CO)_{10}$ system (experiment 5) accelerates catalysis of the methanol homologation reaction. In the mixed system, essentially all of the iron is in the form of nonnucleophilic $Fe(CO)_5$, and the products, therefore, retain the high selectivity toward ethanol formation characteristic of the manganese system.

Although the reactive species in the RhI_3- and $Ru_3(CO)_{12}$-catalyzed reactions (experiments 2 and 3) have not been conclusively identified, spectroscopic observation of the anions $HRu_3(CO)_{11}^-$ and $Rh(CO)_2I_2^-$ in the reaction mixtures is consistent with the reactivity pattern discussed for the Mn and Fe systems. Significantly, $Rh(CO)_2I_2^-$ also is the reactive nucleophile used in the Monsanto acetic acid process.[23]

The ethanol production rates reported here are comparable to the best current homologation technologies (all based on promoted or unpromoted cobalt carbonyls).[24] The mole percent conversion[25] of methanol to ethanol per hour for the mixed $Mn_2(CO)_{10}/Fe(CO)_5$ system (experiment 6) is 10.4% per hour. Maximum values calculated from the data given in each report by workers at Union Carbide (18.8%/h),[26] Exxon (12.0%/h),[27] Gulf (11.7%/h),[28] British Petroleum (9.7%/h), and Celanese (7.5%/h)[30] are similar. In this connection it is noteworthy that the mechanism identified in the new systems uses component reactions that are widespread for metal carbonyls. In contrast, the cobalt systems all appear to require a feature unique to $HCo(CO)_4$, namely, its unusually high acidity.

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Registry No. CH_3OH, 67-56-1; CH_3CH_2OH, 64-17-5; $Fe(CO)_5$, 13463-40-6; RhI_3, 15492-38-3; $Ru_3(CO)_{12}$, 15243-33-1; $Mn_2(CO)_{10}$, 10170-69-1; 1-methylpiperidine, 626-67-5; trimethylamine, 75-50-3; 1,3-bis(1-methyl-4-piperidyl)propane, 64168-11-2.

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(16) (a) We have found other conditions under which methyl transfer is not rate limiting. There are also indications that in the catalytic reactions ion pairing plays a significant role. (b) $CH_3HFe(CO)_4$ and $CH_3C(O)HFe(CO)_4$ and their conjugate bases are in equilibrium. These equilibria do not affect the rate of the reaction and are omitted for clarity.

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(18) In the stoichiometric reactions, EtOH and CH_4 are also the products, and the rate is first order in anion and cation. The kinetic orders indicate that reaction 8 is rate limiting for the reaction between $N(CH_3)_4^+$ and $HFe(CO)_4^-$. This reaction can not be studied in methanol because $HFe(CO)_4^-$ is not stable in the absence of free amines.

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(24) In addition to the products shown in Table I, liquid side products were also observed in experiments 1 and 2. However, in experiments 3–6 ethanol and methane (easily separated as a gas) account for more than 99% of the organic product. To compare the multitude of liquid products that can be obtained with cobalt catalysts, see ref 30.

(25) (a) Defined as: (EtOH produced, mmol/MeoH initially, mmol) × 100%. (b) The metal carbonyl catalysts used in these studies are intrinsically more thermally stable than the cobalt carbonyl catalysts, and higher concentrations can be used to partially compensate for their lower specific activity (turnover frequency).

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Synthesis, Characterization, and Crystal Structure of the $[Ru_{10}C_2(CO)_{24}]$ Dianion. An Edge-Fused Bioctahedral Dicarbide Cluster

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The formation, structures, and properties of metal clusters incorporating carbon atoms (carbides) relate importantly to the problem of activating carbon monoxide.[1] Recently, it was observed[2] that pyrolysis of $Ru_6(CO)_{18}^{2-}$ (refluxing diglyme, 162 °C)

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