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Homologation of Methanol Catalyzed by Manganese Carbonyl in Alkali-Metal Formate–Methanol Solutions[†]

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In this work, $Mn_2(CO)_{10}$ was found to be an active catalyst for the homologation of methanol in alkali-metal formate–methanol solutions at 200 °C and elevated CO and H_2 pressures. $Mn_2(CO)_{10}$ is converted to $Mn(CO)_5^-$ by its reaction with H_2 and/or HCO_2^-, and methanol is activated by the formation of methyl formate. The latter reaction is catalyzed by HCO_2^-. It is proposed that HCO_2^- catalyzes the formation of methyl formate by the reverse of the known pathway for base-catalyzed hydrolysis of carboxylate esters. The methyl-transfer reaction between $Mn(CO)_5^-$ and HCO_2CH_3 to give $CH_3Mn(CO)_5$ is rate-limiting in the homologation process and follows second-order kinetics, with a rate constant of 2.4×10^{-3} M^{-1} s^{-1} at 200 °C. Subsequent reactions of $CH_3Mn(CO)_5$ lead to the formation of ethanol, acetaldehyde, acetals, methane, and traces of ethyl formate and methyl acetate. Methane is produced with a yield of 5–50%, decreasing with increasing partial pressure of CO. The homologation reaction generates CO_2 as the coproduct according to the reaction $CH_3OH + 2CO + H_2 \rightarrow CH_3CH_2OH + CO_2$.

Catalytic homologation of alcohols with synthesis gas has been extensively studied as a route for producing coal-based ethanol and fuels.[1] Most of these studies[2-5] have been directed toward the modification of the well-known $HCo(CO)_4$ catalyst, which is believed to activate alcohols by protonation. The unusually high acidity of $HCo(CO)_4$ is essential for the activation of these alcohols.[6] The catalytic homologation of methanol utilizing iron pentacarbonyl in tertiary amine–methanol solutions is an alternative process for producing coal-based ethanol.[7] In contrast to the cobalt carbonyl hydride system, the iron pentacarbonyl–tertiary amine–methanol system is very active for the homologation of methanol, but not for its homologues, and methanol is activated via the formation of methyl formate. The tertiary amine functions as a base to stabilize the metal carbonylate ion and to catalyze the formation of methyl formate. It also serves as a catalyst for the methyl-transfer reaction between methyl formate and the metal carbonylate ion. This chemistry is generally applicable to a variety of metal carbonyls as catalysts.

In this paper, we describe a related system in which $Mn_2(CO)_{10}$ is the catalyst and the tertiary amines are replaced by alkali-metal formate salts. Although the product selectivity for ethanol is reduced by this modification,[8] mechanistic interpretations are facilitated by the absence of amines. The results of kinetic and other studies on the $Mn_2(CO)_{10}$–alkyli-metal formate–methanol system are presented here, and the homologation mechanism is discussed.

Results and Discussion

Methanol solutions containing $Mn_2(CO)_{10}$ and HCO_2K (10% excess) produce HCO_2CH_3, $Mn(CO)_5^-$, and CH_3CH_2OH at temperatures near 200 °C under synthesis gas pressure. A typical plot showing the variation of the concentrations of these products as a function of time is given in Figure 1. The concentration of methyl formate remains fairly constant during the reaction. Apparently methyl formate rapidly reaches its equilibrium value, and small fluctuations in its concentration during the reaction simply reflect small changes in the partial pressure of CO.

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Table I. Product Distributions as a Function of H_2 and CO Pressures[a]

expt. no.	pressure, psi		reactn time, h	product distribution, mol %						
	H_2	CO		EtOH	HCO_2Et	CH_3CHO	$(MeO)_2$–$CHCH_3$	EtO(MeO)–$CHCH_3$	AcOMe	CH_4
1	280 (± 50)	410 (± 50)	5.0	61		1	7	*d*		31
2	260 (± 50)	2600 (± 400)	5.1	66	3	1	13	3	1	13
3	2800 (± 300)	560 (± 130)	8.0	54		1	2	1		42
4	750 (± 50)	2300 (± 400)	6.0	75	3	1	8	2	1	10
5[b]	600 (± 300)	1300 (± 300)	5.9	72	1	1	8	3	1	14
6[b,c]	800 (± 300)	1800 (± 300)	7.0	76	1	1	3	3	1	15
8	265 (± 25)	410 (± 40)	5.4	47	4	1	5	d		43
9[e]	370 (± 20)	440 (± 80)	5.0	45	3		3	d		49
10[e]	430 (± 110)	2800 (± 800)	5.0	66	2	2	11	d		18
11[f]	25 (± 25)	3200 (± 300)	4.6	37	3	18	34	d	3	5

[a] $[Mn_2(CO)_{10}]$ = 0.025 M and $[HCO_2K]$ = 0.15 M, except for experiments 5, 6, and 11; T = 200 °C. [b] $[Mn_2(CO)_{10}]$ = 0.075 M and $[HCO_2K]$ = 0.17 M. [c] Containing 0.10 M $Fe(CO)_5$. [d] Not determined. [e] No samples were taken during the experiment. [f] Initial solution contains 0.041 M $NaMn(CO)_5$ and 1.57 M HCO_2Me. H_2 was not added.

Manganese carbonyl is quantitatively converted to $Mn(CO)_5^-$, the concentration of which decreases gradually during the reaction due to the precipitation of $MnCO_3$. In addition to ethanol and CO_2, other organic products (Table I) are generated.

If the reaction is carried out without HCO_2K, only 30% of $Mn_2(CO)_{10}$ is converted to $HMn(CO)_5$, which remains constant for hours. Moreover, the solution becomes slightly acidic (pH 5.5); the concentration of methyl formate gradually increases to 0.1 M in 3 h; and no ethanol (<0.1 mM) is detected. Therefore, potassium formate (or other alkali-metal formate) is an important constituent of the catalyst solutions.

The following reactions in Scheme I are proposed to account for the production of ethanol in the $Mn_2(CO)_{10}$–alkali-metal formate–methanol solutions. The mechanism also satisfactorily accounts for the product distributions and the kinetics, which are discussed later.

Scheme I

$$Mn_2(CO)_{10} + H_2 \rightleftharpoons 2HMn(CO)_5 \quad (1)$$

$$CH_3OH + CO \xrightleftharpoons{HCO_2^-} HCO_2CH_3 \quad (2)$$

$$HMn(CO)_5 + HCO_2^- \rightarrow Mn(CO)_5^- + H_2 + CO_2 \quad (3)$$

$$Mn(CO)_5^- + HCO_2CH_3 \rightarrow CH_3Mn(CO)_5 + HCO_2^- \quad (4)$$

$$CH_3Mn(CO)_5 + CO \rightleftharpoons CH_3C(O)Mn(CO)_5 \quad (5)$$

$$CH_3C(O)Mn(CO)_5 + H_2 \rightarrow HMn(CO)_5 + CH_3CHO \quad (6)$$

$$CH_3CHO + H_2 \rightarrow CH_3CH_2OH \quad (7)$$

In the absence of HCO_2^-, the equilibrium reaction between $Mn_2(CO)_{10}$ and H_2 (eq 1) to form the inactive $HMn(CO)_5$ is rapidly established, and the solution becomes weakly acidic. The concentration of HCO_2CH_3 (eq 2) is low because of the absence of any catalyst. Because of the low concentrations of $Mn(CO)_5^-$ and HCO_2CH_3, the production of ethanol is too slow to be detected. The addition of HCO_2K brings about the quantitative conversion of $Mn_2(CO)_{10}$ to $Mn(CO)_5^-$ (eq 3) and accelerates the formation of HCO_2CH_3 so that its equilibrium concentration is quickly established.

The methyl-transfer reaction to form $CH_3Mn(CO)_5$[9] from $Mn(CO)_5^-$ and HCO_2CH_3 (eq 4) is rate-limiting, and subsequent fast reactions (eq 5–7) lead to the production of ethanol. The reactions in eq 5,[10,11] 6,[12,13] and 7[12] have been studied previously. The sum of eq 2–7 yields the overall stoichiometry depicted by eq 8.

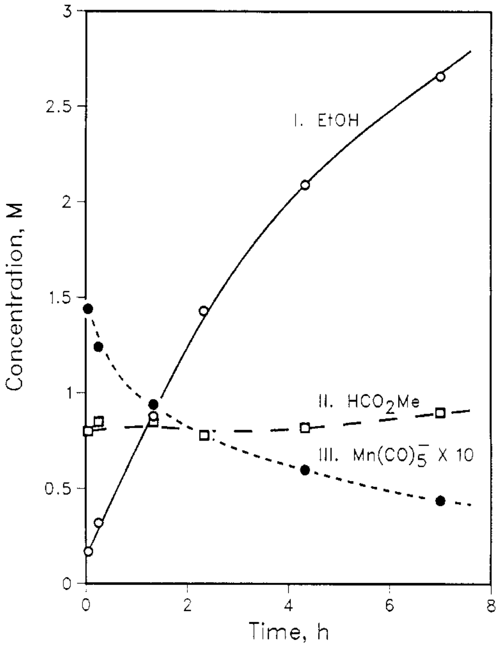

Figure 1. Typical rate plots for EtOH, HCO_2Me, and $Mn(CO)_5^-$ in $Mn_2(CO)_{10}$–HCO_2K–MeOH solutions (initial solutions: $[Mn_2(CO)_{10}]$ = 0.075 M and $[HCO_2K]$ = 0.17 M; T = 200 °C and P = 4500 psi of 3:1 CO/H_2): curve I (○), EtOH; curve II (□), HCO_2Me; curve III (●), $Mn(CO)_5^-$.

$$CH_3OH + 2CO + H_2 \rightarrow CH_3CH_2OH + CO_2 \quad (8)$$

Owing to the presence of CO_2 generated as the byproduct in eq 3, any base that is stronger than $CH_3OCO_2^-$ is converted to its conjugate acid by CO_2, and the pH of the solution is eventually controlled by the equilibrium in eq 9. The system can be kept at high pH values by maintaining a low partial pressure of CO_2. This may be accomplished by purging the reactor with synthesis gas.

$$CO_2 + CH_3OH + B \rightleftharpoons CH_3OCO_2^- + BH^+ \quad (9)$$

Product Distributions. In addition to ethanol, several other products, including ethyl formate, acetaldehyde,

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[9] An attempt to detect $CH_3Mn(CO)_5$ and $CH_3C(O)Mn(CO)_5$ was not successful because H_2 was produced from a methanol solution of $NaMn(CO)_5$. A solution of 0.041 M $NaMn(CO)_5$ and 1.57 M HCO_2Me was heated at 200 °C under 4000 psi of CO. Loss of 70% of $Mn(CO)_5^-$ and formation of H_2 and $Mn_2(CO)_{10}$ were observed immediately after the temperature reached 200 °C, presumably due to eq 1. The system was catalytic for methanol homologation, even though H_2 was not added (see Table I, experiment 11).

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acetals, methyl acetate, and methane, were also generated. The distribution of products under different CO and H_2 pressures is shown in Table I. Ethyl formate may be generated from the carbonylation of ethanol or by the transesterification reaction between ethanol and methyl formate. The production of acetaldehyde as an intermediate is shown in eq 6. Acetaldehyde is either reduced to ethanol (eq 7) or converted to acetals by its reaction with the alcohols. Methyl acetate may be generated from the reaction of $CH_3C(O)Mn(CO)_5$ with MeOH directly or with H_2O followed by the esterification of the acetic acid generated. Water is the byproduct in the reaction of acetaldehyde and alcohols to give acetals.

We have also examined the product distribution in the hydrogenation of $CH_3Mn(CO)_5$ with and without CO. Conversion of 60% of $CH_3Mn(CO)_5$ to $CH_3C(O)Mn(CO)_5$ was observed when a solution of 14.4 mmol of $CH_3Mn(CO)_5$ in 90 mL of benzene was heated at 100 °C and 600 psi of CO for 2 h. Some methane (0.3 mmol) was detected in the gas phase. The solution reacted immediately with H_2 at 1000 psi to give CH_3CHO (4.1 mmol), EtOH (8.1 mmol), HCO_2Et (0.60 mmol), and CH_4 (0.3 mmol). The Mn complex was converted to $Mn_2(CO)_{10}$ in this reaction. Apparently eq 5 and 6 dominated and no CH_4 was produced after the addition of hydrogen.

In another experiment, 14.4 mmol of $CH_3Mn(CO)_5$ in 75 mL of benzene was heated at 100 °C and 600 psi of argon for 1 h to produce 0.45 mmol of CH_4. The solution reacted immediately with H_2 at 1000 psi to give CH_3CHO (0.14 mmol), EtOH (6.5 mmol), HCO_2Et (0.46 mmol), CO (6.6 mmol), and CH_4 (0.87 mmol). These products accounted for only 55% of the methyl group on $CH_3Mn(CO)_5$ used. The product solution was reddish orange instead of the yellow solution of $Mn_2(CO)_{10}$ obtained in the presence of CO. This finding suggests the presence of polynuclear Mn complexes. The fact that only 6.6 mmol of CO was detected in the gas phase indicates that most of the CO that is not incorporated into the organic products is retained by the manganese. It appears that some of the methyl groups are also retained by the manganese product.

As shown in Table I, the production of CH_4 varies from 5% to 49% in these experiments. These variations may be attributed to the suppression of CH_4 production by CO, since change in H_2 pressure (compare experiment 3 with experiments 1, 8, and 9) does not appear to affect CH_4 selectivity. The results on the hydrogenation of $MeMn(CO)_5$ under CO and under argon pressures are also consistent with suppression of CH_4 production by CO. The diverse mechanisms by which alkanes and aldehydes may be formed from an alkyl–manganese carbonyl complex have been identified in a recent study by Halpern and workers.[14] In view of Halpern's work, it seems likely that at low CO pressures, the formation of acetaldehyde from $CH_3(O)Mn(CO)_5$ (eq 6) proceeds through a prior dissociation of one CO, followed by reaction with H_2 or $HMn(CO)_5$. However, at high CO pressures, the suppression of CO dissociation is expected and a path involving the homolysis of $MeC(O)–Mn(CO)_5$ becomes more important. The acetyl radical thus formed would then abstract the H atom from $HMn(CO)_5$. Similarly, at low CO pressures, CH_4 may be produced from $CH_3Mn(CO)_5$ by initial CO dissociation, followed by reaction with H_2 or $HMn(CO)_5$. At high CO pressures, this path is suppressed. Furthermore, high CO pressure also reduces the concentration of $CH_3Mn(CO)_5$ and, therefore, the production of CH_4, by driving eq 5 to the right. It should be noted that dissociation of acetyl radical to give $CH_3^{\bullet}$ and CO may also contribute to the production of CH_4. The rate constant is calculated to be 1.0×10^4 s^{-1} ($k = 2.4 \times 10^3$ M^{-1} s^{-1} for the reverse reaction) at 200 °C based on the activation parameters of Calvert[15] and Benson.[16] Loss of CO from acyl radicals may compete with the abstraction of an H atom from $HMn(CO)_5$. This type of competition has also been observed by Halpern and co-workers on a related system.[14]

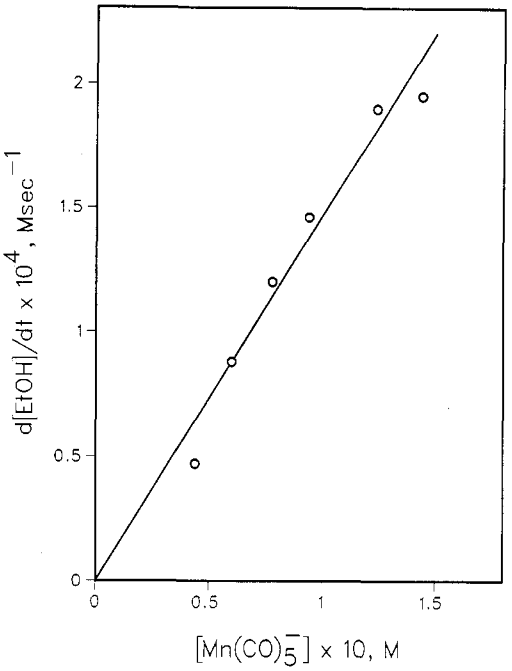

Figure 2. Typical plot of d[EtOH]/d*t* vs. $[Mn(CO)_5^-]$, derived from the data in Figure 1.

The results in Table I and the hydrogenation of $MeMn(CO)_5$ also indicate that CO suppresses the reduction of acetaldehyde to ethanol, since acetaldehyde and its acetals were produced at the expense of ethanol at higher CO pressures. Similar results were obtained in the hydrogenation of $MeMn(CO)_5$ by Dombek.[12] It is most likely that ethanol was also a major product in the related study by King et al.[13] It is interesting to note that Orchin et al.[17] have shown that $RC(O)Mn(CO)_5$ [$R = Ph(CH_2)_x$, $x = 1$ or 2] reacts with high pressure of synthesis gas at 70 °C to give aldehyde in sulfolane, but the same reaction gives $RCH_2OC(O)Mn(CO)_5$ in hexane. The corresponding formate ester is produced when the temperature is raised to 230 °C.

Kinetics. Methanol solutions containing $Mn_2(CO)_{10}$ (0.025–0.075 M) and an excess of HCO_2K (0.15–0.60 M) were used in our kinetic studies. The reactions were carried out at a temperature of 200 °C, an H_2 partial pressure of 260–2800 psi, and a CO partial pressure of 410–2600 psi. The kinetic data are summarized in Table II.

The plots in Figure 1, produced from the results of experiment 5, are used to illustrate the analysis of the rate data. The instantaneous rates of production of ethanol, d[EtOH]/d*t*, are obtained from the tangents to curve I. The linear correlation between d[EtOH]/d*t* and the concentration of $Mn(CO)_5^-$, as shown in Figure 2, indicates that the rate of production of ethanol is first-order in

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Table II. Rate Data for the Homologation of Methanol[a]

expt. no.	t, h	$10^2 \times$ [$Mn(CO)_5^-$], M	[HCO_2Me], M	[EtOH], M	$10^5 \times$ d[EtOH]/dt, M s^{-1}	10^3k_{11}, M^{-1} s^{-1}	χ_{EtOH}	k_4, M^{-1} s^{-1}
1	0	5.53	0.44	0.033				
	1.0	4.13	0.34	0.165	3.7[b]	2.0	0.61	3.3[c]
	2.0	2.67	0.34	0.179				
	3.0	1.87	0.39	0.195				
	5.0	0.43	0.38	0.218				
	6.0	0.10	0.52	0.249				
2	0	4.47	1.13	0.03	7.0	1.4		
	1.0	3.40	1.42	0.28	7.0	1.4		
	2.0	2.93	1.35	0.52	5.9	1.5		
	3.2	2.80	1.46	0.76	4.7	1.2		
	5.1	2.27	1.41	0.96				
						av 1.4	0.66	2.1
3	0	5.43	0.42	0	5.2	2.3		
	1.0	4.83	0.50	0.13	4.1	1.7		
	2.0	4.13	0.46	0.33	3.1	1.6		
	4.0	2.97	0.42	0.52				
	6.0	1.60	0.43	0.54				
	8.0	0.58	0.44	0.53				
						av 1.9	0.54	3.5[c]
4	0	4.77	0.68	0				
	0.17	4.53	1.28	0	11.0	1.9		
	1.0	3.73	1.25	0.30	9.2	2.0		
	2.0	3.43	1.19	0.55	7.2	1.8		
	3.0	3.13	1.17	0.83	6.4	1.8		
	4.0	3.07	1.03	1.05	5.4	1.7		
	6.0	2.63	1.19	1.36				
						av 1.8	0.75	2.4
5	0.05	14.4	0.80	0.17	19.5	1.7		
	0.25	12.4	0.85	0.32	19.0	1.8		
	1.33	9.4	0.85	0.88	14.6	1.8		
	2.33	7.8	0.78	1.43	12.0	2.0		
	4.33	6.0	0.82	2.09	8.8	1.8		
	7.00	4.4	0.90	2.66	4.7			
						av 1.8	0.72	2.5
7[d]	0	4.6	0.71	0.10	7.9	2.4		
	2.5	3.8	0.92	0.77	6.9	2.0		
	4.4	3.4	1.02	1.20	5.9	1.7		
	6.3	2.9	1.02	1.49	4.1	1.4		
	9.6		1.08	1.85				
						av 1.9	(0.75)[e]	2.5

[a] The experiment numbers correspond to those in Table I. [b] Average rate in the first hour. [c] These values have higher uncertainty because of fewer data points taken and are not used to calculate the average value for k_4. [d] P_{CO} = 2300 (± 400) psi and P_{H_2} = 750 (± 150) psi. [e] Estimated value.

$Mn(CO)_5^-$. This is also true for other experiments in Table II. Therefore, the rate of production of ethanol may be depicted by eq 10.

$$d[EtOH]/dt = k_{10}[Mn(CO)_5^-] \qquad (10)$$

Such a good correlation between d[EtOH]/dt and [$Mn(CO)_5^-$] exists only because the concentration of HCO_2CH_3 is relatively constant throughout an experiment, as shown by the data in Table II. In order to derive the dependence of the rate constant k_{10} on the concentration of HCO_2CH_3, the data are tested against eq 11, in which $k_{10} = k_{11}[HCO_2CH_3]$. The k_{11} values calculated from eq

$$d[EtOH]/dt = k_{11}[HCO_2CH_3][Mn(CO)_5^-] \qquad (11)$$

11 are shown in Table II. The agreement among these values obtained from our experiments, in which the initial concentration of $Mn(CO)_5^-$ varies by a factor of 3 and the steady-state concentration of HCO_2CH_3 varies by a factor of 4, indicates that eq 11 is a good rate law. Therefore, d[EtOH]/dt is first-order in HCO_2CH_3 and first-order in $Mn(CO)_5^-$.

The second-order rate law for the production of ethanol is consistent with the mechanism of Scheme I, in which eq 4 is the rate-limiting step. As discussed earlier, ethanol only accounts for part of the products derived from eq 4, and k_{11} is not equal to k_4. If we assume that during the course of an experiment ethanol accounts for a constant mole fraction (χ_{EtOH}) of the products derived from eq 4, then eq 12 may be used to calculate k_4. This assumption

$$d[EtOH]/dt = k_4\chi_{EtOH}[HCO_2CH_3][Mn(CO)_5^-] \qquad (12)$$

may not be strictly true. However, it is suitable for the analysis of our data if only small variations in the mole fraction of ethanol occur during the course of the reaction. The results in Table II justify the assumption. As expected, the k_4 values shown in Table II are fairly constant. The average value of 2.4×10^{-3} M^{-1} s^{-1} for k_4 is comparable to the second-order rate constant of 2.7×10^{-3} M^{-1} s^{-1} for the reaction of NMe_4^+ with $Mn(CO)_5^-$ in N-methylpyrrolidinone at infinite dilution.[18] The values obtained in experiments 1 and 3 have higher uncertainty because the rapid loss of the catalysts in these experiments prevents the acquisition of better data.

In Table III, the rate constant k_4 for reactions in different catalyst solutions is summarized. These experiments demonstrate that the rate constant is not significantly affected by the change in the concentration of HCO_2K, by the replacement of HCO_2K with HCO_2Cs, or by the addition of 18-crown-6. The addition of $Fe(CO)_5$

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Table III. Second-Order Rate Constant for the Reaction of $Mn(CO)_5^-$ with HCO_2Me: Effect of Solution Composition[a]

expt no.	compositn, M $[Mn_2(CO)_{10}]$	$[HCO_2K]$	[others]	10^3k_4, M^{-1} s^{-1}
1	0.025	0.15		2.3
2	0.025	0.15	0.25 (18-crown-6)	1.9
3	0.025	0.60		2.4
4	0.025		0.15 (HCO_2Cs)	1.7
5[b]	0.075	0.17	0.10 $[Fe(CO)_5]$	2.4

[a] Reaction at 200 °C and 4500 psi, maintained with a 3:1 CO/H_2 gas mixture. [b] Corresponds to experiment 6 of Table I.

also has no effect on the rate or the selectivity of the $Mn_2(CO)_{10}$–HCO_2K–methanol solutions.

Formation of $Mn(CO)_5^-$ from $Mn_2(CO)_{10}$ and HCO_2^-. $Mn_2(CO)_{10}$ (0.075 M) was rapidly and quantitatively converted to $Mn(CO)_5^-$ at 200 °C and 4500 psi of CO in an HCO_2K–methanol solution (0.17 M). The first gas sample, taken at 10 min after the test temperature was reached, had the composition (mol %): H_2, 1.9; CO, 84.2; CH_4, 0.6; CO_2, 13.2. The mole percent of hydrogen remained practically unchanged for 12 h while that of methane and carbon dioxide increased continuously. Methyl formate was rapidly formed and was at equilibrium throughout the experiment. During this period, ethanol, acetaldehyde, and acetals were continuously produced. Ethanol only accounts for about 30% of the liquid products, the balance being acetaldehyde and the acetals.

The formation of $Mn(CO)_5^-$ and H_2 may be depicted by reaction 13. Hydrogen generated in eq 13 is used in the production of ethanol and other products. A low steady-state concentration of H_2 is maintained, and the system is, therefore, catalytic in the homologation of methanol. It seems likely that, instead of reacting with HCO_2^- directly as shown in eq 3, $HMn(CO)_5$ is converted to $Mn(CO)_5^-$ via eq 1 and 13. Reduction of metal carbonyls by formate

$$Mn_2(CO)_{10} + 2HCO_2^- \rightarrow 2\ Mn(CO)_5^- + H_2 + 2CO_2 \quad (13)$$

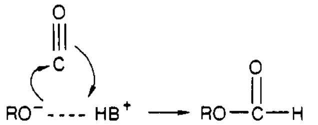
ion and its reverse reaction have been reported for some group VI (6^{30}) metal carbonyls.[19,20] Both reactions 1 and 13 are fast under our reaction conditions, and our results do not show which path dominates under these conditions. In any case, quantitative conversion of $Mn_2(CO)_{10}$ to $Mn(CO)_5^-$ was achieved in our catalyst solutions.

Carbonylation of Methanol Catalyzed by HCO_2^-. The carbonylation of alcohols in the presence of a strong base to give the corresponding formate esters is a well-documented industrial process.[21-22] The reaction has been proposed to proceed through the preequilibrium formation of the carbanion $RO(O)C^-$, which picks up a proton to form alkyl formate (eq 14 and 15).[23] However, later attempts

$$RO^- + CO \rightleftharpoons RO(O)C^- \quad (14)$$

$$RO(O)C^- + ROH \rightarrow RO(O)CH + RO^- \quad (15)$$

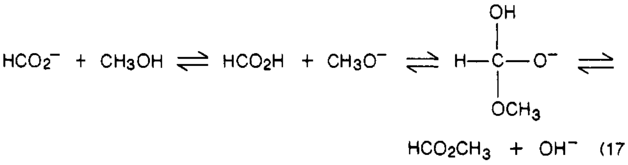
to substantiate the formation of the intermediate carbanion in the decarbonylation of methyl formate by trapping experiments and by isotope-labeling experiments failed.[24] A concerted mechanism, involving direct reaction of carbon monoxide with an alkoxide ion that is hydrogen-bonded to an acid, was suggested (eq 16).



(16)

Earlier we adopted the base-catalyzed carbonylation of methanol as a route for the formation of methyl formate in amine–methanol solutions.[7,8] An unexpected observation was that HCO_2^- ion, which raises the pH of the methanol solution by only 1 pH unit, was very effective in catalyzing reaction 2 in the homologation reaction. This observation cannot be explained in terms of the basicity of the solution, since formate ion is more effective in catalyzing reaction 2 than dimethylneopentylamine and proton sponge, the conjugate acids of which have pK_a values of 10 and 13, respectively. We have also shown that HCO_2^- catalyzes this reaction in the absence of $Mn_2(CO)_{10}$.

We believe that formate ion is the catalyst for reaction 2 in HCO_2K–methanol catalyst solutions, as well as in amine–methanol catalyst solutions. The reaction may simply proceed by the reverse of the base-catalyzed hydrolysis of the formate ester, namely, eq 17. The OH^- is



$$HCO_2^- + CH_3OH \rightleftharpoons HCO_2H + CH_3O^- \rightleftharpoons H\text{—}\underset{OCH_3}{\overset{OH}{C}}\text{—}O^- \rightleftharpoons HCO_2CH_3 + OH^- \quad (17)$$

readily converted back to HCO_2^- by CO to complete the cycle.[25] A recent study suggests that formic acid serves as an intermediate in the catalytic conversion of alcohols to their formate esters.[26]

The inefficiency of the bulky amines, such as dimethylneopentylamine and proton sponge, in catalyzing reaction 2 may be attributed to the difficulty for these amines to displace the formate ion from methyl formate. Such S_N2 reactions are known to be very much affected by the steric hindrance of the reactants.[27,28]

Catalyst Stability. One common problem in the $Mn_2(CO)_{10}$ catalyst system, both in the amine–methanol solutions and in the HCO_2K–methanol solutions, is the loss of the catalyst due to the formation of $MnCO_3$ or $Mn(HCO_2)_2$. Depending on the reaction conditions, both $MnCO_3$ and $Mn(HCO_2)_2$ have been found to precipitate from the solutions. Efforts to prevent their formation have not been successful.

We believe that the loss of the catalyst is initiated by the disproportionation of $Mn_2(CO)_{10}$ according to eq 18.

$$3Mn_2(CO)_{10} \rightarrow 2Mn^{2+} + 4Mn(CO)_5^- + 10CO \quad (18)$$

We have observed that higher CO pressures prolong the lifetime of the catalyst. This is taken as an indication that reaction 18 proceeds with the prior, reversible dissociation of one CO. Hydrogen was also found to prolong the lifetime of the catalyst. The effect of hydrogen presumably is to reduce the steady-state concentration of $Mn_2(CO)_{10}$ (eq 1). Consistent with this explanation, no correlation between the rate of catalyst loss and the partial pressure of CO_2 was found. Addition of potassium formate apparently destabilizes the catalyst, since no loss of Mn

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Table IV. Survey of Catalysts in HCO_2K–MeOH Solutions[a,b]

expt no.	cat. (concn, M)	$[HCO_2K]$, M	T, °C	t, h	[EtOH], M
1	$Mn_2(CO)_{10}$ (0.075)	0.17	200	7.0	2.7
2	$Fe(CO)_5$ (0.10)	0.50	230	1.0	0.03
3	$NiI_2{\cdot}6H_2O$ (0.10)	0.30	230	4.7	0.06
4	$Ru_3(CO)_{12}$ (0.017)	0.15	230	4.2	0
5	RhI_3 (0.05)	0.15	200	4.8	0.03

[a] P = 4500 psi, maintained with a 3:1 CO/H_2 gas mixture. [b] The concentrations of methyl formate were about 1 M in all these experiments.

catalyst was found when a methanol solution of $Mn_2(CO)_{10}$ was heated at 200 °C for 3 h in 4500 psi of 3:1 CO/H_2.

Other Metal Catalysts. Several other transition-metal complexes were tested for catalytic activity in this system. The results in Table IV indicate that none is as active as $Mn_2(CO)_{10}$. Since methyl formate is present at its equilibrium concentrations in all these experiments, the lower reactivity in these systems simply reflects the lack of reactive nucleophiles.

Experimental Section

Material. The following chemicals were reagent grade and were used as received: $Mn_2(CO)_{10}$ and $Ru_3(CO)_{12}$ (Strem Chemicals); $Fe(CO)_5$ and 18-crown-6 (Aldrich); $NiI_2{\cdot}6H_2O$, RhI_3, HCO_2Cs, and HCO_2K (Alfa). Hydrogen and carbon monoxide were of CP grade from Matheson. The $3CO/H_2$ gas mixture was blended from the CP-grade gases and had the composition (%): H_2, 24.0; CO, 73.8; N_2, 2.2.

Analyses. The analyses of the gas samples were carried out isothermally at 80 °C on a 3.5-ft spherocarb column in a Varian 3700 GC, equipped with a thermal conductivity detector. Analyses of the liquid products, except for acetals, were carried out on a 6-ft porapak Q column in a Varian 3700 GC equipped with a flame ionization detector with the program: 60 °C (10 min) to 220 °C (12 min) at 10 °C/min. Analyses of acetals were carried out on a 6-ft 1% Alltech 1000 on Graphpac GC with the program: 50 °C (5 min) to 130 °C (5 min) at 10 °C/min. The identification of the organic products by GC–MS was performed on a Hewlett-Packard 5888 GC-5984 MS system. The analyses were done on a 60-m SE-30 column with the program: 50 °C (6 min) to 220 °C at 8 °C/min.

The quantitative analysis of $Mn(CO)_5^-$ was performed by a modification of the method developed by Iwanaga[29] for the titration of $Co(CO)_4^-$. A 1.0 mM methylene blue solution in 20% acetic acid–ethanol was used in the titration. $Mn(CO)_5^-$ titrates as a one-electron reductant.

The quantitative analysis of dimethylpiperidinium ion was carried out by precipitation of the ammonium ion as its Reineckate salt followed by the spectrophotometric determination of the Reineckate ion. The procedure has been described elsewhere.[18]

Catalytic Reactions. The system for the high-pressure reactions has been described previously.[18] In a typical experiment, $Mn_2(CO)_{10}$ and HCO_2K were weighed into the autoclave, which was then assembled and filled with argon after the air was pumped off. Deaerated methanol was then added against a counterflow of argon and the solution heated to 200 °C with the desired CO and H_2 pressures. Pressure drops due to reaction and samplings were restored with H_2 and CO. The amounts of CO and H_2 to be added to maintain the desired partial pressures of CO and H_2 were estimated from the stoichiometry of the reaction, the pressure drop, and the composition of the head gas, as monitored from the gas samples. The fluctuations of P_{H_2} and P_{CO} in Table I reflect the difficulty in controlling them in these batch operations.

The white precipitate in the cold product solution was collected, washed with methanol, and dried. The compound was identified as $MnCO_3$ from its infrared spectra: ν_{CO} = 1415 cm^{-1} (vs).

Reaction of $Mn_2(CO)_{10}$ with HCO_2K. $Mn_2(CO)_{10}$ (13.5 mmol) and HCO_2K (30.6 mmol) were weighed into the autoclave, which was sealed and filled with argon. Deaerated methanol (180 ml) was then added to the autoclave against an argon flow. After the argon gas was replaced with CO, the autoclave was heated to 200 °C with an initial pressure of 2500 psi of CO. The reaction was maintained at 200 °C and 4500 psi with CO for 21 h, but the reaction apparently stopped after 12 h due to loss of the Mn catalyst.

Hydrogenation of $MeMn(CO)_5$ in the Absence of CO. A benzene solution (75 mL) containing 14.4 mmol of $MeMn(CO)_5$ was heated at 100 °C under 600 psi argon for 1.1 h. A sample of the head gas showed that 0.45 mmol of CH_4 was produced. A liquid sample showed only the presence of a small amount of CH_3CHO, presumably due to decomposition of $MeMn(CO)_5$ on the injector. Hydrogen was then admitted to raise the pressure from 600 to 1600 psi. A gas sample was taken 20 min later, and the reactor was then cooled. A liquid sample was taken from the reactor. Analyses of the samples gave the following products: CH_3CHO, 0.14 mmol; EtOH, 6.5 mmol; HCO_2Et, 0.46 mmol; CH_4, 0.87 mmol; CO, 6.6 mmol. The product solution was reddish orange and contained no precipitate.

Hydrogenation of $MeMn(CO)_5$ in the Presence of CO. A benzene solution (90 mL) containing 14.4 mmol of $MeMn(CO)_5$ was loaded into the autoclave against a steady flow of argon. After the admission of 500 psi of CO, the solution was heated to 100 °C. A gas sample taken 2 h later indicated the presence of 0.3 mmol of CH_4. A liquid sample revealed, by its $^{13}C(^1H)$ NMR spectra, that 60% of $MeMn(CO)_5$ had been converted to $MeC(O)Mn(CO)_5$. Analyses of the sample by GLC showed only a trace of CH_3CHO and no other organic products. Hydrogen was then admitted to raise the pressure from 600 to 1600 psi. A gas sample was taken 10 min later, and the reactor was cooled. A liquid sample was taken from the reactor at room temperature. Analyses of the gas sample and the liquid sample gave the following products: CH_3CHO, 4.1 mmol; EtOH, 8.1 mmol; HCO_2Et, 0.6 mmol; CH_4, 0.3 mmol.

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Registry No. MeOH, 67-56-1; $Mn_2(CO)_{10}$, 10170-69-1; HCO_2K, 590-29-4; EtOH, 64-17-5.

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(30) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13–18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)