Homologation of Methanol Catalyzed by Manganese Carbonyl in Tertiary Amine–Methanol Solutions[†]

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Dimanganese decacarbonyl catalyzes the homologation of methanol to ethanol at 200 °C in the presence of CO and H_2 (300 atm) in *N*-methylpiperidine ($MeNC_5H_{10}$)–MeOH solutions. At reaction conditions, $Mn_2(CO)_{10}$ is converted to $Mn(CO)_5^-$, while MeOH is carbonylated to give HCO_2Me. The reaction of $Mn(CO)_5^-$ with HCO_2Me or with $Me_2NC_5H_{10}^+$, the latter being generated from the reaction between $MeNC_5H_{10}$ and HCO_2Me, yields $MeMn(CO)_5$. Subsequent fast reactions convert $MeMn(CO)_5$ to ethanol and other products. With a synthesis gas mixture of 3:1 CO/H_2, ethanol and other liquid products are produced in 85% yield, the balance being CH_4. Minor liquid products include HCO_2Et, CH_3CHO, acetals, and *n*-PrOH. These minor products, produced at the expense of ethanol, may account for up to 10% of the products. As with other base-promoted systems, CO_2 rather than H_2O is the coproduct of this reaction, and the homologation reaction may be depicted as $CH_3OH + 2CO + H_2 \rightarrow CH_3CH_2OH + CO_2$. The rate constants for the two competing reactions to generate $MeMn(CO)_5$ have been measured under conditions in which only one of these reactions is operative. The reaction of $Me_2NC_5H_{10}^+$ with $Mn(CO)_5^-$ in methanol exhibits a strong salt effect and follows second-order kinetics with a rate constant of 1.0×10^{-2} M^{-1} s^{-1} at 200 °C and an ionic strength of 0.2 M. This rate constant is comparable to the value of 2.4×10^{-3} M^{-1} s^{-1} for the reaction of HCO_2Me with $Mn(CO)_5^-$. Thus, both $Me_2NC_5H_{10}^+$ and HCO_2Me are effective in methylating $Mn(CO)_5^-$, and either reaction may be made the dominant pathway for the formation of $MeMn(CO)_5$ in the catalytic process.

We previously reported a process for the catalytic homologation of methanol to ethanol under the pressure of synthesis gas in tertiary amine–methanol solutions.[1,2] The process is applicable to a variety of transition-metal carbonyls. Among those examined, $Mn_2(CO)_{10}$ was chosen for further study; high selectivity for ethanol production is obtainable with this catalyst while the relevant organomanganese intermediates may be independently synthesized and studied. A recent paper[3] describes $Mn_2(CO)_{10}$ catalyzed homologation of methanol in alkali-metal formate–methanol solutions. In that system, the methyl transfer reaction between methyl formate and $Mn(CO)_5^-$ to give $MeMn(CO)_5$ was shown to be rate-limiting, and second-order kinetics were observed. To understand the kinetics of the catalytic homologation of methanol in $Mn_2(CO)_{10}$–tertiary amine–methanol solutions, we used *N*-methylpiperidine as the base and evaluated the rate constant for the other methyl transfer reaction, i.e., the reaction between $Mn(CO)_5^-$ and $Me_2NC_5H_{10}^+$. The results have allowed us to understand the seemingly complicated kinetics of the catalytic homologation of methanol in $Mn_2(CO)_{10}$–tertiary amine–MeOH solutions.

Results and Discussion

When a methanol solution of $Mn_2(CO)_{10}$ (0.075 M) and *N*-methylpiperidine ($MeNC_5H_{10}$) (2.0 M) was heated to 200 °C under synthesis gas (3:1 CO/H_2 at 300 atm), 40% of the $Mn_2(CO)_{10}$ was converted to $Mn(CO)_5^-$ and ethanol was produced. The results are shown in Figure 1 and in Table I, experiment 1.

In contrast to the catalyst solutions of $Fe(CO)_5$ and other metal carbonyls investigated earlier,[1,2] both methyl formate and dimethylpiperidinium ion ($Me_2NC_5H_{10}^+$) were at very low concentrations, approximately 0.03 and 0.01 M, respectively. Despite these low concentrations, the rate of ethanol production was comparable to that found in Fe(CO)$_5$–amine–methanol solutions. Analyses of samples taken at various times indicated that, except for the gradual decrease in the concentration of $Mn(CO)_5^-$, the reaction proceeded under conditions close to a steady state. The loss of $Mn(CO)_5^-$ was accompanied by the precipitation of $MnCO_3$ (ν_{CO} = 1415 cm^{-1} (vs)). The apparent pH of the solution remained at 10.0 ± 0.1. The concentrations of HCO_2Me and $Me_2NC_5H_{10}^+$ remained fairly constant, while that of ethanol increased steadily and reached 1.7 M in the 12-h reaction time. Traces of HCO_2Et (0.018 M), *n*-PrOH (0.010 M), CH_3CHO(0.010 M), and $CH_3CH(OCH_3)_2$ (0.014 M) were also found in the product solution. The only gaseous product was methane, which accounted for 15% of the products. As with other base-promoted systems, CO_2 rather than H_2O is the coproduct of the homologation reaction.

Further studies of this system initially led to puzzling results, since the rate of ethanol production failed to respond to factors expected to alter it. In the experiment illustrated in Figure 2 (experiment 2), the reaction just described was allowed to reach steady state, and methyl formate (enough to increase its concentration by 2.3 M) was then added under pressure. As expected, methyl formate decarbonylated to achieve its equilibrium concentration of 1.1 M immediately after the addition was completed, and $MeNC_5H_{10}$ was quantitatively converted to $Me_2NC_5H_{10}^+$ in about 1 h. The concentration of $Mn(CO)_5^-$ also rapidly increased from 0.05 to 0.15 M, corresponding to the quantitative conversion of $Mn_2(CO)_{10}$. The apparent pHs of the solutions were at 10.5 ± 0.1. Surprisingly, the rate of production of ethanol hardly changed, even though the concentrations of $Mn(CO)_5^-$, HCO_2Me, and $Me_2NC_5H_{10}^+$ had increased by factors of 3, 40, and 300, respectively. The subsequent decrease in the concentration of methyl formate correlated with a drop in the partial

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(1) Chen, M. J.; Feder, H. M.; Rathke, J. W. *J. Am. Chem. Soc.* **1982**, *104*, 7346.

(2) Chen, M. J.; Feder, H. M.; Rathke, J. W. *J. Mol. Catal.* **1982**, *17*, 331.

(3) Chen, M. J.; Rathke, J. W. *Organometallics* **1987**, *6*, 1833.

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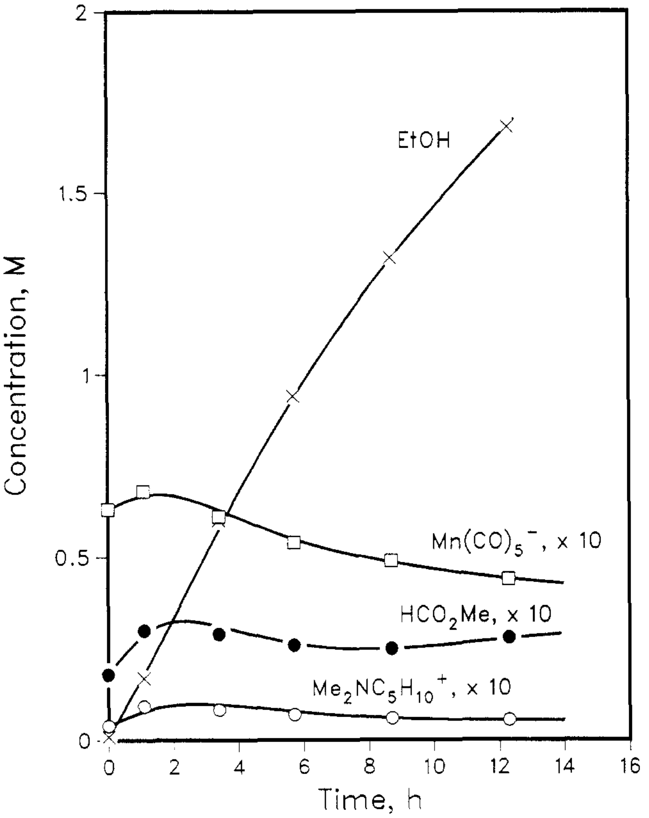

Figure 1. Typical rate plots for the homologation of methanol in $Mn_2(CO)_{10}$-$MeNC_5H_{10}$-MeOH solutions at high concentration of $Mn_2(CO)_{10}$ (initial solution, $[Mn_2(CO)_{10}]$ = 0.075 M and $[MeNC_5H_{10}]$ = 2.0 M; T = 200 °C and P = 300 atm of 3:1 CO/H_2).

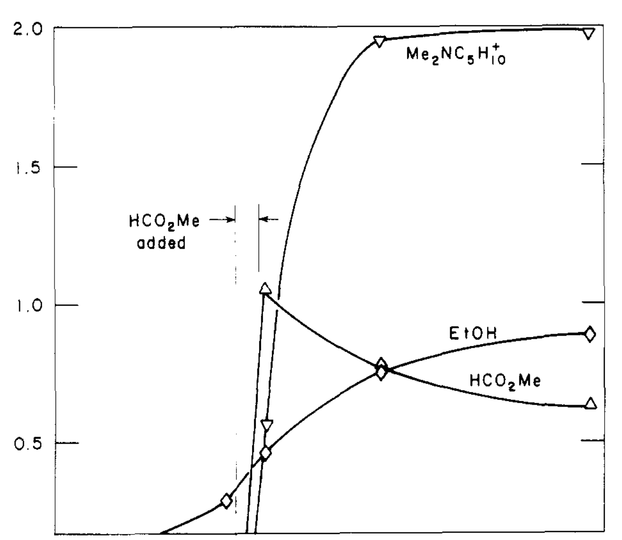

Figure 2. Effect of the addition of methyl formate on the homologation of methanol in $Mn_2(CO)_{10}$-$MeNC_5H_{10}$-MeOH solutions (initial solution, $[Mn_2(CO)_{10}]$ = 0.075 M and $[MeNC_5H_{10}]$ = 2.0 M; T = 200 °C and P = 300 atm of 3:1 CO/H_2).

pressure of CO. The decrease in the concentration of $Mn(CO)_5^-$ was accompanied by the precipitation of a white solid, which has been identified as $Mn(HCO_2)_2$ by its IR spectra[4] (ν_{CO} at 1570 (vs), 1350 (s), and 775 cm^{-1} (m)).

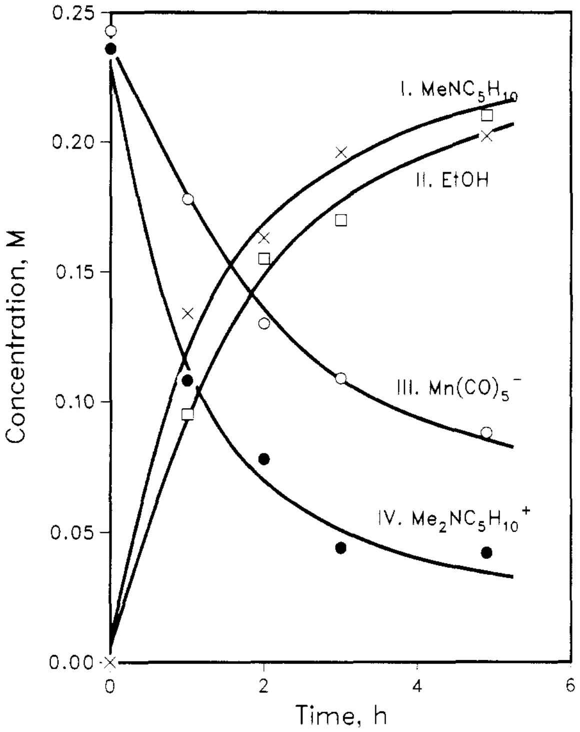

Figure 3. Rate plots for the reaction of $Mn(CO)_5^-$ with $Me_2NC_5H_{10}^+$ in methanol (initial solution, 0.24 M $[Me_2NC_5H_{10}][Mn(CO)_5]$; T = 180 °C and P = 300 atm of H_2).

In another experiment, the effect of a change in the concentration of $Mn_2(CO)_{10}$ on the homologation of methanol was examined. By simply reducing the concentration of $Mn_2(CO)_{10}$ from 0.075 to 0.025 M (experiment 3), we found that 75% of the $MeNC_5H_{10}$ was converted to $Me_2NC_5H_{10}^+$, and both HCO_2Me and $Mn(CO)_5^-$ reached their equilibrium concentrations within 2 h at 200 °C. The average rate of ethanol production in the first 2 h was comparable to that of a solution containing 0.075 M $Mn_2(CO)_{10}$ (experiment 1), but thereafter the rate dropped more quickly because of faster loss of the catalyst. The pHs of the solutions were at 10.8 ± 0.1. White precipitate of $Mn(HCO_2)_2$ was found in later samples.

The change in the composition of the catalyst solution, brought about by adding methyl formate or by varying the initial concentration of $Mn_2(CO)_{10}$, may be understood in terms of changes in the relative rates of the various steps in the catalytic cycle. However, it is not obvious why the rate of ethanol production changed so little, even though the composition of the solutions changed greatly. To understand the complex chemistry of the catalytic homologation of methanol in $Mn_2(CO)_{10}$-amine-methanol solutions, we continued to study the kinetics of the individual steps in the catalytic cycle. Some of these studies were reported earlier.[3]

Methyl Transfer Reactions between $Me_2NC_5H_{10}^+$ and $Mn(CO)_5^-$ in Methanol Solution. The methyl transfer reaction between $Me_2NC_5H_{10}^+$ and $Mn(CO)_5^-$ in methanol was carried out under 300 atm of H_2 and in the absence of CO so that formation of methyl formate and the regeneration of $Mn(CO)_5^-$ could be eliminated or minimized.

Figure 3 presents the rate plots for the reactants and the products in the reaction of equimolar $Me_2NC_5H_{10}^+$ and $Mn(CO)_5^-$ at 180 °C. These results indicate that 1 mol of

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[4] Ogata, T.; Taga, T.; Osaki, K. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1674.

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

	initial solution							
expt no.	$[Mn_2(CO)_{10}]$, M	$[HCO_2K]$, M	$[MeNC_5H_{10}]$, M	*t*, h	$10^2[Mn(CO)_5^-]$,[b] M	$[HCO_2Me]$, M	$[Me_2NC_5H_{10}^+]$, M	[EtOH], M
1	0.075	0	2.0	0	6.3 (16.2)	0.018	0.0040	0.01
				1.1	6.8 (15.6)	0.030	0.0093	0.17
				3.4	6.1 (14.4)	0.029	0.0083	0.60
				5.7	5.4	0.026	0.0070	0.94
				8.7	4.9 (11.8)	0.025	0.0060	1.32
				12.3	4.4 (10.0)	0.028	0.0055	1.68[c]
2	0.075	0	2.0	0	5.0	0.02	0.008	0.04
				1.1	4.3	0.02	0.004	0.29
				1.17 -1.35	methyl formate (25 mL) added			
				1.38	14.8	1.05	0.56	0.43
				2.22	13.4	0.77	1.85	0.59
				3.62	9.0	0.63	1.88	0.71
3	0.025	0	2.0	0	3.8	0.02	0[d]	0.01
				2.0	5.2	0.72	1.5[d]	0.48
				4.0	4.0	0.74	1.9[d]	0.58
				6.0	2.4	0.70	1.9[d]	0.64
4	0.025	0	0.050	0	0.6	1.23[e]	0.017[d]	0.02
				1.1	2.6 (5.2)	0.94	0.013	0.18
				2.4	1.9	0.96	0.006	0.31
				4.1	2.2	0.83	0.007	0.50
				7.6	1.9	0.60	0.007	0.72
				22.2	1.2 (2.0)	0.36[f]	0.012	1.19
5	0.025	0.15	0	0	4.6	0.71	0	0.10
				2.5	3.8	0.92	0	0.77
				4.4	3.4	1.02	0	1.20
				6.3	2.9	1.02	0	1.49
				9.3		1.08	0	1.85
6	0.025	0.15	0.050	0	4.8	0.76	0.019	0.03
				1.0	4.2	0.98	0.029	0.26
				2.0	3.6	0.96	0.026	0.45
				4.0	2.7	0.91	0.023	0.83
				6.0	1.7	0.90	0.025	0.97
7	0.025	0.15	0.30	0	5.8	1.00	0.184	0.13
				1.0	4.3	1.23	0.257	0.42
				2.0	3.1	1.16	0.243	0.67
				3.3	1.5	1.07	0.256	0.75
8	0.025	0.15	2.0	0	5.1	0.89	1.52	0.07
				1.0	4.7	0.72	1.99	0.15
				2.0	3.9	0.71	1.99	0.24
				3.0	3.7	0.69	1.94	0.30
				4.6	2.6	0.70	1.99	0.40
				6.6	2.0	0.67	2.09	0.45

[a] Reactions were at 200 °C and 300 atm, maintained with a 3:1 CO/H_2 gas mixture. [b] Numbers in parentheses are the concentration of total manganese. [c] The sample also contained 0.010 M CH_3CHO, 0.018 M HCO_2Et, 0.010 M *n*-PrOH, and 0.014 M $CH_3CH(OCH_3)_2$. Concentrations of side products increased steadily with time. [d] Deduced from the concentration of $MeNC_5H_{10}$. [e] The initial solution contains 1.50 M HCO_2Me. [f] Pressure, not maintained since last sampling, dropped down to 210 atm.

$MeNC_5H_{10}$ was produced for each mole of $Me_2NC_5H_{10}^+$ consumed and that ethanol accounted for 90% of the $Me_2NC_5H_{10}^+$ consumed. Consistent with these results, the methane produced corresponds to 10% of the products. Therefore, the reaction may be expressed as

$$Me_2NC_5H_{10}^+ + Mn(CO)_5^- \xrightarrow{H_2} 0.9MeCH_2OH + 0.1CH_4 + MeNC_5H_{10} + (\text{Mn products} + CO) \quad (1)$$

Comparison of curves III and IV suggests that partial regeneration of $Mn(CO)_5^-$ did occur, since less than 1 mol of $Mn(CO)_5^-$ was consumed for each mole of $Me_2NC_5H_{10}^+$ reacted. This regeneration occurred mostly in the first hour, after which there was nearly a 1:1 correspondence in the consumption of $Mn(CO)_5^-$ and $Me_2NC_5H_{10}^+$. A white precipitate, with the empirical formula of $Mn_1C_{1.25}H_{4.30}N_{0.17}O_{2.08}$, was collected from the product solution. A trace of methyl formate was found in the product solution (≤0.004 M), but its contribution to the methyl transfer reaction may be neglected.

Table II lists the concentrations of $Mn(CO)_5^-$ and $Me_2NC_5H_{10}^+$ and the rates of disappearance of $Me_2NC_5H_{10}^+$ as derived from the tangents to curve IV at various sampling times. The ratio of $-d[Me_2NC_5H_{10}^+]/dt$ to the concentration product $[Mn(CO)_5^-][Me_2NC_5H_{10}^+]$, shown as k_2 in the last column, is fairly constant. Therefore, reaction 2 follows second-order kinetics with a rate constant of 9.2×10^{-4} $M^{-1}s^{-1}$ at 180 °C.

$$Me_2NC_5H_{10}^+ + Mn(CO)_5^- \xrightarrow{k_2} MeMn(CO)_5 + MeNC_5H_{10} \quad (2)$$

A similar experiment carried out at 200 °C gave $k_2 = 1.0$ (±0.3) × 10^{-2} M^{-1} s^{-1}. Methane accounted for 15% of the products derived from the methyl group. Because of the rapidness of the reaction, this rate constant is evaluated from fewer data points and has higher uncertainty. It should be noted that, in an earlier study of reaction 2 in *N*-methyl-2-pyrrolidinone solution, a primary kinetic salt effect was observed, and a value of 2.7×10^{-3} M^{-1} s^{-1} at 200 °C was obtained for k_2 at infinite dilution.[5] The data in Table II are too limited to yield information concerning the salt effect for reaction 2 in methanol.

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(5) Roth, S. A.; Stucky, G. D.; Feder, H. M.; Chen, M. J.; Rathke, J. W. *Organometallics* **1984**, *3*, 708.

Table II. Second-Order Rate Constant for the Reaction of $Mn(CO)_5^-$ with $Me_2NC_5H_{10}^+$ in Methanol[a]

T, °C	t, h	$[Mn(CO)_5^-]$, M	$[MeNC_5H_{10}]$, M	$[Me_2NC_5H_{10}^+]$, M	[EtOH], M	$-10^5 d[Me_2NC_5H_{10}^+]/dt$, M s^{-1}	$10^4 k_2$,[c] M^{-1} s^{-1}
180	0	0.243	0	0.236	0	5.7[b]	9.9
	1.0	0.178	0.134	0.108	0.095	1.7[b]	8.8
	2.0	0.130	0.163	0.078	0.155	0.90[b]	8.9
	3.0	0.109	0.196	0.044	0.170	*d*	
	4.9	0.088	0.202	0.042	0.210	*d*	
							av 9.2
200	0	0.176	0.062	0.154	0.038	17[e]	71
	0.33	0.070	0.185	0.044	0.138	4.0[e]	130
	0.67	0.046	0.023	0.007	0.166	*d*	
	1.00	0.028	0.227	0.002	0.178	*d*	
							av 100

[a] Initial solution: 0.243 M and 0.216 M $[Me_2NC_5H_{10}][Mn(CO)_5]$ for reactions at 180 and 200 °C, respectively. P = 300 atm of H_2 (no CO added). [b] These rates are estimated to be good to 15%. [c] $k_2 = (-d[Me_2NC_5H_{10}^+]/dt)/[Mn(CO)_5^-][Me_2NC_5H_{10}^+]$. [d] Uncertainties are too high to be useful. [e] These rates are estimated to be good to 30%.

Table III. Observed and Calculated Rates of Ethanol Production

	initial solution				"steady-state" concn[b]			rate,[c] d[EtOH]/dt		
expt[a] no.	$[Mn_2(CO)_{10}]$, M	$[MeNC_5H_{10}]$, M	$[HCO_2K]$, M	t,[b] h	$10^2[Mn(CO)_5^-]$, M	$[Me_2NC_5H_{10}^+]$, M	$[HCO_2Me]$, M	$10^5 R_{obsd}$, M s^{-1}	$10^5 R_2$, M s^{-1}	$10^5 R_3$, M s^{-1}
1	0.075	2.0	0	1.1	6.8	0.0093	0.030	5.7	0.47	0.37
2	0.075	2.0	0	2.2	13.4	1.85	0.77	5.6	187	1.9
3	0.025	2.0	0	2.0	4.0	1.9	0.72	1.7	60	5.2
4	0.025	0.050	0	1.1	2.6	0.013	0.94	4.0	0.3	4.4
5	0.025	0	0.15	2.5	3.8	0	0.92	6.9	0	6.3
6	0.025	0.050	0.15	1.0	4.2	0.029	0.98	7.0	0.9	7.4
7	0.025	0.30	0.15	1.0	4.3	0.26	1.23	7.9	11	9.5
8	0.025	2.0	0.15	1.3	4.3	2.0	0.72	2.3	65	5.6

[a] The experiment numbers correspond to those in Table I. [b] The "steady-state" concentrations are the values for each experiment at time t, at which the reaction is close to a steady state. [c] R_{obsd} = observed rate, R_2 = calculated rate for reaction 2, and R_3 = calculated rate for reaction 3. See text.

Methyl Transfer Reactions in $Mn_2(CO)_{10}$–$MeNC_5H_{10}$–MeOH Solutions. The second-order rate constant at 200 °C for reaction 3 in methanol containing 0.15 M HCO_2K was earlier determined to be 2.4×10^{-3} M^{-1} s^{-1}.[3]

$$HCO_2Me + Mn(CO)_5^- \rightarrow MeMn(CO)_5 + HCO_2^- \quad (3)$$

Since the rate constants for eq 2 and 3 are comparable, both $Me_2NC_5H_{10}^+$ and HCO_2Me have to be considered as methylating species in the catalytic homologation reactions. To determine the contribution of eq 2 and 3 to the formation of $MeMn(CO)_5$ in $Mn_2(CO)_{10}$–$MeNC_5H_{10}$–MeOH solutions, we studied the kinetics of the homologation of methanol at varied concentrations of $Me_2NC_5H_{10}^+$. Alteration of the initial concentration of $MeNC_5H_{10}$ was used to achieve variation in the concentration of $Me_2NC_5H_{10}^+$. The reactions were studied in the presence and in the absence of HCO_2K. The pressure was maintained at 300 atm with a 3:1 CO/H_2 gas mixture. Rate data are summarized in Table I. In experiments 5–8, HCO_2K was added. Quantitative conversion of $Mn_2(CO)_{10}$ to $Mn(CO)_5^-$ was achieved by the time the temperature reached 200 °C. In the absence of HCO_2K (experiments 1–4), the formation of $Mn(CO)_5^-$ was slower and, in most cases, incomplete. In these cases, quantitative conversion of $Mn_2(CO)_{10}$ to $Mn(CO)_5^-$ was achieved only by building up HCO_2^- (its presence as the counter anion of $Me_2NC_5H_{10}^+$ was confirmed by its ^{13}C NMR spectrum) in the reaction (experiment 3) or by adding HCO_2Me (experiment 2). It should be noted that the concentration of HCO_2^- remained low throughout the reaction in experiments 1 and 4. The correlation between the concentrations of $Mn(CO)_5^-$ and HCO_2^- strongly suggests that the reaction of $Mn_2(CO)_{10}$ with HCO_2^- is the main pathway for the formation of $Mn(CO)_5^-$ in solutions containing high concentrations of HCO_2^-.

Very low steady-state concentrations of methyl formate and $Me_2NC_5H_{10}^+$ were maintained in experiment 1 throughout the reaction. When the concentration of $Mn_2(CO)_{10}$ was lowered by a factor of 3 (experiment 3), both methyl formate and $Me_2NC_5H_{10}^+$ (and HCO_2^-) were found to build up to their equilibrium concentrations gradually. In contrast, the rates of formation of methyl formate and $Me_2NC_5H_{10}^+$ were faster in solutions containing HCO_2K (experiments 5–8), and their equilibrium concentrations were achieved or nearly achieved by the time the temperature reached 200 °C. Apparently, the formate ion catalyzes the formation of methyl formate, which then reacts with $MeNC_5H_{10}$ to give $Me_2NC_5H_{10}^+$ and HCO_2^-. The mechanism by which HCO_2^- catalyzes the carbonylation of methanol has been discussed.[3]

The rate of ethanol production decreased slowly in these experiments because of the gradual loss of $Mn(CO)_5^-$ through formation of $Mn(HCO_2)_2$ or $MnCO_3$. Had it not been for the catalyst instability, the reactions would have proceeded at steady state. Table III gives the "steady-state" concentrations of $Mn(CO)_5^-$, $Me_2NC_5H_{10}^+$, and HCO_2Me at selected reaction times. The criterion for choosing the reaction time is that the rate of ethanol production could be accurately measured at the selected time. To evaluate the contributions of reactions 2 and 3 to the formation of $MeMn(CO)_5$, we compared the observed rates of ethanol production at "steady-state" conditions with the calculated rates, which were based on the concentrations of the reacting species, the average mole fraction of 0.75 for ethanol (see discussion below on product selectivity), and the second-order rate constants of $k_2 = 1.0 \times 10^{-2}$ M^{-1} s^{-1} and $k_3 = 2.4 \times 10^{-3}$ M^{-1} s^{-1}. These rates are given as R_{obsd}, R_2, and R_3 in Table III.

In experiment 5, $Me_2NC_5H_{10}^+$ was absent, so the observed rate is nearly equal to R_3. In experiments 4 and 6 (low concentration of $Me_2NC_5H_{10}^+$), the agreement between R_{obsd} and the sum of R_2 and R_3 is good, and reaction 3 is the dominant path under these conditions. In experiments 2, 3, and 8 (high concentration of $Me_2NC_5H_{10}^+$), the observed rate is much lower than the sum of R_2 and R_3. In the last experiment, R_2 is equal to 28 times R_{obsd}. Therefore, k_2 in experiment 8 must be at least 28 times (depending on the contribution from eq 3) lower than the value of $1.0 \times 10^{-2}\ M^{-1}\ s^{-1}$ obtained from the stoichiometric study. Similar comparison leads to the conclusion that k_3 in experiment 8 is at least 2.4 times lower than the value of $2.4 \times 10^{-3}\ M^{-1}\ s^{-1}$ obtained in HCO_2K–methanol solutions. Therefore, both k_2 and k_3 (but especially k_2, which involves reactions between two oppositely charged ions) decrease in the presence of high concentrations of the salt $Me_2NC_5H_{10}^+,HCO_2^-$. We believe that an increase in k_2 is responsible for R_{obsd} being higher than the sum of R_2 and R_3 in experiment 1. Since the ionic strength in experiment 1 is not very different from the value of 0.02 M at which k_2 is measured, the increase in k_2 must stem from other causes. It seems reasonable to attribute the higher k_2 to the presence of a high concentration of *N*-methylpiperidine; its dielectric constant ($\epsilon_{25} = 3$) is much lower than that of methanol ($\epsilon_{25} = 32.6$). Reactions between two oppositely charged ions proceed more rapidly in less polar solvents.

The only effect from the addition of HCO_2K to $Mn_2(CO)_{10}$–amine–MeOH solutions is to catalyze the formation of HCO_2Me, $Me_2NC_5H_{10}^+$, HCO_2^-, and $Mn(CO)_5^-$. Consistent with this explanation, no rate enhancement was observed (experiment 8) when HCO_2K was added to the solution of experiment 3, in which the concentrations of HCO_2Me, $Me_2NC_5H_{10}^+$, HCO_2^-, and $Mn(CO)_5^-$ were high, presumably all at their equilibrium values.

Mechanism for the Catalytic Homologation of Methanol. The results obtained for the reactions in $Mn_2(CO)_{10}$–$MeNC_5H_{10}$–MeOH solutions (experiments 1–4) may be understood in terms of the mechanism shown in Scheme I, which shares many common features with the reactions in the $Fe(CO)_5$–amine–methanol system[1] and the $Mn_2(CO)_{10}$–HCO_2K–MeOH system.[3] The net reaction is

Scheme I

$$Mn_2(CO)_{10} + H_2 \rightleftharpoons 2HMn(CO)_5 \quad (4)$$

$$HMn(CO)_5 + R_3N \rightleftharpoons R_3NH^+ + Mn(CO)_5^- \quad (5)$$

$$MeOH + CO \rightleftharpoons HCO_2Me \quad (6)$$

$$HCO_2Me + R_3N \rightarrow R_3NMe^+ + HCO_2^- \quad (7)$$

$$R_3NMe^+ + Mn(CO)_5^- \rightarrow R_3N + MeMn(CO)_5 \quad (2)$$

$$HCO_2Me + Mn(CO)_5^- \rightarrow HCO_2^- + MeMn(CO)_5 \quad (3)$$

$$MeMn(CO)_5 + CO \rightleftharpoons MeC(O)Mn(CO)_5 \quad (8)$$

$$MeC(O)Mn(CO)_5 + H_2 \rightarrow MeCHO + HMn(CO)_5 \quad (9)$$

$$MeCHO + H_2 \xrightarrow{cat.} MeCH_2OH \quad (10)$$

$$R_3NH^+ + HCO_2^- \rightarrow R_3N + H_2 + CO_2 \quad (11)$$

$$MeOH + 2CO + H_2 \rightarrow MeCH_2OH + CO_2 \quad (12)$$

For the experiment described in Figure 1, both $Mn(CO)_5^-$ and HCO_2Me were at low steady-state concentrations, far away from their equilibrium values dictated by eq 4–6. The concentration of $Me_2NC_5H_{10}^+$ was also very low because of the low concentration of HCO_2Me. Apparently, the methyl transfer reaction to form $MeMn(CO)_5$ by eq 2 (see discussion in the previous section for ignoring eq 3) is so efficient that neither $Mn(CO)_5^-$, HCO_2Me, nor $Me_2NC_5H_{10}^+$ builds up its concentration under these conditions.

As mentioned earlier, the rate of ethanol production in experiment 2 was relatively unaffected by the addition of methyl formate, despite the large increase in the concentrations of $Mn(CO)_5^-$, HCO_2Me, and $Me_2NC_5H_{10}^+$. It is apparent that the decrease in the second-order rate constants, k_2 and k_3, due to the build-up of high concentrations of $Me_2NC_5H_{10}^+$ and HCO_2^-, more or less cancels the expected rate increase from the higher concentrations of the reacting species in reactions 2 and 3. Under these conditions, the formation of $MeMn(CO)_5$ becomes rate-limiting.

The observed partial conversion of $Mn_2(CO)_{10}$ to $Mn(CO)_5^-$ before the addition of HCO_2Me in experiment 2 is derived from kinetic rather than thermodynamic reasons. Since hydrogen under comparable conditions reversibly converts $Mn_2(CO)_{10}$ to $HMn(CO)_5$ in the absence of a base,[3] the presence of $MeNC_5H_{10}$ would have driven reaction 4 to completion if it were fast under the reaction conditions. Therefore, the observed increase in the concentration of $Mn(CO)_5^-$ after the addition of HCO_2Me is also of kinetic origin. Since the rate of its consumption, as judged by the rate of ethanol production, did not decrease, there was a net increase in the rate of formation of $Mn(CO)_5^-$ after the addition of methyl formate. This rate enhancement is attributed to the reaction of $Mn_2(CO)_{10}$ and HCO_2^- (eq 13), which becomes important as

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

HCO_2^- accumulates from the reaction of HCO_2Me with $MeNC_5H_{10}$. We previously showed that reaction 13 is fast at 200 °C.[3] The reduction of metal carbonyls by formate ion is also known for other systems.[6-8]

For reactions in which HCO_2K was added (experiments 5–8), eq 13 becomes the main pathway for the production of $Mn(CO)_5^-$, and the mechanism in Scheme I may be modified accordingly.

We have established here a strong correlation between the concentration of HCO_2^- and the production rate of HCO_2Me, $Me_2NC_5H_{10}^+$, and $Mn(CO)_5^-$. The mechanism by which the formate ion catalyzes the carbonylation of methanol has been discussed.[3] Since formate ion is generated in reaction 7 at a rate comparable to reaction 6, the presence of a tertiary amine leads to a continuous increase in the concentration of formate ion during the time in which equilibria 6 and 7 are being established. The formation of methyl formate should, therefore, be autocatalytic in the presence of a tertiary amine during this period. Work is in progress to establish the HCO_2^- catalyzed (as differentiated from RO^- catalyzed)[9] carbonylation of methanol.

Product Selectivity. We previously noted[1] that the homologation of methanol, but not ethanol, in this system derives from the more facile transfer of the methyl group from methyl formate, as compared with the transfer of its homologues from their formate esters in S_N2 reactions such as eq 3 and 7.[10] In our earlier work on the $Mn_2(CO)_{10}$–

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amine–methanol system,[1,2] the reaction conditions were such that $Mn(CO)_5^-$, HCO_2Me, and $Me_2NC_5H_{10}^+$ were all at low concentrations and, except for methane (~15% of the products) and traces of methyl formate and ethyl formate, ethanol was the only organic product detected. In this study, traces of acetaldehyde, dimethylacetals, and 1-propanol were also observed when the reactions were allowed to proceed to higher conversions (Table I, footnote *c*). Apparently, reduction of acetaldehyde to ethanol in eq 10 is the dominant reaction for acetaldehyde under these conditions. We later found that acetaldehyde and acetals may account for as much as 50% of the liquid products in HCO_2K–methanol solutions.[3] These products were also found at fair concentrations, as high as 10%, in amine–methanol solutions when the concentration of $Me_2NC_5H_{10}^+,HCO_2^-$ was high (experiments 2–8). Methane production, which was not significantly affected by change in the composition of the solution, accounted for 15 (±3)% of the products. The formation of acetals in the HCO_2K–methanol solutions may be attributed to the lower basicity of these solutions, the pHs of which are three units lower. The conversion of acetaldehyde to acetals is an acid-catalyzed reaction and apparently becomes competitive in the less basic HCO_2K–methanol solutions. In amine–methanol solutions, the formation of acetals appears to correlate with the formation of $Me_2NC_5H_{10}^+,HCO_2^-$. It is not clear whether the increased yield of acetals in these solutions is due to the decrease in the rate of reaction 10 or the increase in the rate of formation of acetals, or both.

Conclusions

We have shown that in the catalytic homologation of methanol to ethanol in $Mn_2(CO)_{10}$–tertiary amine–methanol solutions, the system is very selective for ethanol production. Only a trace of propanol was produced, even when the reaction was carried out to high conversion. This selectivity arises because methyl transfer reactions in eq 2, 3, and 7 are more facile than similar reactions for the ethyl group or other homologues. It is known[10] that the rate difference between methyl and ethyl transfers is larger when displacement of poor leaving groups, HCO_2^- and $MeNC_5H_{10}$ in this case, is involved in such S_N2 reactions. In contrast, in the $HCo(CO)_4$ catalyzed homologation of methanol,[11,12] ethanol and other higher alcohols are also produced. The selectivity is poorer in this system because the rate-limiting methyl transfer reaction involves displacement of H_2O, which is a better leaving group, from $MeOH_2^+$.

The kinetic studies establish that the rate-limiting step in the catalytic cycle is the two competing methyl transfer reactions, namely, the reactions of $Mn(CO)_5^-$ with methyl formate and with dimethylpiperidinium ion. The latter reaction, which involves reaction between two oppositely charged ions, is more sensitive to the ionic strength.

Experimental Section

Material. The following chemicals were of reagent grade and were used as received: $Mn_2(CO)_{10}$ (Strem Chemical); methyl formate and *N*-methylpiperidine (Aldrich); and methanol (Fisher Scientific). The synthesis of $[Me_2NC_5H_{10}][Mn(CO)_5]$ has been described previously.[5] Hydrogen and carbon monoxide were of CP grade from Matheson. The certified gas mixture blended from these CP gases had the composition: CO, 74 (±1)%; H_2, 24 (±1)%; and N_2 2.0 (±0.1)%.

Instruments. The following instruments were used in this study: Perkin-Elmer 1500 FT-IR, Varian FT-80 NMR, Varian 3700 GC, Hewlett-Packard 5888 GC-5984 MS system, and Orion 901 ionalyzer.

Analyses. The quantitative analysis of $Mn(CO)_5^-$ and $Me_2NC_5H_{10}^+$ has been described elsewhere.[3] $Mn(CO)_5^-$ was determined by redox titration with methylene blue, and $Me_2NC_5H_{10}^+$ was determined spectrophotometrically as its salt of Reinecke ion, $[Cr(NH_3)_2(SCN)_4]^-$. The total amount of manganese in solution was determined by titration with EDTA.[13] A solution of 1.0 mL of the sample and 10 mL of 1% KOH was boiled until a brown precipitate formed, and 2 mL of 1.2 M HCl was then added to dissolve the precipitate. The solution was prepared for titration with the addition of 10 mL of a pH 10 buffer (NH_4Cl–NH_4OH), a few small crystals of calmagite as indicator, and approximately 0.1 g of ascorbic acid to stabilize the metal–indicator complex.

Analyses of the organic compounds in the solution phase were carried out on a 6-ft porapak Q column with an FID detector and with the program: 60 (10 min) to 220 °C (12 min) at 10 °C/min. The gas samples were analyzed isothermally at 80 °C on a 3.5-ft spherocarb column with a TCD detector. The identification of the organic products was performed on the Hewlett-Packard GC–MS system with a 200-ft SE-30 capillary column. The oven temperature was programmed from 50 (6 min) to 200 °C at 8 °C/min.

The apparent pHs of the solutions were measured with an electrode calibrated with an aqueous pH 10 buffer.

Catalytic Reactions. The system and the general procedures for the high-pressure experiments have been described previously.[5] All the experiments, unless otherwise specified, were carried out in batch operation, and a 3:1 CO/H_2 gas mixture was used to restore the drop in pressures due to reaction or sampling. Because of CO_2 production, the partial pressure of CO, as well as H_2, gradually decreased during the reaction.

A precision metering pump (Laboratory Data Control) was used to pump liquids into the reactor under reaction conditions.

Methyl Transfer Reaction between $Mn(CO)_5^-$ and $Me_2NC_5H_{10}^+$. A solution of 0.24 M $[Me_2NC_5H_{10}][Mn(CO)_5]$ in 120 mL of methanol, prepared under argon, was loaded into the autoclave against a countercurrent flow of argon. The autoclave was heated to 180 °C with an initial pressure of 200 atm of H_2. Hydrogen was used to maintain the pressure at 300 atm. Liquid samples were taken and analyzed at various times. Analysis of a gas sample taken at the conclusion of the experiment yielded a value of 2.0 mmol of CH_4.

A white solid (1.0 g) was collected from the product solution, washed with methanol, and suction-dried. The IR spectra of the solid gave no band for carbonyl. The elementary analyses (Galbraith Laboratories) gave the composition (%): Mn, 49.53; C, 13.60; H, 3.91; N, 2.15; O, 30.81 (by difference), corresponding to the empirical formula $Mn_1C_{1.25}H_{4.30}N_{0.17}O_{2.03}$.

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Registry No. $Mn_2(CO)_{10}$, 10170-69-1; $MeNC_5H_{10}$, 626-67-5; $Mn(CO)_5^-$, 14971-26-7; EtOH, 64-17-5; HCO_2Me, 107-31-3; $Me_2NC_5H_{10}^+$, 15302-91-7; HCO_2K, 590-29-4; MeOH, 67-56-1.

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