in 89%. During photolysis, GC analysis at intervals showed that ct-1,5-COD and tt-1,5-COD were present in about 2.5% and 1.7%, respectively.

A solution of the complex (675 mg) and cc-1,5-COD in methanol (180 mL) was purged under nitrogen and irradiated as above for 30 min. After being stirred for 30 min, the photolysate was quickly filtered and washed with cold methanol (2 × 5 mL) to give a solid (593 mg, 88%): UV, see Figure 3c; IR, showed all major peaks of [CuCl(ct-1,5-COD)]$_2$ between 1250 and 650 cm^{-1} (Figure 4b). This solid was decomposed as above and the ether extract was analyzed by GC to give ct-1,5-COD (76%) and cc-1,5-COD (23%).

Pyrex Filter. A methanol suspension containing [CuCl(cc-1,5-COD)]$_2$ (414 mg, 2 mmol) and cc-1,5-COD (4 mmol) was photolyzed through a Pyrex filter under nitrogen. In 5 min, white precipitates were formed and increased considerably. The solution samples at intervals were treated as above and analyzed by GC to give no peaks other than cc-1,5-COD up to 4 h of irradiation. The white solid was filtered and washed with cold methanol; the solid was treated with concentrated ammonium hydroxide and sodium cyanide and was extracted with ether as above. GC analysis of the ether solution gave peaks at 4.18 (ct-1,5-COD, 28%) and 5.28 min (cc-1,5-COD, 70%). While three minor peaks ($\approx$1%) were also observed, they did not correspond to TCO or tt-1,5-COD.

Preparation of the [CuCl-ct-1,5-COD]$_2$ Complex. CuCl$_2$ (3 g), an ether solution of ct-1,5-COD, and methanol (25 mL) were treated with SO$_2$ at 0 °C. The solid was filtered and washed with cold methanol to give a white powder of [CuCl(ct-1,5-COD)]$_2$ (524 mg): UV and IR spectra, see Figures 3b and 4c; NMR (CDCl$_3$) 2.12 (br m, 8 H), 5.79 (br m, 4 H) ppm; MS (EI), *m/e* (%) 54 (100), 67 (54), 79 (48), 259 (10), 261 (15), 263 (12), 265 (5), 294 (12), 296 (10), 298 (20), 300 (12), 394 (5), 396 (7), 398 (5), 400 (2). The solid (20 mg) was decomposed with NH$_4$OH and NaCN as before and extracted with ether. GC of the ether solution showed the peaks of ct-1,5-COD (96%) and two unknown peaks at 1.76 (<3%) and 2.11 min ($\approx$1%). The dried sample gave the following elemental analysis: sample 1, C, 26.25; H, 3.27; C/H, 8.03; sample 2, C, 33.43; H, 4.17; C/H, 8.02 (calcd for CuClC$_8$H$_{12}$, C, 46.38; H, 5.80; C/H 8.00).

Photolysis of [CuCl(ct-1,5-COD)]$_2$ in Methanol. The complex (40 mg) in methanol (25 mL) was photolyzed through a Corex filter under nitrogen, and the total mixtures were analyzed at intervals as described above. The results are shown in Figure 6; tt-1,5-COD was not detected in 90 min of irradiation.

A similar suspension was photolyzed through a Pyrex filter and analyzed as above. The percentage of ct-1,5-COD decreased and that of cc-1,5-COD increased to 60:40 in 2 h, but no TCO was formed.

Acknowledgment. We gratefully acknowledge the generous financial support of the work provided by the Natural Science and Engineering Council of Canada.

Registry No. [CuCl(cc-1,5-COD)]$_2$, 89015-37-2; CC-1,5-COD, 1552-12-1; ct-1,5-COD, 5259-71-2; tt-1,5-COD, 17612-50-9; [CuCl(ct-1,5-COD)]$_2$, 89015-38-3; Cu(acac)$_2$, 46369-53-3; acack, 19393-11-4; Ph$_2$CO, 119-61-9; Cu(hfac)$_2$, 14781-45-4; cc-1,5-COD–Ph$_2$CO oxetane, 88947-01-7; Cu(acac)(PPh$_3$)$_2$, 25427-02-5; Cu(acac)(cc-1,5-COD), 88947-02-8.

Methyl Transfer to Nucleophilic Metal Carbonylate Anions in Catalytic Methanol Homologation

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Received December 2, 1983

The kinetics of the stoichiometric reaction of methyltrialkylammonium cations with nucleophilic metal carbonylate anions was investigated in terms of its relationship to a new catalytic methanol homologation method. At high temperatures and pressures of H$_2$ and CO, a methyl group from each cation is incorporated into methane or ethanol. In the ionizing solvent, *N*-methylpyrrolidinone, the reaction using iron tetracarbonyl hydride anion is first order in both the methylammonium cation and iron carbonylate anion concentrations and zero order with respect to the partial pressures of hydrogen or carbon monoxide. The enthalpy and entropy of activation, in the temperature range of 180–210 °C, are 44 kcal/mol and +17 eu, respectively. The second-order rate constants exhibit a primary kinetic salt effect, increasing with decreasing salt concentration. The rate constants also increased with decreasing dielectric constant of the solvent. The data are consistent with methyl group transfers (S$_N$2) between ions as the rate-limiting step. At 200 °C and 245 atm (3:1 CO/H$_2$) the second-order rate constants, 2.0 × 10^{-4} M^{-1} s^{-1} for HFe(CO)$_4^-$, 5.3 × 10^{-4} M^{-1} s^{-1} for Mn(CO)$_5^-$, are a measure of the nucleophilicities of these carbonylates toward tetramethylammonium ion. In the case of the manganate system, the product selectivity (ethanol vs. methane) was found to be independent of H$_2$ or CO partial pressure between 61 and 184 atm but slightly dependent on the concentration of Mn(CO)$_5^-$. These factors are discussed in terms of reaction mechanism.

Introduction

The homologation of alcohols using cobalt carbonyls was first reported by Wender et al.[2a] in the late 1940s although an earlier (1941) patent using a CoO/NiO catalyst exists.[2b] At 180 °C and 200 atm of synthesis gas (1:1 CO/H$_2$), the homogeneous catalyst, HCo(CO)$_4$, was observed to ho-

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mologate alcohols according to eq 1. The homologation

$$ROH + CO + 2H_2 \xrightarrow[180\ ^\circ C,\ 200\ atm\ of\ CO/H_2]{HCo(CO)_4} RCH_2OH + H_2O \quad (1)$$

of methanol is of particular current interest. Typical product selectivities have been described by Koermer.[3] In addition to ethanol, the reaction products may include methane, acetaldehyde, higher alcohols, formate and acetate esters, acetals, glycols, and glycol esters. An explanation for the frequent lack of selectivity in this process lies in its reaction mechanism,[4-6] which is proposed to involve protonation of the alcohol by the strongly acidic $HCo(CO)_4$, followed by attack by the cobalt carbonylate anion and the elimination of water. Since 1976, several groups[7-12] have patented numerous variations that utilize promoters and metallic cocatalysts in attempts to increase the rate and selectivity of this reaction.

The discovery[13a] of the catalytic homologation of methanol by $Fe(CO)_5$ in the presence of a tertiary amine, according to eq 2, has opened a new approach to this

$$CH_3OH + 2CO + H_2 \xrightarrow[200\ ^\circ C,\ 300\ atm\ of\ CO/H_2]{Fe(CO)_5/NR_3} CH_3CH_2OH + CO_2 \quad (2)$$

transformation that does not depend on acid catalysis. The method is advantageous in that the homologation stops at ethanol and the product is anhydrous. The mechanism proposed[13b-d] for the $Fe(CO)_5$-catalyzed reaction is shown in eq 3–11.

$$CH_3OH + CO \overset{NR_3}{\rightleftharpoons} HCO_2CH_3 \quad (3)$$

$$HCO_2CH_3 + NR_3 \rightleftharpoons CH_3NR_3^+ + O_2CH^- \quad (4)$$

$$Fe(CO)_5 + H_2 + NR_3 \rightleftharpoons HFe(CO)_4^- + CO + HNR_3^+ \quad (5)$$

$$HNR_3^+ + O_2CH^- \xrightarrow{Fe(CO)_5} H_2 + CO_2 + NR_3 \quad (6)$$

$$HCO_2CH_3 + HFe(CO)_4^- \rightarrow CH_3HFe(CO)_4 + O_2CH^- \quad (7a)$$

$$CH_3NR_3^+ + HFe(CO)_4^- \rightarrow CH_3HFe(CO)_4 + NR_3 \quad (7b)$$

$$CH_3HFe(CO)_4 + CO \rightarrow CH_3C(O)HFe(CO)_4 \quad (8)$$

$$CH_3HFe(CO)_4 + CO \rightarrow CH_4 + Fe(CO)_5 \quad (9)$$

$$CH_3C(O)HFe(CO)_4 + CO \rightarrow CH_3C(O)H + Fe(CO)_5 \quad (10)$$

$$CH_3C(O)H + H_2 \xrightarrow{HFe(CO)_4^-} CH_3CH_2OH \quad (11)$$

The new method is applicable to a variety of metal centers,[13b,c] and with most of these, methyl transfers from alkylammonium ions to metal carbonylate anions, as in eq 7, are crucial steps. Although Dessey[15] has measured the relative nucleophilicities of several transition-metal anionic complexes toward alkyl halides, while alkyl and aryl transfers from quaternary ammonium, phosphonium, and arsonium cations to $CpFe(CO)_2^-$ and $Re(CO)_5^-$ have been used synthetically by Ellis,[14] the earlier works lack quantitative kinetic studies applicable to the new catalytic systems. We, therefore, have undertaken a study of reaction 7b and its analogues under stoichiometric conditions. These kinetic measurements reveal much about the overall catalytic reactions without introducing the complicating factors of the initiating steps, eq 3–6.

Experimental Section

Syntheses. All syntheses of oxygen-sensitive carbonylate salts were performed in an inert atmosphere glovebox with recirculated helium atmosphere. All organic solvents were dried prior to use. Tetramethylammonium salts of $HFe(CO)_4^-$ and $Mn(CO)_5^-$ were prepared by using the methods of Pettit[16] and King.[17] Corresponding salts of the *N,N*-dimethylpiperidinium ion were prepared similarly. Solutions of $NaHFe(CO)_4$ in *N*-methylpyrrolidinone solution were obtained by acidifying $Na_2Fe(CO)_4\cdot 1.5\ \overline{O(CH_2)_2\text{-}O(CH_2)}$ (Aldrich Chemical Co.) with formic acid in the NMP solution. Insoluble NaO_2CH was removed by filtration, and the solutions were prepared immediately before use.

Kinetic Studies. Pressure reactions were conducted in a 300-mL, type 316 stainless steel electrically heated autoclave (Autoclave Engineers). The autoclave was equipped with a "MagneDrive" gas-circulating stirrer and an internal cooling coil. Temperature control was by means of an anticipatory proportional controller. A Gould-Statham strain-gauge transducer (0–340 atm of pressure) was used to measure the pressure in the system. CO (99.99%), H_2 (99.999%), or CO/H_2 mixtures (obtained from Matheson Gas Co.) were introduced into the autoclave and brought up to pressure by a Haskel double-piston gas booster.

The autoclave was equipped with the capability for removal of gas and liquid samples during the course of an experiment. A valved, liquid sample line, chilled by circulating ice water, was used for the withdrawal of quenched liquid samples into inert-

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Table I. Reaction with Unequal Concentrations of $Me_2NC_5H_{10}^+$ and $HFe(CO)_4^-$ in NMP Solution[a]

sample	time, h	$[HFe(CO)_4^-]$, M	$[Me_2NC_5H_{10}^+]$, M	$\Delta[HFe(CO)_4^-]$, M	$\Delta[Me_2NC_5H_{10}^+]$, M
0	0	0.583	0.197	0	0
1	1.5	0.533	0.146	0.050	0.051
2	3.0	0.493	0.108	0.080	0.088
3	4.5	0.465	0.0850	0.118	0.112
4	6.0	0.450	0.0636	0.133	0.133

[a] At 200 °C and 245 atm (3:1 CO/H_2). Initial concentration: $NaHFe(CO)_4$, 0.40 M; $Me_2NC_5H_{10}^+$, 0.20 M.

gas-filled, septum-capped vials. Gaseous aliquots (3 mL) were expanded into a 300-mL pressure vessel and then transferred into preevacuated bulbs for analysis. Because sampling perturbs the system, feed gas was added via the gas booster to restore the nominal gas pressure.

In a typical experiment the autoclave was charged with the solution of intended composition via a filling port and against a countercurrent flow of helium. The autoclave was then purged by at least three compression/vent cycles with CO and filled with a synthesis gas of the desired composition. The contents of the autoclave were brought to the desired temperature and pressure, usually in about a half-hour, and a "time-zero" sample of the liquid and gaseous phases were obtained. The reaction was run for the necessary length of time, was periodically sampled, and was finally quenched. Final gas and liquid samples were then taken at room temperature and the gas and liquid volumes noted.

Analytical Procedures. Analytical instrumentation included a Perkin-Elmer Model 340 double-beam recording spectrometer, a Varian Model FT-80 NMR spectrometer, and a gas chromatograph (Varian 3700) electronically coupled to an automatic integrator (Varian CDS-111).

Gas samples in an argon carrier stream were analyzed (GLC thermal-conductivity detection) for H_2, CO, CO_2, and CH_4 on a 2.5-ft Spherocarb column held isothermal at 70 °C. A synthetic gas mixture (Matheson Gas Co.) containing 60.23% CO, 24.79% H_2, 10.01% CO_2, and 4.97% CH_4 was used for standardization.

Liquid samples were analyzed (flame-ionization detection) for methanol, acetaldehyde, methyl formate, ethanol, and ethyl formate on a 6-ft Porapak Q column, temperature programmed from 100 to 230 °C at a rate of 10 °C/min. Standard solutions for calibration were prepared from known concentrations of reagent grade compounds dissolved in appropriate solvents.

Carbonylate Anions. Modifications of Iwanaga's methylene blue titration[18] for $Co(CO)_4^-$ were developed for analysis of $HFe(CO)_4^-$ and $Mn(CO)_5^-$ concentrations in liquid samples. $HFe(CO)_4^-$ titrates as a four-electron reductant against 1.00 mM methylene blue in a 50% solution of acetic acid in toulene. $Mn(CO)_5^-$ titrates as a one-electron reductant against 1.00 mM methylene blue in a 20% solution of acetic acid in ethanol. In these titrations methylene blue has the dual role of oxidant and indicator.

Quaternary Ammonium Cations. A modified literature[19] procedure for the analysis of quaternary ammonium cations by precipitation of their Reineckate $[Cr(NH_3)_2(SCN)_4^-]$ salts was employed. Selective precipitation took place in a basic methanol solution. To eliminate coprecipitation of tertiary ammonium cations, the pH of the solution must be kept sufficiently high,[20] e.g., for $MeHNC_5H_{10}^+$ ($pK_a = 10.1$ in water) the pH was adjusted to >13 with NaOH in methanol. The precipitated salt was redissolved in acetone and the absorbance measured at 525 nm. The Beer's plot for *N,N*-dimethylpiperidinium Reineckate was linear over the experimental range ($\epsilon = 103\ M^{-1}\ cm^{-1}$).

Results

Reaction of $MeNR_3^+$ with $HFe(CO)_4^-$. Kinetic information for this reaction was obtained by heating NMP solutions[21a] containing both ions and following the disappearance of each as a function of time. A solution containing $NaHFe(CO)_4$ and $[Me_2NC_5H_{10}][HFe(CO)_4]$ was first investigated (Table I). It may immediately be recognized that the $Me_2NC_5H_{10}^+$ and $HFe(CO)_4^-$ both decrease in concentration at the same rate, consistent with the stoichiometry[22] of eq 12 (where the coefficient $a \leq 1$, which determines the relative amounts of CH_4 and C_2H_5OH, is dependent on the reaction conditions).

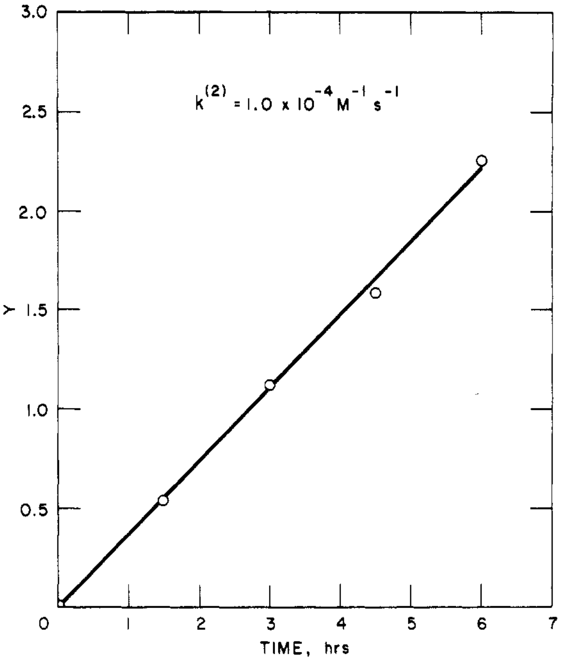

Figure 1. Second-order rate plot for methyl transfer to $HFe(CO)_4^-$ at 200 °C and 245 atm (3:1 CO/H_2) in NMP solution.

$$MeNR_3^+ + HFe(CO)_4^- + aH_2 + (a+1)CO = Fe(CO)_5 + NR_3 + aCH_3CH_2OH + (1-a)CH_4 \quad (12)$$

For a reaction having the form A + B → products, with a reaction rate given by $r = k^{(2)}[A][B]$, eq 13 is valid. The

$$Y = \frac{1}{[A]_0 - [B]_0} \ln \frac{[A][B]_0}{[A]_0[B]} = k^{(2)}t \quad (13)$$

linearity of a second-order rate plot of Y vs. t (Figure 1) confirmed the reaction to be first order in each ion; the slope yielded a rate constant[23] $k^{(2)} = 1.0 \times 10^{-4}\ M^{-1}\ s^{-1}$.

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[22] Also consistent with this stoichiometry, the sum of the methane and ethanol measured at the end of the reaction corresponded well (>90%) with the amount of $Me_2NC_5H_{10}^+$ consumed and the ^{13}C NMR peak due to $Fe(CO)_5$ increased, at least approximately, in proportion to the decrease in the peak due to $HFe(CO)_4^-$, while no other metal carbonyl resonances were observed.

Table II. Rate Constants and Product Selectivities for Reaction of $MeNR_3^+$ with $HFe(CO)_4^-$ in NMP Solution[a]

expt	temp, °C	CO/H_2	cation	$10^4k^{(2)}$, $M^{-1}\,s^{-1}$	selectivity $[EtOH]/\Delta[MeNR_3^+]$
1	180	3/1	NMe_4^+	0.24	0.11
2	190	3/1	NMe_4^+	0.71	0.08
3	200	3/1	NMe_4^+	2.0	
4	210	3/1	NMe_4^+	5.5	0.07
5	200	1/1[b]	NMe_4^+	1.8	0.15
6	200	1/3	NMe_4^+	1.6	0.11
7	200	3/1	$Me_2NC_5H_{10}^+$	1.6	0.06

[a] Total pressure = 245 atm, initial concentration of $MeNR_3^+HFe(CO)_4^-$ = 0.20 M. [b] Total pressure = 123 atm.

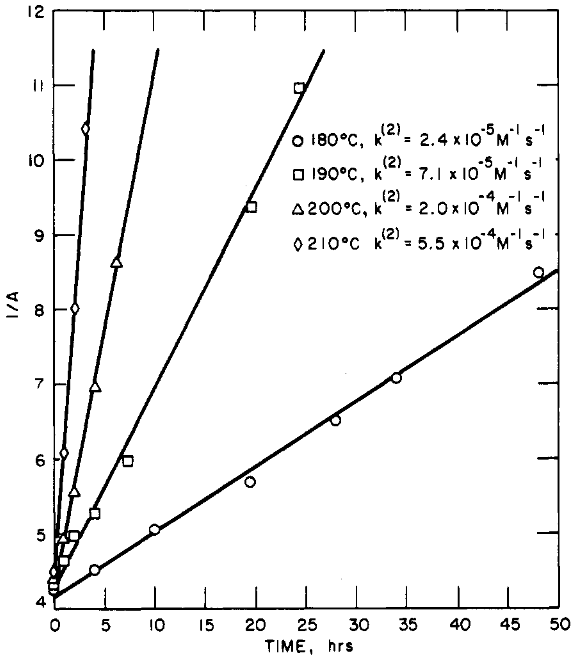

Figure 2. Effect of temperature on the second-order rate constants for methyl transfer to $HFe(CO)_4^-$ in NMP solution 245 atm (3:1 CO/H_2).

Because a reaction between ions in a medium of modest dielectric constant is readily subject to primary kinetic salt effects, subsequent reactions were carried out with stoichiometric (1:1) salts at nearly constant initial ionic strength. When $[A]_0 = [B_0]$, the reaction rate is given by $r = k^{(2)}[A]^2$ and the integrated rate equation becomes

$$[A]^{-1} = k^{(2)}t + [A_0]^{-1} \qquad (14)$$

The results of seven experiments of this type, all initially conforming to eq 14, are given in Table II; typical plots of $1/A$ vs. t are shown in Figure 2. The variables investigated were nature of electrophile, temperature, and partial pressures of H_2 and CO.

The effect of the electrophile may be seen in comparison of experiments 3 and 7 of Table II. A purely statistical effect, determined by the concentration of available methyl groups, would require the rate constant for NMe_4^+ to be twice that for $Me_2NC_5H_{10}^+$. Experimentally it is only about 20% larger, indicating that other effects are operative.

The enthalpy of activation ($\Delta H^\ddagger$ = 44 kcal/mol) and entropy of activation ($\Delta S^\ddagger$ = +17 eu) were obtained directly from the slope and the intercept, respectively, of an Eyring plot (Figure 3). The large positive $\Delta H^\ddagger$ is consistent with the extreme temperature sensitivity expected of a reaction involving the cleavage of a Me–N bond ($D \approx$ 90–100 kcal/mol) and formation of a Me–Fe bond ($D \approx$ 40–50 kcal/mol). The large positive $\Delta S^\ddagger$ is attributable to the release of molecules of solvation as the ions combine to produce a neutral, activated complex.

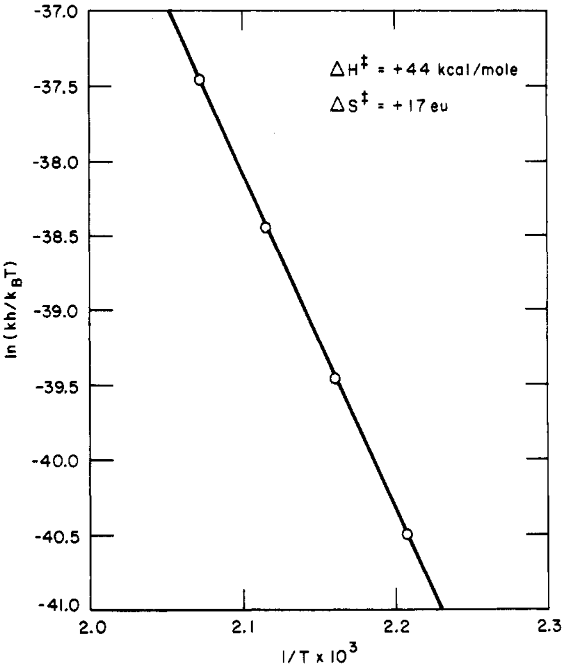

Figure 3. Eyring plot for methyl transfer to $HFe(CO)_4^-$ between 180 and 210 °C and 245 atm (3:1 CO/H_2) in NMP solution.

Entries 3, 5, and 6 in Table II show the effect on the second-order rate constants of hydrogen and carbon monoxide partial pressures of 61.5 and 184.5 atm, 61.5 and 61.5 atm, and 184.5 and 61.5 atm, respectively. No kinetically significant rate dependence on hydrogen or carbon monoxide pressure can be adduced, and it may be concluded that the rate of methyl transfer is independent of either H_2 or CO partial pressure.

As would be expected for a reaction in which there is a destruction of charge across the reaction coordinate, a profound effect was observed when the polarity of the reaction solvent was decreased. With use of THF (ϵ_{25} = 7.32) as the solvent, the reaction of $[NMe_4][HFe(CO)_4]$ (0.23 M) at 190 °C and 245 atm (3:1 CO/H_2) was too fast to monitor. The half-life in THF at 150 °C (2.0 h) was similar to that in NMP at 210 °C (2.3 h). At 150 °C reaction 12 follows *first-order* reaction kinetics in the solution, with an initial rate constant of $k^{(1)} = 9.5 \times 10^{-5}$ s^{-1}. First-order kinetics is expected if the bulk of the reagent is in the form of tight ion pairs and the rate-limiting step is internal motion within each pair. Apparently the tight ion pairing that occurs in THF at low temperatures[21b,c] also occurs at 150 °C.

In Table II the column headed "selectivity" expresses the ratio of ethanol formed in the reaction to the ammonium ion that had disappeared. Except for traces of other organic products, the remainder of the organic products was accounted for by the formation of methane. The selectivity (6–15%) in the stoichiometric reaction in NMP is considerably less than that in the catalytic reaction (30–70%) with methanol as the solvent. An effect of solvent on the alkyl-to-acyl transformation that is presumed to lie on the pathway for ethanol formation is well-documented.[24] The decrease in selectivity with in-

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(23) Note that the constants throughout this work are based on concentrations measured at room temperature; for more exact comparisons, allowance for the expansion of the solutions at temperature must be made.

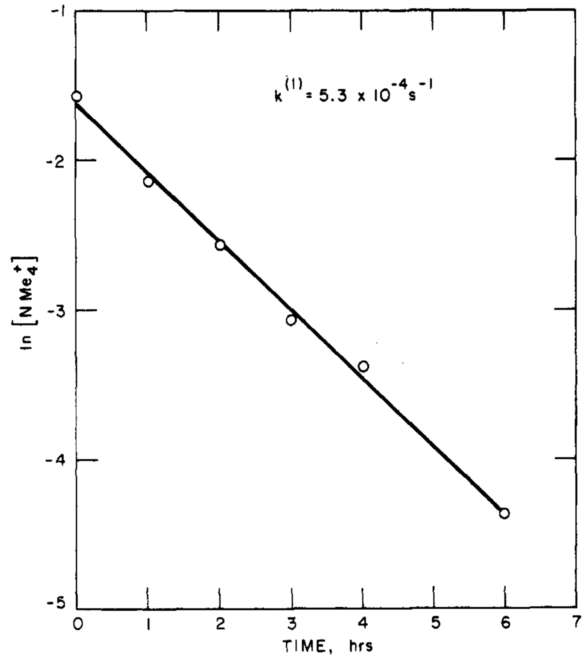

Figure 4. First-order rate plot for methyl transfer to $Mn(CO)_5^-$ at 200 °C and 245 atm (3:1 CO/H_2) in NMP solution.

creasing temperature seems, in contrast, to be a relatively small effect.

Reaction of $MeNR_3^+$ with $Mn(CO)_5^-$. A series of kinetic experiments were performed in which the nucleophile $Mn(CO)_5^-$ was substituted for $HFe(CO)_4^-$. These nucleophiles differ in a significant way. Thus, while the equilibrium

$$Fe(CO)_5 + NR_3 + H_2 \rightleftharpoons NR_3H^+ + HFe(CO)_4^- + CO \qquad (15)$$

proceeds significantly to the right in methanol (allowing $Fe(CO)_5$ to be used catalytically), it proceeds negligibly to the right in NMP or THF, thus permitting the purely stoichiometric reaction (eq 12) to be studied in these solvents. In contrast, the analogous reaction, eq 16, pro-

$$^1/_2Mn_2(CO)_{10} + NR_3 + {}^1/_2H_2 \rightleftharpoons NR_3H^+ + Mn(CO)_5^- \qquad (16)$$

ceeds rapidly and completely to the right so that the overall reaction of NMe_4^+ with $Mn(CO)_5^-$ was catalytic, even in NMP solution, and $[Mn(CO)_5^-]$ remained constant. The latter fact was ascertained via the constancy of broad absorption bands[25] at 1895 and 1860 cm^{-1} and the absence of carbonyl frequencies near 2000 cm^{-1} characteristic of $Mn_2(CO)_{10}$, $HMn(CO)_5$, $MeMn(CO)_5$, and $MeCOMn(CO)_5$.[26]

Because of the constancy of $[Mn(CO)_5^-]$, the disappearance of the quaternary ammonium cation was expected to occur under pseudo-first-order reaction conditions. A typical experimental result showing over 4 half-lives is shown in Figure 4. It may be noted that the principal organic product, ethanol, appeared synchronously with the disappearance of NMe_4^+, illustrated in Figure 5. In Table III are recorded the results of experiments conducted to determine the effect of concentration on the rate constant of the reaction. The first-order rate constants $k^{(1)}$ were obtained from the slopes of the rate plots similar to Figure 4. On the assumption that the reaction rate is also first order in $[Mn(CO)_5^-]$, a second-order rate constant, $k^{(2)}$, may be obtained via $k^{(2)} = k^{(1)}/[Mn(CO)_5^-]$. The values so obtained are also given in Table III. The primary kinetic salt effect on the rate constants was large and in the direction expected for oppositely charged ions as demonstrated by comparison of experiments. It is easily evaluated, because in contrast with the $HFe(CO)_4^-$ system, the ionic strength remains constant during the net reaction (eq 17).

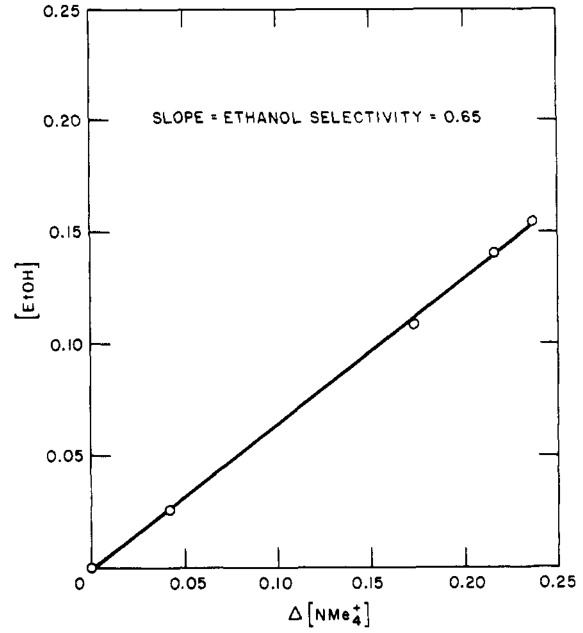

Figure 5. Product selectivity following the methyl transfer to $Mn(CO)_5^-$ at $[Mn(CO)_5^-]$ = 0.238, 200 °C, and 245 atm (3:1 CO/H_2) in NMP solution.

Table III. Rate Constants and Product Selectivities for Reaction of NMe_4^+ with $Mn(CO)_5^-$ at 200 °C in NMP Solution[a]

$[Mn(CO)_5^-]$, M	CO/H_2	$10^4k^{(1)}$, s^{-1}	$10^4k^{(2)}$, $M^{-1} s^{-1}$	selectivity [EtOH]/Δ[NMe_4^+]
0.238	3/1	1.3	5.3	0.65
0.124	3/1	0.90	7.3	0.56
0.061	3/1	0.78	13	0.46
0.032	3/1	0.47	14	0.38
0.115	1/1[b]	0.90	7.8	0.61
0.125	1/3	0.95	7.6	0.56

[a] Total pressure = 245 atm. [b] Total pressure = 123 atm.

$$NMe_4^+ + (H_2, CO) \xrightarrow{Mn(CO)_5^-} NMe_3H^+ + (CH_4, C_2H_5OH) \qquad (17)$$

A plot of ln $k^{(2)}$ against the square root of the ionic strength[27] is shown in Figure 6. The result is consistent[28] with the expected primary salt effect, with an extrapolated value of $k^{(2)}$ of 2.7×10^{-3} M^{-1} s^{-1}. For the $HFe(CO)_4^-$

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(24) (a) Calderazzo, F.; Cotton, F. A. *Inorg. Chem.* **1962**, *1*, 30. (b) Mawby, R. J.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 3994.

(25) Hileman, J. C.; Huggins, D. K.; Kaesz, H. D. *Inorg. Chem.* **1962**, *1*, 933.

(26) King, R. B.; King, A. D.; Iqbal, M. Z.; Frazier, C. C. *J. Am. Chem. Soc.* **1978**, *100*, 1687.

(27) The primary kinetic salt effect requires a dependence of the rate constant on the ionic strength of the solution, of the form $\ln k^{(2)} = \ln k_0^{(2)} + DZ_AZ_BI$ where $k_0^{(2)}$ is the rate constant at infinite dilution, D is a function of the dielectric constant, Z is the ionic charge of the ith ion, and I is the ionic strength.

(28) The kinetic data of Table III are also consistent with a reaction that is first order in $[N(CH_3)_4^+]$ and half order in $[Mn(CO)_5^-]$ with no kinetic salt effect. This interpretation has been rejected because it appears to lack physicality; the near constancy of the values of $k^{(1)}[Mn(CO)_5^-]^{1/2}$ is regarded as an adventitious result of the form of the kinetic salt effect.

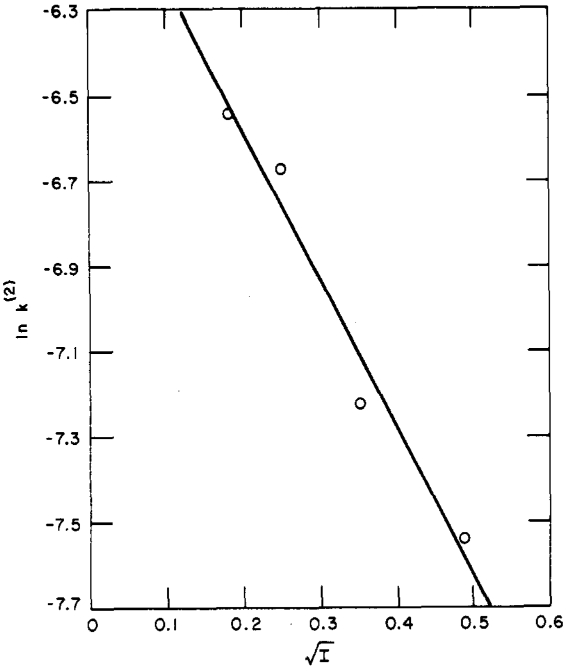

Figure 6. Effect of ionic strength on the methyl transfer to $Mn(CO)_5^-$ at 200 °C and 245 atm (3:1 CO/H_2) in NMP solution.

system, the kinetic salt effect was also noticeable in slight upward curvature of the data points in plots of $1/A$ vs. t, an effect presumably due to the decrease in ionic strength (resulting in an increase in rates) as the reaction progresses (Figure 2).

A comparison of the second-order rate constants for experiments 2, 5, and 6 further shows no significant effect of hydrogen or carbon monoxide partial pressures on the rate of the ionic reaction.

For the reaction of NMe_4^+ with $Mn(CO)_5^-$, the selectivity for ethanol ranged from 36% to 65% and appears to be relatively unaffected by the partial pressures of CO and H_2. A slight increase in selectivity with increasing concentration of the reagents is noticeable. This effect will be discussed later.

Discussion

The results of this work indicate that when tetramethylammonium ion reacts with $HFe(CO)_4^-$ or $Mn(CO)_5^-$ in the presence of H_2 and CO to produce ethanol and methane, the rate-limiting step is a methyl group transfer from the cation to the metal carbonylate neucleophile:

$$R_3NMe^+ + M(CO)_x^{-n} \xrightarrow{k^{(2)}} R_3N + MeM(CO)_x^{-(n-1)} \quad (18)$$

The observations supporting this mechanism are the experimental second-order reaction kinetics (M = Fe) and pseudo-second-order reaction kinetics (M = Mn); the strong, inhibitory primary kinetic salt effect; the enthalpy of activation, 44 kcal mol^{-1}, which is reasonable for Me–N bond breaking synchronous with Me–M bond formation; and the selectivity against the transfer of alkyl groups other than methyl observed in the catalytic homologation experiments,[13] in common with other S_N2 reactions. Other results supporting the mechanism are the large increase (~1400-fold for THF vs. NMP) of reaction rate in less polar medium and the large positive entropy of activation (+17 eu) in the strong donor solvent, NMP, which suggests the extrusion of solvent molecules when the ions react to form a neutral intermediate.

The ultimate products of these reactions, almost exclusively methane and ethanol, arise from fast reactions following the formation of the methyl–metal bond. These reactions would include hydrogenation to methane and methyl migration followed by hydrogenation to acetaldehyde/ethanol. The relatively poor selectivity for ethanol formation in the $HFe(CO)_4^-$ reaction compared with that of the $Mn(CO)_5^-$ reaction might be explained by cis elimination from $(Me)HFe(CO)_4$. The formation of methane from $MeMn(CO)_5$ is unlikely to proceed by an internal monometallic reductive elimination but may proceed by hydrogenation, by a bimolecular elimination via small equilibrium concentrations of $HMn(CO)_5$, or by free-radical formation and hydrogen abstractions.[29] Whatever the mechanism, the H_2 and CO dependencies for this branch must be the same as for the branch to ethanol to account for selectivity unchanged by CO/H_2 ratios. One possibility is that there is no H_2 or CO dependence in either branch. This could be the case if, for example, the methyl group in $CH_3Mn(CO)_5$ dissociates homolytically to form a methyl radical that reacts (faster than the dissociation occurs) with $HMn(CO)_5$ to form CH_4. Meanwhile, at a rate slightly faster than the homolytic dissociation, the methyl group in $CH_3Mn(CO)_5$ could also migrate to carbon to form $CH_3C(O)Mn(CO)_4$, resulting eventually in ethanol formation, apparently with all steps on this pathway faster than the initial methyl-migration step. Under the hypothetical circumstances just described, the selectivity for ethanol or methane would depend only on the relative rate of methyl migration or homolytic dissociation in $CH_3Mn(CO)_5$ and not on the H_2 or CO pressures. With respect to the ethanol branch the literature deals only with lower temperatures and pressures. The presumed precursor $MeC(O)Mn(CO)_5$ has been reported by King[26] to yield acetaldehyde and $Mn_2(CO)_{10}$ at 95 °C in the presence of H_2, while Dombek[30] reports the principal product at 75 °C under 6.8 atm of H_2 is ethanol, with the relative amount of the CO insertion product decreasing under lower hydrogen pressures.

The curious increase in ethanol selectivity with increasing $Mn(CO)_5^-$ concentration, previously noted, may relate to a report by Casey[31] of methyl migration during reaction 19. If the dimetallic acetylmanganese anion in

$$Mn(CO)_5^- + MeMn(CO)_5 \rightarrow (CO)_5Mn{-}Mn(CO)_4(COMe)^- \quad (19)$$

eq 19 makes some contribution as a precursor of acetaldehyde/ethanol, and the methane path is monometallic, the observation may be rationalized. The selectivity differences may also be due to a medium effect resulting from the ionic strength differences in these solutions. Significant medium effects on the selectivity using $HFe(CO)_4^-$ as the nucleophile were mentioned earlier. In any case, it should be noted that the effect is not large.

Experiments 2-3 and 3-1 indicate that $Mn(CO)_5^-$ is approximately 2.7 times as nucleophilic toward $N(CH_3)_4^+$ as $HFe(CO)_4^-$.

Conclusion

The kinetics of the reaction of quaternary ammonium ions bearing methyl groups with nucleophilic metal carbonylate anions at elevated temperatures and pressures has been investigated for the first time. The reaction is first order in each reactant and zero order in either H_2 or CO, indicating a rate-limiting S_N2 methyl transfer step.

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[29] Nappa, M. J.; Santi, R.; Diefenbach, S. P.; Halpern, J. *J. Am. Chem. Soc.* **1982**, *104*, 619.

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[31] Casey, C. P.; Clifford, R. C.; Anderson, R. L.; Marten, D. F. *J. Am. Chem. Soc.* **1975**, *97*, 3053.

The products of the reactions investigated are methane and ethanol in proportions that are relatively sensitive to solvent and metal center but relatively insensitive to H_2 and CO pressure.

Acknowledgment. This research was supported by the Office of Chemical Science, Division of Basic Energy Sciences, U.S. DOE. We thank Prof. J. Halpern for helpful discussions.

Registry No. CH_3OH, 67-56-1; NMe_4^+, 51-92-3; $Me_2NC_5H_{10}^+$, 15302-91-7; $HFe(CO)_4^-$, 18716-80-8; $NaHFe(CO)_4$, 53558-55-7; $NMe_4^+HFe(CO)_4^-$, 63814-56-2; $Me_2NC_5H_{10}^+HFe(CO)_4^-$, 89043-30-1; $Na_2Fe(CO)_4$, 14878-31-0; $Mn(CO)_5^-$, 14971-26-7; NMe_4^+-$Mn(CO)_5^-$, 74343-84-3; $Me_2NC_5H_{10}^+Mn(CO)_5^-$, 89043-31-2.

Direct Synthesis, Reactivity, Fluxional Behavior, and Molecular Structure of $Cp_2Mo_2(CO)_3[PhP(OCH_2CH_2)_2NH]$ (Cp = η^5-C_5H_5), a Compound with a Dissymmetrically Substituted Mo≡Mo Bond. Synthesis and Molecular Structure of $Cp_2Mo_2(CO)_3P(OMe)_3$[1]

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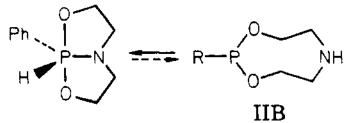
Received September 26, 1983

The reaction of $[Cp(CO)_2Mo]_2$ (Cp = η^5-C_5H_5) with the bicyclic aminophosphorane $\overline{PhP(H)(OCH_2CH_2)_2N}$ results, at room temperature, in the formation of $Cp_2Mo_2(CO)_3$(phoran) (III) (major product), $Cp_2Mo_2(CO)_5$(phoran) (IV), and $Cp_2Mo_2(CO)_4(\text{phoran})_2$ (V) (in which "phoran" represents the open tautomeric form, i.e., $PhP(OCH_2CH_2)_2NH$, of the phosphorane). The unexpected and direct formation of the dissymmetrically CO substituted complex III, in which the Mo≡Mo triple bond is retained, appears to be restricted to phoran and was not observed for $PhP(OMe)_2$, which may indicate that the nitrogen atom transannular to phosphorus in phoran plays a role in the reaction. Complex III undergoes addition reactions with CO and isocyanides to form IV and $Cp_2Mo_2(CO)_3(\mu,\eta^2$-CNR)(phoran) (R = CMe_3, CH_2Ph), respectively. Its reaction with $P(OMe)_3$ results in the formation of $Cp_2Mo_2(CO)_3P(OMe)_3$ (VI). X-ray diffraction studies have been carried out on III and VI. Characteristic of both structures are relatively short Mo–Mo bonds (2.504 Å, average), semibridging CO ligands, and nonlinear Cp–Mo–Mo–Cp arrangements. The dissymmetric substitution of the Mo≡Mo bond allowed the investigation of the dynamic behavior of the CO ligands by means of variable-temperature ^{13}C NMR studies of the ^{13}CO-enriched complex III. Evidence was obtained for a one-for-one switch process of two carbonyls, during which the third one remains unexchanged.

Introduction

The chemistry of the metal–metal triple bond in $[Cp(CO)_2Mo]_2$ (I), (Cp = η^5-C_5H_5) has been the subject of numerous investigations. Its reactions with nucleophiles or small unsaturated organic molecules[3] usually lead to the symmetrical addition products, $Cp_2Mo_2(CO)_4L_2$, in which the metal–metal bond order is 1. By contrast, CO substitution reactions in which the Mo≡Mo bond is retained remain practically unknown. The first direct substitution of *one* CO ligand on the Mo≡Mo bond was relized by using the bicyclic aminophosphorane IIA, which coordinates to the metal through the phosphorus site of its open tautomeric form IIB (eq 1).[2] The resulting complex,



(1)

IIA IIB

$Cp_2Mo_2(CO)_3$(phoran) (III), represents a rare example of an easily and directly accessible dissymmetric derivative. More recently, direct substitution of *all* CO groups of I was achieved by using elemental sulfur[4] or selenium.[5] Other

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