Nucleophilic Activation of Coordinated Carbon Monoxide. Reaction of Tungsten Hexacarbonyl with Methoxide Salts

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Kinetics studies of the reactions of $[Na^+][OCH_3^-]$ and $[((C_6H_5)_3P)_2N^+][OCH_3^-]$ with $W(CO)_6$ are reported. The preparation of acetonitrile solutions of $((C_6H_5)_3P)_2NOCH_3$, a convenient source of solubilized methoxide ion in aprotic media, is described. Second-order rate constants (730 ± 130 M^{-1} s^{-1} and 743 ± 61 M^{-1} s^{-1}) and equilibrium constants (3200 ± 300 M^{-1} and 1400 ± 200 M^{-1}) for the formation of the methoxycarbonyl complexes $[M^+][W(CO)_5CO_2CH_3^-]$ ($M^+ = Na^+$ and $((C_6H_5)_3P)_2N^+$, respectively) at 25 °C are several orders of magnitude lower than those reported for the formation of group VIII methoxycarbonyl complexes. Addition of trace quantities of water to THF/CH_3OH solutions of $[Na^+][W(CO)_5CO_2CH_3^-]$ suprisingly resulted in the formation of $W(CO)_6$ and not the expected metal hydride $HW(CO)_5^-$. These observations are consistent with the previously reported variation in catalytic activity of group VI and VIII metal carbonyl compounds for the water gas shift reaction.

Introduction

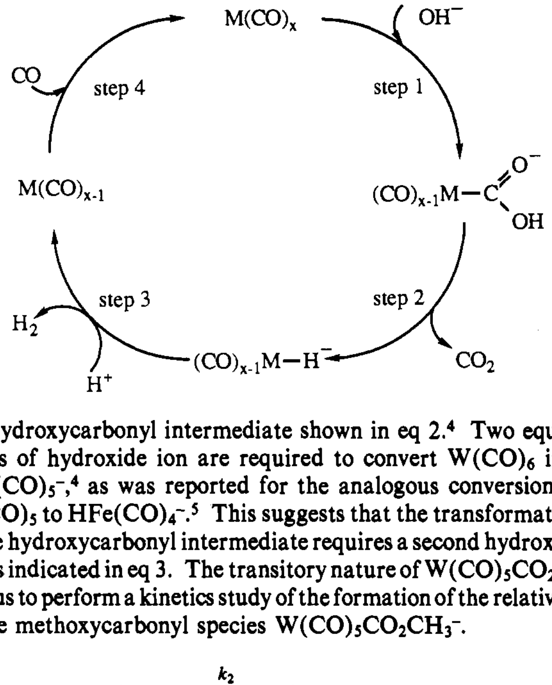
The homogeneously catalyzed activation of carbon monoxide has been an area of intense research in recent years,[2] because of the use synthesis gas (CO/H_2 mixture) as a feedstock for the production of organic chemicals and fuels. The $CO:H_2$ ratio is adjusted by the water gas shift (WGS) reaction, eq 1, to yield

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (1)$$

the optimum ratio for the formation of the desired organic compound. The catalyzed formation of CO_2 and H_2 in the WGS reaction results from nucleophilic attack upon a metal-activated CO molecule. Nucleophilic attack is also utilized in a variety of metal-catalyzed reactions such as the hydrogenation and hydroformylation of alkenes, the oxidation or reduction of CO, and the reductive carbonylation of nitroaromatics. The important role of nucleophilic activation of carbon monoxide in catalysis is illustrated by steps 1 and 2 in Scheme I, the proposed mechanism for the WGS reaction catalyzed by metal carbonyl complexes in alkaline solution.[3] The nucleophilic attack of a coordinated CO ligand by hydroxide yields the hydroxycarbonyl complex, $M(CO)_{x-1}CO_2H^-$, step 1; this species undergoes decarboxylation to give a metal hydride species as shown in step 2. Kinetics studies have shown that the rate constant for the reaction of coordinated CO with hydroxide is many orders of magnitude ($\sim 10^6$) higher than that for free CO.[2]

The relatively low turnover numbers reported for the group VI and VIII metal carbonyl compound-catalyzed WGS reaction is attributed to the opposing basic and acidic pH requirements of steps 1 and 3 in the proposed catalytic scheme. Nevertheless, the lower reactivity of these systems offers the opportunity to study several important steps in the WGS reaction and their dependence upon the specific catalytic species. To this end, we began a detailed kinetics study of the reaction of hydroxide and methoxide salts with group VI metal carbonyls. Addition of hydroxide salts to $W(CO)_6$ results in the formation of $HW(CO)_5^-$, presumably via the hydroxycarbonyl intermediate shown in eq 2.[4] Two equivalents of hydroxide ion are required to convert $W(CO)_6$ into $HW(CO)_5^-$,[4] as was reported for the analogous conversion of $Fe(CO)_5$ to $HFe(CO)_4^-$.[5] This suggests that the transformation of the hydroxycarbonyl intermediate requires a second hydroxide ion as indicated in eq 3. The transitory nature of $W(CO)_5CO_2H^-$ lead us to perform a kinetics study of the formation of the relatively stable methoxycarbonyl species $W(CO)_5CO_2CH_3^-$.

Scheme I



$$W(CO)_6 + [M'^+][OH^-] \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} [M'^+][W(CO)_5CO_2H^-] \qquad (2)$$

$$[M'^+][W(CO)_5CO_2H^-] + OH^- \xrightarrow{k_3} [M'^+][HW(CO)_5^-] + HCO_3^- \qquad (3)$$

Addition of methoxide salts to $W(CO)_6$ results in the formation of the moderately stable methoxycarbonyl adduct, as described by eq 4.[6] We report here a detailed kinetics study of eq 4 and some chemistry of the methoxycarbonyl adduct as a prelude to a similar study of reactions 2 and 3 which involve the transient hydroxycarbonyl adduct. These studies, combined with the previously reported detailed kinetics studies of the addition of

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hydroxide and methoxide to group VIII mononuclear and trinuclear carbonyls,[7] will enable an evaluation of the reported catalytic activity of groups VI and VIII mononuclear carbonyl complexes[8] in terms of the relative values of the rate constants k_2, k_{-2}, and k_3 for the different metal complexes.

$$W(CO)_6 + [M'^+][OCH_3^-] \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} [M'^+][W(CO)_5CO_2CH_3^-] \quad (4)$$

Experimental Section

Materials. All manipulations and reactions were carried out under an Ar or CO atmosphere using standard Schlenk techniques unless stated otherwise. Tetrahydrofuran (THF) was distilled from sodium–benzophenone. Acetonitrile was distilled from CaH_2, and water was doubly distilled. Freshly distilled solvents were degassed with three or more freeze–pump–thaw (f–p–t) cycles and then stirred under CO or Ar. Hexanes and methanol were vacuum distilled from CaH_2 into a Schlenk tube cooled to −78 °C followed by introduction of Ar. All solvent mixtures were prepared as volume to volume ratios. In general, solutions of $W(CO)_6$ were kept under a CO atmosphere, and stock base solutions were kept under Ar.

Bis(triphenylphosphoranylidene)ammonium[9] chloride, [PPN]Cl (Aldrich), was dried in vacuum at 100 °C for at least 3 h. 15-Crown-5 (Lancaster) was dried in vacuum at room temperature overnight. $NaBPh_4$ and $W(CO)_6$ (Strem) were used as received. $W(CO)_5PPh_3$ was prepared following literature procedures.[10] Chemical analyses were performed by the Microanalytical Laboratory at the University of California, Berkeley, CA.

Methanolic $NaOCH_3$ was prepared by reacting freshly cleaned sodium with distilled, Ar-saturated methanol. After the reaction was complete, the solution was degassed with f–p–t cycles and stored under Ar. Base concentrations were determined by aqueous titration with HCl solutions standardized against NaOH solutions prepared from J. T. Baker "Dilut-it" standards using phenolphthalein. Methanolic $LiOCH_3$ was similarly prepared using Li wire.

Synthesis of $[PPN^+][OCH_3^-]$. This salt was prepared following the metathesis procedure described by Martinsen and Songstad.[11] In a typical reaction, 3.20 g (5.53 mmol) of [PPN]Cl were added to a test tube fitted with a 24/40 taper joint. The salt was then dried in vacuo at 100 °C for at least 3 h. Following introduction of Ar, 35 mL of CH_3CN were added. A methanolic solution of $NaOCH_3$ (2.07 M, 3.0 mL, 6.21 mmol) was slowly added to this solution by syringe. The resulting mixture was sonicated for 15 min and then cooled in an ice/water bath for 10 min. The gas inlet was replaced by a Suba-Seal septum and the mixture centrifuged at 2500 rpm for 10 min. The clear solution obtained was removed via syringe and either used immediately or subjected to the following procedure to exchange methanol for acetonitrile: The solution was transferred by syringe to a Schlenk tube and 60 mL of CH_3OH was added. The solution volume was reduced to ~20 mL by vacuum distillation at room temperature. Another 60 mL of CH_3OH was added and the volume again reduced to 20 mL. This process was repeated a third time. Complete removal of CH_3CN was confirmed by ^1H NMR spectroscopy by noting the absence of the $-CH_3$ resonance of acetonitrile. A minimum solution volume of ~15 mL is required to prevent formation of $Ph_2P(O)NPPh_3$.[12] Base concentrations were determined by aqueous titration against standardized HCl using the indicator resazurin.

Synthesis of $[PPN^+][W(CO)_5CO_2CH_3^-]$. A solution of $[PPN^+][OCH_3^-]$ in CH_3CN (0.15 M, 1.7 mL, 0.255 mmol) was added to 90 mg (0.256 mmol) of $W(CO)_6$ dissolved in 30 mL of CO saturated CH_3CN. The solvent was removed under reduced pressure, yielding bright orange crystals. The product was washed with hexanes, dried under vacuum, and stored under CO. Attempts to precipitate the salt by the addition of hexanes or other nonpolar solvents to the acetonitrile solution resulted in the formation of oils, impure material, or $[PPN^+][W(CO)_5OCH_3^-]$. Similar results were obtained when the synthesis was performed in 90/10 THF/CH_3OH solution. Anal. Calc C, 56.0; H, 3.60; N, 1.52. Found: C, 56.7; H, 3.59; N, 1.68. IR (ν_{CO}) in 90/10 THF/CH_3OH: 2052 w, 1909 s, 1868 m cm^{-1}. ^{13}C NMR agreed with literature values.[6] λ_{max} = 416 nm (ϵ = 3500) in 90/10 THF/CH_3OH.

Instrumentation. Electronic and infrared spectra were recorded on Cary 17 or Varian DMS 200 and Nicolet 20DXB spectrophotometers, respectively. ^1H and ^{13}C NMR spectra were obtained with a General Electric QE-300 operating at 300.173 and 75.486 MHz, respectively, or a GE GN-300 operating at 300.100 and 75.468 MHz. Deuterated solvents were used for both lock and internal calibration of ^1H and ^{13}C spectra.[13] $\{^1H\}^{31}P$ spectra were obtained on the GN-300 at 121.65 MHz in CH_3CN or CH_3OH. A capillary tube containing H_3PO_4 was used as an internal standard (δ = 0 ppm).

Stopped-flow kinetics studies were carried out with a Durrum-Gibson D110 stopped-flow spectrophotometer equipped with a MGW Lauda RC3 constant temperature water bath. The absorbance signal at 416 nm was digitized and captured by an Apple IIe microcomputer using an Interactive Microwave Model AI13 12-bit A/D interface. The sampling rate was controlled by a variable software delay counter.[14] The sampling rates were calibrated using a Wavetek Model 114 signal generator whose pulse durations were standardized against a Tektronic 7603 oscilloscope. This system gave a k_{obs} for the rate of reaction between $Fe(CO)_5$ and $NaOCH_3$ in 90/10 THF/CH_3OH that was within 5% of the literature value.[7a] Solutions for kinetics studies were prepared from stock metal carbonyl and base solutions and were transferred via syringes to the stopped-flow spectrophotometer syringes under CO. The absorbance data were transferred to an IBM-PC and rate data analyzed using the kinetic overrelaxation method (KORE) of Swain et al.[15] or from curve-fitting routines in ASYSTANT.[16]

The conductance assembly consisted of a sine wave generator which provided a 1 kHz input voltage to a Wheatstone bridge, and an oscilloscope connected to the output terminals of the bridge. Some measurements were made using an Electro Scientific Instruments impedence meter, Model 253. Conductivity cells consisting of electrodes with an area of 3 cm^2 separated by a distance of 3 cm or an area of 1 cm^2 separated by a distance of 0.5 cm were used. Solutions with $[NaOCH_3]$ from 0.01 to 0.20 M in 90/10 THF/CH_3OH were prepared by dilution of a ~1 M methanolic $NaOCH_3$ solution with Ar-saturated THF and CH_3OH. Solutions with $[(PPN)OCH_3]$ from 4×10^{-4} to 0.017 M were prepared by dilution of a 0.17 M methanolic $(PPN)OCH_3$ solution.

Results and Discussion

Preparation of $[PPN^+][OCH_3^-]$ Solutions. This salt is conveniently prepared via the metathesis reaction of (PPN)Cl and $NaOCH_3$. It is unstable in CH_3CN solution, converting to the oxides $Ph_2P(O)NPPh_3$ and Ph_3PO,[17] but is stable in CH_3OH.[18] The solvent system can be changed from CH_3CN to CH_3OH by repeated azeotropic distillation. An abrupt conversion to the oxide occurs if the solution is pumped to dryness.[12] The methanolic solution of $[PPN^+][OCH_3^-]$ is a convenient, stable source of both the methoxide ion and the excellent crystallizing cation $[PPN^+]$. The CH_3CN solution is an excellent source of solubilized methoxide ion in an aprotic media. This solution is convenient for synthetic purposes, but must be used immediately upon preparation.

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(9) The bis(triphenylphosphine)iminium ion is the usual name for this ion, but since this ion is fundamentally not an iminium ion, various names have been suggested. See ref 11.

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(13) Reported peak positions are referenced to Me_4Si by assigning the reported chemical shift for the observed resonance of the residual protons in the solvent.

(14) Software programs for data acquisition, transfer and analysis are available upon request from the authors.

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(18) Freshly prepared samples contained ~6.5% of the two oxides; after 4 days their concentration had increased to 8.9%.

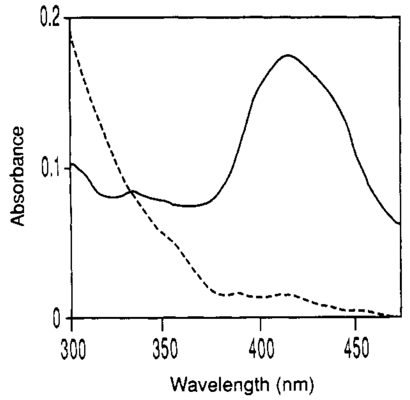


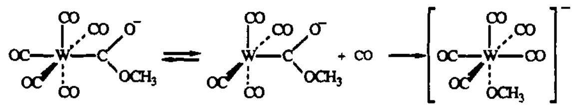
Figure 1. UV/vis spectrum of $W(CO)_6$ (dashed line) and $[Na^+][W(CO)_5CO_2CH_3^-]$ (solid line) in 90/10 THF/CH_3OH.

Table I. Infrared Spectral Data for the Terminal CO Ligands of Tungsten Carbonyl Complexes in 90/10 THF/CH_3OH

compound	ν_{CO}, cm^{-1}
$W(CO)_6$	1975 s
$[Na][W(CO)_5CO_2CH_3]$	2051 w, 1909 s, 1876 m
$[PPN][W(CO)_5CO_2CH_3]$	2052 w, 1907 s, 1868 m
$[PPN][W(CO)_5OCH_3]$	2065 w, 1919 s, 1865 m
$[PPN][HW(CO)_5]$	2029 w, 1889 s, 1879 m
$[PPN][\mu^2\text{-}H(W(CO)_5)_2]$	2041 w, 1941 s, 1879 m

Reaction of $W(CO)_6$ with Methoxide Ion. Addition of $[Na^+][OCH_3^-]$ in CH_3OH to $W(CO)_6$ in 90/10 THF/CH_3OH results in the formation of $[Na^+][W(CO)_5CO_2CH_3^-]$, with the UV/vis changes shown in Figure 1. Similar spectral changes are obtained for $[Li^+][OCH_3^-]$ and $[PPN^+][OCH_3^-]$ in both 90/10 THF/CH_3OH and CH_3CN solution. The reaction can also be monitored by the IR (ν_{CO}) changes observed upon addition of methoxide to the metal carbonyl solution. The relevant infrared data are reported in Table I. The strongest ν_{CO} band for $[M'^+][W(CO)_5CO_2CH_3^-]$ shifts from 1909 cm^{-1} when M′ = Na or Li to 1907 cm^{-1} when M′ = PPN. These small but significant differences suggest that a tighter ion pair is obtained with the Na^+ cation than the large PPN^+ ion. Similar findings have been reported for the Na^+ and PPN^+ salts of $M(CO)_4CO_2CH_3^-$ (M = Fe, Ru, and Os);[7a] however frequency shifts of ~10 cm^{-1} were observed. The smaller frequency shifts observed for the tungsten complex can be attributed to the distribution of the extra electron density over five terminal CO ligands compared to the four terminal carbonyl groups of the group VIII complexes. Unlike the group VIII methoxycarbonyl complexes, no ν_{CO} ester absorbance is observed for the CO_2CH_3 group of $W(CO)_5CO_2CH_3^-$ in 90/10 THF/CH_3OH. Although this seems surprising, no ester absorbance was reported by Darensbourg and co-workers for $[K(crypt222)^+][W(CO)_5CO_2CH_3^-]$.[6] In CH_3CN solution the ν_{CO} band of the CO_2CH_3 group is observed at 1658 and 1668 cm^{-1} for the Na^+ and PPN^+ salts of $W(CO)_5CO_2CH_3^-$, respectively. The lower frequency observed for the Na salt confirms that a tighter ion pair is formed with the Na^+ cation. Infrared spectral data for the terminal carbonyl ligands of tungsten complexes relevant to this study are collected in Table I.

Crystallization of $[PPN^+][W(CO)_5CO_2CH_3^-]$ from solution was difficult. Rapid addition of hexanes yielded a yellow oil which gave ν_{CO} absorbances characteristic of the bridging hydride complex $[PPN^+][\mu^2\text{-}H(W(CO)_5)_2^-]$.[19] If the precipitation was carried out slowly (over several hours), CO was lost and significant quantities of $[PPN^+][W(CO)_5OCH_3^-]$ were obtained.[6] The isolated $[PPN^+][W(CO)_5CO_2CH_3^-]$ solid slowly loses CO, even under a CO atmosphere, indicating the instability of the complex. In contrast the sodium salt is stable in 90/10 THF/CH_3OH solution for several days before appreciable conversion to $[Na^+][W(CO)_5OCH_3^-]$ is noted. Attempts to crystallize the sodium salt were unsuccessful. Since the formation of $W(CO)_5OCH_3^-$ is likely to occur via a CO loss followed by migration of the methoxide group, eq 5, the difference in stability



(5)

of the $[PPN^+]$ and $[Na^+]$ salts most likely results from differences in the lability of the two $[M'^+][W(CO)_5CO_2CH_3^-]$ species or differences in the methoxide ion migration of the $[M'^+][W(CO)_4CO_2CH_3^-]$ intermediate.[20] The distribution of more electron density onto the W atom for the PPN salt compared to the Na salt should result in increased lability of the trans carbonyl ligand for the PPN salt. Furthermore, the tight ion pair formed with the Na^+ ion should require greater conformational changes during the OCH_3^- migration. The importance of such counterion interaction with anionic organometallics has been reported by Collman and co-workers, who demonstrated that the alkyl migratory insertion reactions of $[M^+][RFe(CO)_4^-]$ were strongly influenced by the cation.[21]

Addition of methoxide to metal carbonyl clusters has been shown to cause significant labilization of CO, as evidenced by enhanced substitution rate constants.[22] The rapid conversion of $[PPN^+][W(CO)_5CO_2CH_3^-]$ to $[PPN^+][W(CO)_5OCH_3^-]$ suggests that methoxide addition to $W(CO)_6$ results in a similar labilization of CO. The substitution of CO by PPh_3 in the methoxycarbonyl complex, eq 6, was explored to quantify the labilization effect. No reaction was observed, even after 24 h. This can be contrasted to the enhanced rate of phosphine substitution found for $Ru_3(CO)_{11}CO_2CH_3^-$ compared with $Ru_3(CO)_{12}$.[21] In addition, we find no evidence for the addition of methoxide ion to $W(CO)_5PPh_3$, as discussed later. These two observations suggest that $[PPN^+][W(CO)_4(PPh_3)CO_2CH_3^-]$ is energetically unfavorable, and that the substitution reaction is not observed because of thermodynamic, rather than kinetic, constraints.

$$[M'^+][W(CO)_5CO_2CH_3^-] + PR_3 \underset{k_{-6}}{\overset{k_6}{\rightleftarrows}} [M'^+][W(CO)_4PR_3CO_2CH_3^-] + CO \quad (6)$$

Kinetics of Reactions of $W(CO)_6$ with Methoxide. Reaction kinetics for eq 4 were investigated by monitoring the absorbance changes (A_t) at 416 nm with the stopped-flow spectrophotometer. The concentration of $W(CO)_6$ was ~0.10 mM, while that of $[M'OCH_3]$ was varied from ~1 to 40 mM, always in a large stoichiometric excess to ensure pseudo-first-order conditions. Under these conditions, plots of ln ($A_t - A_{inf}$) were linear for at least 5 half-lives. The plots of the observed rate constants versus concentration of base were linear below 7 mM, as shown in Figure 2 for M′ = PPN. An abrupt departure from linearity was observed at higher base concentrations, as shown in Figure 3 for M′ = PPN and Na. The linear relationship observed at lower methoxide concentrations is consistent with a reversible adduct formation

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(20) It is possible that $W(CO)_5OCH_3^-$ formation also results from the reaction of $W(CO)_5CO_2CH_3^-$ with CH_3OH, as suggested by D. Darensbourg and co-workers.[6] Since $W(CO)_5OCH_3^-$ is obtained from acetonitrile solutions of $W(CO)_5CO_2CH_3^-$ and from the isolated salts $[M'^+][W(CO)_5CO_2CH_3^-]$, a pathway not involving CH_3OH must also be operative.

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(22) (a) Taube, D. J.; van Eldik, R.; Ford, P. C. *Organometallics* **1987**, *6*, 125–129. (b) Taube, D. J.; Ford, P. C. *Organometallics* **1986**, *5*, 99–104.

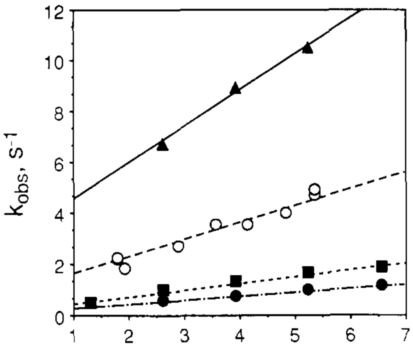

Figure 2. Observed rate constants for the reaction of $W(CO)_6$ with $[PPN^+][OCH_3^-]$ at 7.1 (●), 13.2 (■), 25.0 (○), and 33.9 °C (▲).

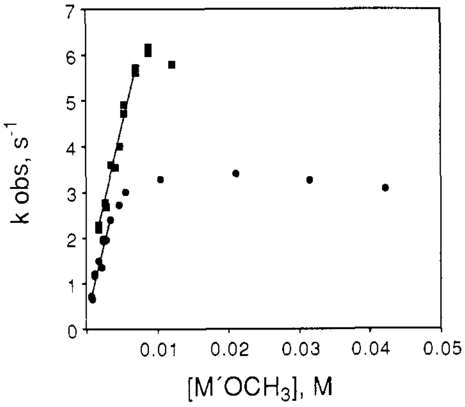

Figure 3. Observed rate constants for the reaction of $W(CO)_6$ with $[PPN^+][OCH_3^-]$ (■) and $[Na^+][OCH_3^-]$ (●) in 90/10 THF/CH_3OH at 25.0 °C.

as described by eq 4. The rate law for this would be

$$\frac{-d[W(CO)_6]}{dt} = (k_4[M'OCH_3] + k_{-4})[W(CO)_6] \quad (7)$$

Thus plots of k_{obs} vs $[M'OCH_3]$ have slopes equal to the forward rate constant (k_4) and nonzero intercepts equal to the reverse rate constant (k_{-4}). The ratio of these rate constants (k_4/k_{-4}) gives the equilibrium constant K_4. Equilibrium data obtained from static infrared experiments are in close agreement with the kinetics results (Table IV). The equilibrium constant K_4 obtained from static IR measurements for M' = PPN in CH_3CN is 500 ± 80 M^{-1}; one-third that found in 90/10 THF/CH_3OH solution (1400 ± 200 M^{-1}). The static equilibrium constants were determined from the concentration of $W(CO)_6$ and $[M'^+][W(CO)_5CO_2CH_3^-]$ present in a solution prepared from known quantities of $W(CO)_6$ and $[M'^+][OCH_3^-]$. These concentrations were deduced by comparing the integrated area of the $\nu_{C\equiv O}$ absorbance of $W(CO)_6$ before and after the addition of $[M'^+][OCH_3^-]$. The agreement between the equilibria constants calculated from the static infrared spectra and those determined by analysis of the linear region of the dependence of k_{obs} upon $[M'OCH_3^-]$ (Figure 2) suggests that eq 4 describes the reaction mechanism. The abrupt departure from pseudo first order kinetics seen at high concentration results from some unidentified solution phenomenon of the methoxide salts in 90/10 THF/CH_3OH rather than a different mechanism for the addition reaction.

Eyring plots of the temperature-dependent rate constants gave the activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ listed in Table II. The value for $\Delta H^\ddagger$ (59 ± 6 kJ mol^{-1}) is about twice that found for methoxide addition to $Ru(CO)_5$.[7a] The small positive value found for $\Delta S^\ddagger$ (6 ± 2 J mol^{-1} K^{-1}) is surprising: a simple addition reaction would be expected to have a negative $\Delta S^\ddagger$. The observed value indicates that there are significant solvation differences between OCH_3^- and $W(CO)_5CO_2CH_3^-$. The large relative errors in k_{-4} preclude calculation of ΔH° and ΔS°, but the reaction is clearly exothermic.

Table II. Rate Constants for the Reaction of $W(CO)_6$ with $[PPN^+][OCH_3^-]$ in 90/10 THF/CH_3OH under CO Atmosphere

T, °C	k_4, M^{-1} s^{-1}	k_{-4}, s^{-1}	K_4,[a] M^{-1}
7.1	148 ± 12	0.10 ± 0.06	1500 ± 900
13.2	263 ± 23	0.24 ± 0.10	1100 ± 470
25.0	743 ± 61	0.65 ± 0.23	1140 ± 420
33.9	1425 ± 270	3.9 ± 1.1	365 ± 125

E_a = 61 ± 1 kJ mol^{-1}
$\Delta H^\ddagger$ = 59 ± 6 kJ mol^{-1}
$\Delta S^\ddagger$ = 6 ± 2 J mol^{-1} K^{-1}

[a] Calculated from k_4/k_{-4} ratio.

Table III. Observed Rate Constants for the Reaction of $[Na^+][OCH_3^-]$ with $W(CO)_6$ in the Presence and Absence of 15-Crown-5 at 25 °C

$10^3[NaOCH_3]$, M	10^3[15-crown-5], × 10^3 M	conductance × 10^5 Ω^{-1} cm^{-1}	k_{obs},[a] s^{-1}
1.71	0	2.52	1.55
1.71	1.71	7.90	1.3
20.6	0	12.5	3.2
20.6	20.6	47.6	2.8

[a] Kinetics values are ± 10%.

Table IV. Equilibrium Constants for the Reaction of $W(CO)_6$ with $[M'^+][OCH_3^-]$ in 90/10 THF/CH_3OH at 25 °C

M'	K_4, M^{-1}	method
Na	2960 ± 1200	kinetics
	3200 ± 300	static IR
PPN	1140 ± 420	kinetics
	1400 ± 200	static IR

The reactivity of $W(CO)_6$ can be compared to those of the group VIII metal carbonyl compounds $M(CO)_5$. A second order rate constant of 97 × 10^3 M^{-1} s^{-1} was found for the reaction of $Fe(CO)_5$ with $NaOCH_3$ in 90/10 THF/CH_3OH, whereas for $Ru(CO)_5$ and $Os(CO)_5$ the reaction rates were too fast to be measured.[7a] It was also observed that the rate of reaction of $Fe(CO)_5$ with $NaOCH_3$ decreased by 2 orders of magnitude as the solvent system varied from 90/10 to 10/90 THF/CH_3OH. In 10/90 THF/CH_3OH k_4 was measured to be 1.8 × 10^3 M^{-1} s^{-1} for $Ru(CO)_5$, while k_4 was 1.36 × 10^4 for $Os(CO)_5$ in 5/95 THF/CH_3OH. Given this observed solvent dependence and the trend in reaction rates of $Os(CO)_5 > Ru(CO)_5 > Fe(CO)_5$, we can estimate a k_4 value for $Os(CO)_5$ of about 1 × 10^6 M^{-1} s^{-1} in 90/10 THF/CH_3OH, 3 orders of magnitude greater than that observed for $W(CO)_6$. This difference is consistent with Darensbourg and Darensbourg's conclusion that the reactivity of metal carbonyls with nucleophiles is dependent upon the extent and location of the positive charge.[23] For example, metal carbonyls with large CO stretching force constants have a large partial positive charge on the carbon atom and are significantly more reactive with nucleophiles than those with low CO vibrational force constants. F_{CO} values of 16.95 and 16.41 mdyn/Å for $Fe(CO)_5$ and $W(CO)_6$, respectively, are consistent with the observed second order rate constants of 0.229 and 0.108 M^{-1} s^{-1} for the addition of benzylmagnesium chloride to $Fe(CO)_5$ and $W(CO)_6$, respectively.[24] However, the difference in reactivity of the groups VI and VIII metal carbonyls with methoxide ion is at least 2 orders of magnitude larger than expected from the differences in F_{CO}. Thus, other factors must be strongly influencing the kinetics. Variation in the specific solvation of the adducts $Fe(CO)_4CO_2CH_3^-$ and $W(CO)_5CO_2CH_3^-$ must dominate the

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(24) Darensbourg, M. Y.; Conder, H. L.; Darensbourg, D. J.; Hasday, C. *J. Am. Chem. Soc.* **1973**, *95*, 5919–5924.

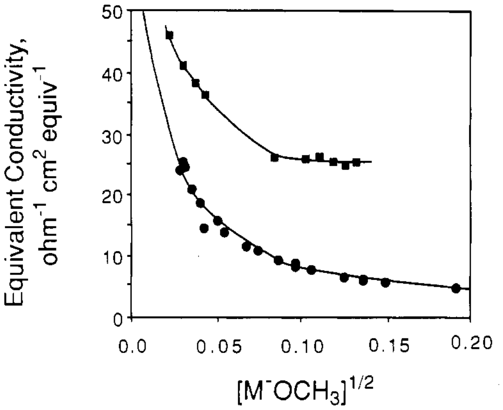

Figure 4. Equivalent conductivity vs [PPNOCH$_3$]$^{1/2}$ (■) and [NaOCH$_3$]$^{1/2}$ (●) in 90/10 THF/CH$_3$OH.

contribution to the observed differences in reactivity. The stable Fe(CO)$_4$CO$_2$CH$_3^-$ species, which has lower activation parameters and does not release CO spontaneously, must be much more strongly solvated than the relatively unstable W(CO)$_5$CO$_2$CH$_3^-$ complex.

The dependence of the observed rate constant on [M'OCH$_3$] revealed an abrupt departure from first order for both [Na$^+$][OCH$_3^-$] and [PPN$^+$][OCH$_3^-$], as seen in Figure 3. Only a linear, first order dependence on [OCH$_3^-$] was observed for the group VIII metals.[7a] For those compounds, however, only base concentrations less than 3 mM could be examined in 90/10 THF/CH$_3$OH because at higher concentrations the reaction rate would exceed the maximum rate observable in the stopped-flow instrument. Thus, it is possible that the abrupt departure from pseudo-first-order kinetics reported here might also be operative for the group VIII metal carbonyls. Examination of the dependence of k_{obs} on methoxide concentration for the reaction with W(CO)$_6$ at nucleophile concentrations less than 3 mM for [Na$^+$][OCH$_3^-$] and 7 mM for [PPN$^+$][OCH$_3^-$] indicate a first order dependence similar to that observed for the group VIII carbonyls, as shown in Figure 2 for [PPN$^+$][OCH$_3^-$]. The second-order rate constant k_4 for reaction with W(CO)$_6$ in 90/10 THF/CH$_3$OH at 25.0 °C was found to be 743 ± 61 M^{-1} s^{-1} for [PPN$^+$][OCH$_3^-$] and 730 ± 130 M^{-1} s^{-1} for [Na$^+$][OCH$_3^-$]. The similarity of the rate constants for these two salts in 90/10 THF/CH$_3$OH is surprising. In the reaction of Fe(CO)$_5$ with [Bu$_4$N$^+$][OCH$_3^-$] in 90/10 THF/CH$_3$OH, the analogous rate constant k_4 was twice that found for the reaction with [Na$^+$][OCH$_3^-$].[7a] A significantly smaller variation in rate constants for the two salts was observed in neat methanol. These results were interpreted to indicate that [Na$^+$][OCH$_3^-$] is much more extensively ion paired in 90/10 THF/CH$_3$OH than in neat methanol and that the ion pair is less reactive.[7a] Therefore, it was expected that there would be a greater difference in the rate of reaction of the two salts with W(CO)$_6$ because of the difference in ion pairing. To gain an understanding of the importance of ions and ion pairs in the nucleophilic addition reaction to W(CO)$_6$, conductivity studies on 90/10 THF/CH$_3$OH solutions of [M'$^+$][OCH$_3^-$] and kinetics studies with [Na$^+$][OCH$_3^-$] in solutions containing 15-crown-5 were investigated.

Conductivity Studies of [M'OCH$_3$] in 90/10 THF/CH$_3$OH. The plot of equivalent conductivity, Λ, vs [NaOCH$_3$]$^{1/2}$ reveals that sodium methoxide is a weak electrolyte in 90/10 THF/CH$_3$OH (Figure 4). The equilibrium constant for eq 8 was

$$[Na^+][OCH_3^-] \rightleftarrows Na^+ + OCH_3^- \qquad (8)$$

determined to be 6 × 10^{-4} M by extrapolation of the observed equivalent conductivity to infinite dilution. Thus the degree of dissociation of sodium methoxide is between 30 and 65% at the concentrations used in the kinetics studies. The Λ of [PPNOCH$_3$] in 90/10 THF/CH$_3$OH reveals that it also acts as a weak electrolyte in 90/10 THF/CH$_3$OH (Figure 4). However, Λ of the PPN salt is significantly greater than that observed for the Na salt at all concentrations studied, consistent with the existence of more solvent-separated ions. Addition of 15-crown-5 to [Na$^+$][OCH$_3^-$] apparently yields an ion distribution similar to that for [PPN$^+$][OCH$_3^-$]: 0.0172 M [PPN$^+$][OCH$_3^-$] had a conductivity of 43.8 × 10^{-5} Ω^{-1} cm^{-1}, larger than that observed for 0.0206 M [Na$^+$][OCH$_3^-$] (12.5 × 10^{-5} Ω^{-1} cm^{-1}) but similar to that observed after the addition of 1 equiv of 15-crown-5 (47.5 × 10^{-5} Ω^{-1} cm^{-1}). The similarity in rate constants found for [Na$^+$][OCH$_3^-$] and [PPN$^+$][OCH$_3^-$] suggests that the ion pair reacts with W(CO)$_6$ at a rate similar to that of the solvated ions.

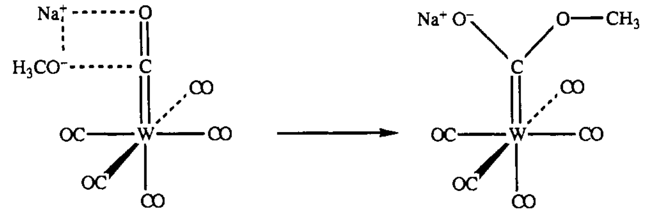

Figure 5. Four-center intermediate for the addition of [Na$^+$][OCH$_3^-$] to W(CO)$_6$.

Dependence of Reaction Rates on 15-Crown-5. The addition of 1 equiv of 15-crown-5 to a solution of [Na$^+$][OCH$_3^-$] in 90/10 THF/CH$_3$OH results in an increase in the conductivity of the solution, consistent with the existence of ion pairs. However, there is a slight *decrease* in the observed rate constant for this reaction with W(CO)$_6$ as shown in Table III, which suggests that the [Na$^+$][OCH$_3^-$] ion pair is slightly more reactive toward W(CO)$_6$ than the free methoxide ion. This strongly supports the formation of the four-center intermediate shown in Figure 5. Theoretical analysis of the photoelectron spectrum of Fe(CO)$_5$ led to the conclusion that the carbon and oxygen atoms of the carbonyl ligands have charges of +0.16 and −0.38, respectively, consistent with coordination of the ion pair.[25] A similar intermediate was proposed for the reaction of LiR (R = CH$_3$, C$_6$H$_5$) with metal carbonyls.[26] Coordination of the Na$^+$ cation to the carbonyl oxygen atom will increase the electrophilicity of the carbon atom, further activating the carbon atom toward nucleophilic attack. Encapsulation of the Na$^+$ ion in the crown ether inhibits its coordination to the carbonyl oxygen, preventing the formation of the four-center intermediate.

Kinetics Studies in CH$_3$CN. To avoid the solution problems encountered in the THF/CH$_3$OH solvent system, we searched for a solvent in which both the metal carbonyl and methoxide salt are soluble. W(CO)$_6$ is sparingly soluble in methanol, but the equilibrium constant for eq 4 is apparently very small.[27] We have not been able to obtain consistent kinetics data for reaction 4 in neat methanol. The two reactants are soluble in CH$_3$CN, so we investigated the kinetics of reaction 4 in this solvent. The reaction of W(CO)$_6$ and [PPN$^+$][OCH$_3^-$] in CH$_3$CN under conditions identical to those used in 90/10 THF/CH$_3$OH was found to be complete with the mixing time (~2 ms) of the stopped-flow spectrophotometer. Attempts to monitor the reaction at lower concentration have not been successful because the absorbance changes at 416 nm are too small to be monitored. The absorbance changes at ~280 nm observed for the disappearance of W(CO)$_6$ when stoichiometric quantities of [PPN$^+$][OCH$_3^-$] are added to dilute solutions (~0.01 mM) are obscured by the absorbances of the PPN$^+$ cation under pseudo-first-order conditions. The dramatic increase in reactivity can be attributed to the decreased solvation of the methoxide ion or ion pair in CH$_3$CN solution.

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The reactivity of $W(CO)_6$ can be compared to that of $W(CO)_5PPh_3$. No changes in either the ν_{CO} infrared or the UV/vis spectra were observed even 6 h after the addition of 10 equiv of $[PPN^+][OCH_3^-]$ to $W(CO)_5PPh_3$ in CH_3CN. Similarly, no reaction was observed in 90/10 THF/CH_3OH solution between $[PPN^+][OCH_3^-]$ and $W(CO)_5PPh_3$. Darensbourg et al. report a decrease in the rate of addition of benzylmagnesium chloride to $LW(CO)_5$ (L = phosphine or phosphite) of 1–2 orders of magnitude compared to the rate of addition to $W(CO)_6$.[23] Similar variation in reactivity was reported for addition of methyllithium to $LW(CO)_5$.[28] It seems likely, therefore, that $W(CO)_4PPh_3(CO_2CH_3)^-$ does not form because of thermodynamic constraints. This is consistent with our observation noted above that PPh_3 does not substitute for CO in $W(CO)_5CO_2CH_3^-$.

Reaction of Water with $[W(CO)_5CO_2CH_3^-]$. The kinetics of methoxide addition to $W(CO)_6$ were studied as a prelude to the addition of hydroxide ion because of the relative stability of $W(CO)_5CO_2CH_3^-$ compared to the proposed intermediate $W(CO)_5CO_2H^-$. The reaction of water and methoxide ion to give methanol and hydroxide, described by the equilibrium process of eq 9, indicates that aqueous solutions of methoxide salts

$$CH_3O^- + H_2O \rightleftarrows CH_3OH + OH^- \qquad (9)$$

should contain significant quantities of hydroxide ion. Accordingly, addition of aqueous solutions of $[Bu_4N^+][OCH_3^-]$ to $W(CO)_6$ in THF results in the formation of $HW(CO)_5^-$, identified by its ν_{CO} spectra.[29] It has been reported that $Fe(CO)_4CO_2CH_3^-$ reacts with trace quantities of water to yield the metal hydride $HFe(CO)_4^-$.[7a] This can be explained by the reversibility of eq 4 and the equilibrium between methoxide and hydroxide in aqueous methanol, eq 9. We find that the sequential addition of stoichiometric quantities of water to a 90/10 THF/CH_3OH solution of $[Na^+][W(CO)_5CO_2CH_3^-]$ results in a decrease in the concentration of the methoxycarbonyl complex and concommitant formation of $W(CO)_6$. As shown in Table V, 86% of the $W(CO)_6$ originally present in solution is recovered after the addition of water. No $HW(CO)_5^-$ was observed in these solutions. In the presence of a large excess of water (~5% by volume), the bridging hydride species $\mu^2\text{-}H(W(CO)_5)_2^-$ forms overnight. This indicates the slow formation of $HW(CO)_5^-$ which reacts with $W(CO)_6$ to yield the bridging hydride dimer. These findings suggest that the equilibria described by eqs 2–4 are highly dependent upon $[H_2O]$ and that the observed catalytic activity of aqueous alkaline solution of metal carbonyls is also strongly dependent upon $[H_2O]$. Darensbourg and co-workers report that alkaline solutions of $W(CO)_6$ show catalytic activity which is lost upon addition of 5% water.[6] In contrast, 30% aqueous methanol solutions of $Fe(CO)_5$ show catalytic activity.[30] The different response of the iron and tungsten catalytic systems to water is consistent with the observation that $HFe(CO)_4^-$ continues to form whereas $HW(CO)_5^-$ does not form under these conditions.

Table V. Percentage of $W(CO)_6$ Observed after Addition of Trace Quantities of Water to $[Na^+][W(CO)_5CO_2CH^-]$ in 90/10 THF/CH_3OH

condition	% $W(CO)_6$[a]
7.5 mM $W(CO)_6$	100
+4.7 equiv of $[Na^+][OCH_3^-]$	0
+3.5 equiv of H_2O[b]	33
+3.0 equiv of H_2O[b]	42
+4.8 equiv of H_2O[b]	71
+3.0 equiv of H_2O[b]	86
+3.0 equiv of H_2O[b]	86

[a] Calculated from the ν_{CO} absorbance of $W(CO)_6$ at 1975 cm^{-1}. [b] Added to solution obtained in previous step.

In contrast to the results obtained in 90/10 THF/CH_3OH, addition of stoichiometric quantities of water to an acetonitrile solution of $[PPN^+][W(CO)_5CO_2CH_3^-]$ resulted in the rapid, complete conversion to $[PPN^+][HW(CO)_5^-]$. The different results obtained in acetonitrile and 90/10 THF/CH_3OH solutions suggest significant differences in the equilibria constants for eqs 2 and 3, which are under investigation.

Conclusions

This study has shown that the nucleophilic addition of methoxide ion to $W(CO)_6$ yields the methoxycarbonyl complex $W(CO)_5CO_2CH_3^-$, analogous to the proposed hydroxycarbonyl intermediate $W(CO)_5CO_2H^-$ in the $W(CO)_6$-catalyzed WGS reaction under alkaline conditions. The stability of $[M'^+][W(CO)_5CO_2CH_3^-]$, including loss of CO, was found to be dependent upon the size and solvation of the counterion M′.

The relatively small values of K_4 compared to analagous reactions of group VIII metals are due to the thermodynamically less favored formation of $W(CO)_5CO_2CH_3^-$. Since eq 4 is similar to eq 2, the small K_4 value suggests that K_2 is also small. This may explain why $W(CO)_6$ has a lower turnover number for the WGS reaction than $Fe(CO)_5$. The fact that no $HW(CO)_5^-$ is formed and only $W(CO)_6$ is observed when water is added to THF/CH_3OH solutions of $W(CO)_5CO_2CH_3^-$ indicates that the lower catalytic activity of $W(CO)_6$ may be due to its inability to readily form the hydride intermediate and that this species is essential to the catalytic cycle, as previously mentioned by Darensbourg.[6]

The addition of methoxide ion to $W(CO)_6$ is at least 3 orders of magnitude faster in CH_3CN solution than in 90/10 THF/CH_3OH, indicating that the methoxide ion is strongly stabilized by methanol.

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