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Oxygen Atom Transfer Reactions to Metal Carbonyls. Kinetics and Mechanism of CO Substitution Reactions of $M(CO)_6$ (M = Cr, Mo, W) in the Presence of $(CH_3)_3NO$

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Detailed kinetic data are reported for the reactions of $M(CO)_6$ (where M = Cr, Mo, and W) with Me_3NO, in the absence and in the presence of triphenylphosphine (PPh_3). The rates of reaction are first-order in concentrations of $M(CO)_6$ and of Me_3NO but zero-order in PPh_3 concentration. The rates of reaction decrease in the order W > Mo $\gtrsim$ Cr. A mechanism is proposed which involves attack on a carbonyl carbon with the formation of coordinatively unsaturated intermediates of the type $M(CO)_5$, which then rapidly react with an entering ligand. Compared with other nucleophiles reported to react by carbonyl attach in $M(CO)_6$ substrates, Me_3NO is a strong nucleophile. Qualitatively, the nucleophilic strengths decrease in the order MeLi > Me_3NO > $PhCH_2MgBr$ $\gg$ N_3^- > NCO^- > NCS^- > Cl^- > Br^- > I^-.

Introduction

The comprehensive reviews by Albers and Coville[1] and by Luh[2] on induced substitution reactions of metal carbonyl complexes have prompted us to initiate a study of oxygen atom transfer reactions to metal carbonyls. Our approach will be to investigate simple systems in order to maximize our chances of better understanding the factors that affect the kinetics and thermodynamics of these reactions. This, our first study, reports data on the kinetics of reactions of the chromium metal triad hexacarbonyls with trimethylamine *N*-oxide (Me_3NO). Further studies will report the effect of other changes in substrates on the rates of CO substitution and the effect of using other known oxygen atom transfer reagents.[3]

Hieber and Lipp[4] first reported the use of pyridine *N*-oxide to facilitate CO release from $Fe(CO)_5$. A decade later, Alper and Edward[5] established the generality of the reaction. The past decade has seen extensive use made of the reaction in syntheses and reactions of metal carbonyl derivatives,[1,2] but to our knowledge this paper is the first report of a quantitative systematic kinetic study of the reaction.

Experimental Section

Compounds and Solvents. Manipulations involving the metal hexacarbonyl compounds were routinely carried out under a N_2 atmosphere by using standard Schlenk techniques. Acetone, acetonitrile, chloroform, and dichloromethane were purified and dried by published[6] procedures. The solvents, which were generally spectroscopic grade, were distilled under a N_2 atmosphere prior to use. The metal complexes $M(CO)_6$ (M = Cr, Mo, W) were obtained from Strem Chemicals and were purified by sublimation. Trimethylamine *N*-oxide (Me_3NO) was obtained either as the dihydrate (Aldrich) and purified by sublimation or it was synthesized by a literature method.[7] The nucleophiles PPh_3 and $AsPh_3$ (Strem) were purified by recrystallization from hexane. The phosphite $P(OEt)_3$ (Strem) was distilled over Na in a N_2 atmosphere prior to use.

Instrumentation. Infrared spectra were recorded on a Nicolet-50X FT-IR using 0.5-mm NaCl cells, on a Nicolet 7199 FT-IR using a Specac P/N 20.500 variable-temperature IR cell which contained a 0.5-mm AgCl cell, or on a Perkin-Elmer 283 using 0.2-mm CaF_2 cells. Ultraviolet–visible measurements were obtained on a Shimadzu UV-240 or on a Perkin-Elmer 320 spectrophotometer using 0.5-cm quartz cells.

Kinetic Measurements. Rate data for the disappearance of reactant metal complexes were obtained by monitoring UV–vis spectral changes and by monitoring spectral changes in the ν(CO) region of the IR. In a typical experiment using a UV spectrophotometer, a solution of $M(CO)_6$ ($\sim 1 \times 10^{-4}$ M) and PPh_3 was prepared in a cuvette, and the cuvette was placed in a temperature-regulated jacket. Constant temperature was maintained by the internal circulating bath of the Shimadzu UV-240 or by an external circulating bath (Neslab RTE-8). After 15 min of temperature equilibration, a CH_2Cl_2 stock solution of Me_3NO was syringed into the cuvette, the cuvette was removed and rigorously shaken, the cuvette was replaced in the light beam, and the resultant spectral changes were monitored.

Infrared spectral changes for the disappearance of the T_{1u} ν_{CO} band were monitored by injecting a solution containing $M(CO)_6$ (7×10^{-4} M), and Me_3NO into a variable-temperature IR cell (Specac P/N 21.000). The reaction solution was prepared at 0 °C by adding a CH_2Cl_2 stock solution of Me_3NO to a CH_2Cl_2 solution containing metal complex and PPh_3.

Plots of $-\ln A$ vs. time for the disappearance of reactant and plots of $-\ln A_\infty - A$ vs. time for the appearance of product were linear over 2–3 half-lives (linear correlation coefficient > 0.995). The slopes of these lines yielded k_{obsd}. Both methods for monitoring the reaction rates yielded similar k_{obsd} values for a given reaction.

Results

The rates of reactions 1 and 2, where M = Cr, Mo, or W, were monitored by following changes in the IR and/or UV–visible absorption spectra with time. Spectral changes

$$M(CO)_6 + Me_3NO \rightarrow M(CO)_5NMe_3 + CO_2 \qquad (1)$$

$$M(CO)_6 + PPh_3 + Me_3NO \rightarrow M(CO)_5PPh_3 + Me_3NO + CO_2 \qquad (2)$$

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[1] Albers, M. O.; Coville, N. J. *Coord. Chem. Rev.* **1984**, *53*, 227.

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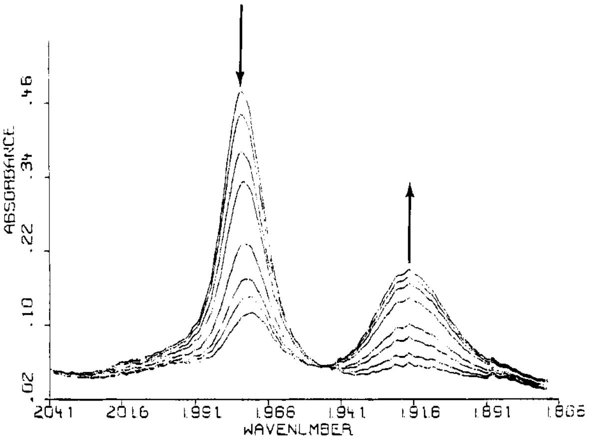

Figure 1. Infrared ν_{CO} absorbance changes vs. time for the reaction $W(CO)_6 + 2Me_3NO + 2PPh_3 \rightarrow W(CO)_4(PPh_3)_2 + 2NMe_3 + 2CO_2$ in CH_2Cl_2 at 11.6 °C.

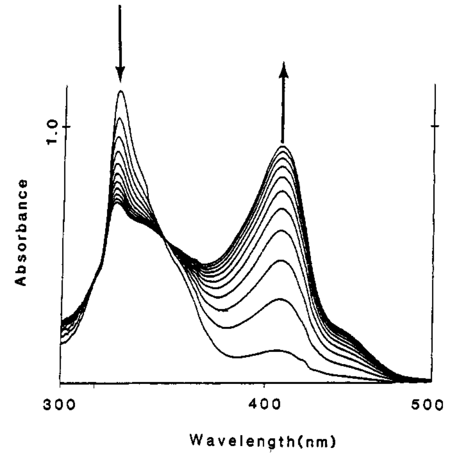

Figure 2. UV–vis absorbance changes vs. time for the reaction $W(CO)_6 + 2Me_3NO \rightarrow W(CO)_4(NMe_3)_2 + 2CO_2$ in CH_2Cl_2 at 30.0 °C.

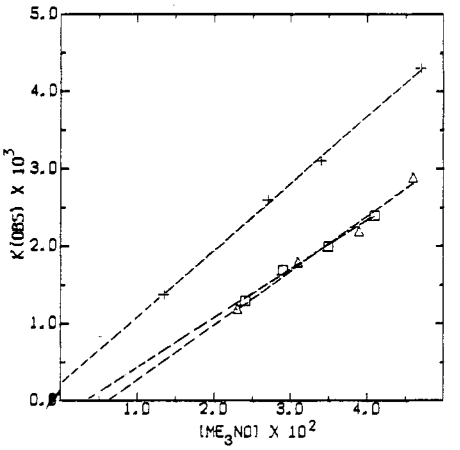

Figure 3. Plot of k_{obsd} vs. Me_3NO concentration for the reaction $M(CO)_6 + Me_3NO \rightarrow M(CO)_5NMe_3 + CO_2$ in CH_2Cl_2 at 12 °C: □, $Cr(CO)_6$, △, $Mo(CO)_6$, +, $W(CO)_6$.

of the reaction mixtures suggest good stoichiometric reactions affording monosubstituted and, after sufficient time, disubstituted products. For the reaction of $W(CO)_6$, the second substitution is fast at these conditions, so no significant amount of monosubstituted product is detected during the reaction as indicated by the good isosbestic points shown by the spectral changes (Figures 1 and 2). In all cases, the reaction products had IR spectra in agreement with reported spectra of the known compounds.[8]

Table I. Second-Order Rate Constants and Activation Parameters for the Reactions of $M(CO)_6$ with Me_3NO (eq 1) in Dichloromethane

M	T, °C	k, M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(mol·deg)
Cr	12.5	5.99×10^{-2}	12.2 ± 0.5	−21.3 ± 1.7
	20.1	9.96×10^{-2}		
	23.5	1.34×10^{-1}		
	32.5	2.59×10^{-1}		
Mo	13.0	6.95×10^{-2}	13.0 ± 0.8	−18.1 ± 2.8
	16.5	1.03×10^{-1}		
	23.5	1.62×10^{-1}		
	29.5	2.71×10^{-1}		
W	11.3	8.72×10^{-2}	16.7 ± 0.8	−4.5 ± 2.7
	17.3	1.67×10^{-1}		
	21.3	2.76×10^{-1}		
	32.0	6.89×10^{-1}		

Table II. Observed Rate Constants, k_{obsd}, for Reaction 2, with Changes in PPh_3 Concentration at a Fixed Me_3NO Concentration in Dichloromethane

M	T, °C	$[Me_3NO]$, M	$[PPh_3]$, M	k_{obsd}, s^{-1}
Cr	14.5	1.75×10^{-2}	4.72×10^{-2}	2.13×10^{-3}
			9.44×10^{-2}	2.28×10^{-3}
			2.36×10^{-1}	2.67×10^{-3}
Mo	11.6	8.33×10^{-3}	6.30×10^{-3}	6.41×10^{-4}
			1.89×10^{-2}	6.79×10^{-4}
			3.34×10^{-2}	3.90×10^{-4}
W	23.5	1.75×10^{-2}	4.27×10^{-3}	7.21×10^{-3}
			1.42×10^{-2}	6.72×10^{-3}
			2.36×10^{-2}	6.71×10^{-3}

Table III. Solvent Effect on the Rates of Reaction 1 for $Cr(CO)_6$ at 16.5 °C

solv	ϵ, M^{-1} cm^{-1}	k, M^{-1} s^{-1}
CH_3CN	38.8	5.50
acetone/CH_2Cl_2 (1:2)	a	0.88
CH_2Cl_2	8.9	0.08
$CHCl_3$/CH_2Cl_2 (3:2)	a	0.01

[a] The dielectric strength of the mixed solutions are not known, but $\epsilon = 20.7$ M^{-1} cm^{-1} for acetone and $\epsilon = 4.73$ M^{-1} cm^{-1} for $CHCl_3$.

Plots of −ln A vs. time were linear for more than 3 half-lives and gave k_{obsd} values reproducible to ±5%. Plots of k_{obsd} vs. $[Me_3NO]$ show (Figure 3) a first-order dependence on Me_3NO, so the reactions (eq 1 or 2) obey the second-order rate law given by eq 3. Rates of reaction 2

$$-d[M(CO)_6]/dt = k[M(CO)_6][Me_3NO] \qquad (3)$$

are zero-order in $[PPh_3]$ (Table III), and the same rates are obtained for corresponding reactions of this type by using either $P(OEt)_3$ or $AsPh_3$. Kinetic data for reaction 1 are given in Table I and for reaction 2 are given in Table II. The effect of solvent on rate constants for the reaction of $Cr(CO)_6$ with Me_3NO is shown in Table III.

Discussion

The reactions of $M(CO)_6$ (M = Cr, Mo, W) with Me_3NO alone afforded the compounds $M(CO)_5NMe_3$[8c] (eq 1), but in the presence of excess PPh_3 the products are $M(CO)_5PPh_3$ (eq 2). For the second substitution, reactions of the metal complexes with Me_3NO and PPh_3 yielded the trans isomers; in the absence of PPh_3, the *cis*-$(Me_3N)_2$ products are formed. Kinetic data for both reactions 1 and 2 obey a second-order rate law (eq 3), first-order in substrate and in Me_3NO concentrations but zero-order in

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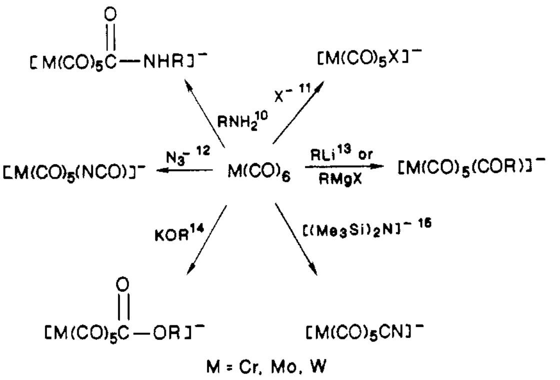
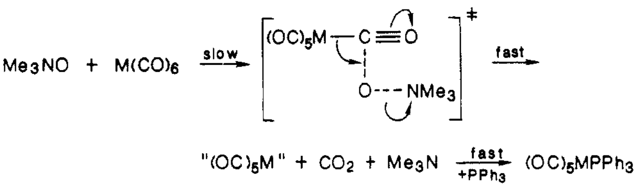
[8] (a) Magee, T. A.; Matthews, C. N.; Wang, Z. S.; Wotiz, J. H. *J. Am. Chem. Soc.* **1961**, *83*, 3200. (b) Cotton, F. A.; Kraihanzel, C. S. *Inorg. Chem.* **1963**, *2*, 534. (c) Koelle, U. *J. Organomet. Chem.* **1977**, *133*, 53.

Scheme I



Scheme II



Scheme III

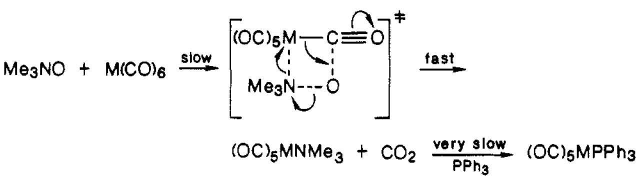


Table IV. Rate Constants for Reaction 1 Estimated at 25 °C and Values of ν_{CO} and of F_{CO} for $M(CO)_6$ in CH_2Cl_2

compd	k, $M^{-1}\ s^{-1}$	ν_{CO},[a] cm^{-1}	F_{CO},[a] mdyn/Å
$Cr(CO)_6$	0.147	1983	16.49
$Mo(CO)_6$	0.190	1985	16.52
$W(CO)_6$	0.366	1980	16.41

[a] Reference 27.

PPh_3. The rate law is consistent with an associative reaction mechanism, where both bond making by attack of the Me_3NO nucleophile and bond breaking of the M–C bond contribute to the energetics of the rate-determining step. This mechanism is supported by experimental values of the activation parameters (table I) which are low for $\Delta H^‡$ and negative for $\Delta S^‡$, whereas for a dissociation (bond-breaking) mechanism values of $\Delta H^‡$ would approximate 30 kcal/mol and values of $\Delta S^‡$ would be positive.

Next it is necessary to decide on the position of attack by the nucleophilic atom 0 of Me_3NO. Attack may occur either on the metal or on the carbonyl carbon. Circumstantial evidence favors attack at a carbonyl carbon chiefly because of the efficient ready evolution of CO_2 by the reaction. Attack at carbonyl carbon, believed to be harder than the metals with a zero oxidation state, also is more in keeping with the concept of hard and soft acids and bases.[9] Likewise, there is a large body of information on reactions of $M(CO)_6$ with different nucleophiles where attack is believed to occur on the carbonyl carbon (Scheme I).

In addition to these reactions where attack on carbonyl carbon results in the formation of a stable product containing the attached carbon (except for reactions forming $[M(CO)_5X]^-$, there are examples where attack at carbon does not result in formation of a stable product but where the added nucleophile functions as a catalyst for CO substitution.[16] For example, Morris[17] reports that CO substitution in $Fe(NO)_2(CO)_2$ with the poor reagent $AsPh_3$ is catalyzed by halide ions and by amines. A similar process could be responsible for the R_3PO catalysis of ^{13}CO exchange in $Mn_2(CO)_{10}$ and in $Co_4(CO)_{12}$,[18] but R_3PO does not catalyze ^{13}CO exchange with the $M(CO)_6$ carbonyls.[19]

Alper and Edward[5] investigated the reaction of $Fe(CO)_5$ with Me_3NO, and they proposed a mechanism which involves nucleophilic attack of Me_3NO on the carbonyl carbon to give Me_3N and CO_2, but no study was made of the iron product. The results of our study concur with their proposed mechanism, and the kinetic data suggest formation of a coordinatively unsaturated active intermediate (Scheme II). An alternative four-centered mechanism (Scheme III) cannot be involved because the rate of CO replacement with PPh_3 in the presence of Me_3NO is much faster than is the rate of Me_3N replacement with PPh_3 in $M(CO)_5NMe_3$.[20]

The effect of solvent on the rates of reaction 1, where the substrate is $Cr(CO)_6$ (Table III), was briefly investigated. The results show an increase in rate with increasing dielectric strength of the solvent, which suggests an increase in polarity in going from the ground state to the transition state. Also to be considered is the fact that CH_3CN and CH_3COCH_3 are better coordinating solvents than is CH_2Cl_2.

Previous studies[21] suggest the ease of nucleophilic attack on carbon of a metal carbonyl correlates the C–O stretching frequency of the carbonyl. The higher the value of ν_{CO}, the greater the ease of attack on the more positive carbon which results from less π back-bonding from the metal. Table IV contains values of ν_{CO}, the CO force constants, and the rate constants estimated for a temperature of 25 °C for the $M(CO)_6$ compounds. On the basis of ν_{CO}, the rates of reaction are expected to vary in the order Mo = Cr > W, but experimental results show W > Mo > Cr. Note the differences in rates are small, and even the rel-

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[20] For example, the associative and dissociative rate constants for the reaction $Mo(CO)_5$ amine + $PPh_3 \rightarrow Mo(CO)_5PPh_3$ + amine are $\sim 10^{-4}\ M^{-1}\ s^{-1}$ and $10^{-5}\ s^{-1}$, respectively, at 35 °C. Covey, W. D.; Brown, T. L. *Inorg. Chem.* **1973**, *12*, 2820.

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Table V. Rates of Nucleophilic Attack at Carbon for $M(CO)_6$ Compounds

compd	nucleophile	*T*, °C	*k*, M^{-1} s^{-1}	ref
$Cr(CO)_6$	Br^-	120.0	2.89×10^{-3}	11a
	I^-	125.0	2.20×10^{-3}	11a
	N_3^-	25.0	0.0	12
	$PhCH_2MgBr$	27.0	0.530	13b
	Me_3NO	25.0	0.150	*a*
	MeLi	25.0	7.29	13a
$Mo(CO)_6$	Br^-	55.0	3.24×10^{-3}	11a
	N_3^-	28.5	0.039	12
	$PhCH_2MgBr$	27.0	0.91	13b
	Me_3NO	25.0	0.182	*a*
	MeLi	25.0	8.67	13a
$W(CO)_6$	Br^-	100.0	2.00×10^{-3}	11a
	I^-	120.0	3.20×10^{-3}	11a
	NCS^-	100.0	4.92×10^{-3}	11b
	NCO^-	100.0	8.33×10^{-3}	11b
	CN^-	95.0	1.07×10^{-1}	11b
	N_3^-	30.0	0.107	12
	$PhCH_2MgBr$	27.0	1.08	13b
	Me_3NO	25.0	0.524	*a*
	MeLi	25.0	14.9	13a

[a] This work.

ative ordering of rate changes for different temperatures. More meaningful are the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (Table I), which also favor reaction in the order W > Mo > Cr. The reason for this behavior is not understood. The observed reactivity may be due to differences in CO to metal σ donation. An earlier report[23] suggests that the metal–CO σ-bond energies increase in the order Cr < Mo < W. This increased electron donation to the metal center would remove electron density from the C atom, thereby making the C atom more electrophilic. The resultant metal to CO π-back-bonding process may be less efficient in transferring electron density than is the σ-donation process. Furthermore,[13b] these two modes of bonding may be active to different extents, as the central metal is changed. Unfortunately, atomic charge calculations for the carbon atoms have only been reported[23] for $Cr(CO)_6$ (+0.20). However, considering that the metal with the highest ionization potential would have the highest positive charge on its carbonyl carbons, it follows that the rates of reaction (as found) should decrease in the order W > Mo > Cr.[24] Of course, all these considerations relate only to the ground states of the substrates and tell us nothing about the transition states for reaction. It is significant that the activation parameters (Table I) for Cr and Mo are about the same and different from W. The more rapid rate of reaction of $W(CO)_6$ is due to its more favorable entropy term, which suggests a less restricted transition state, perhaps, because W is the largest metal of the triad.

Rate data for reactions of $M(CO)_6$ with nucleophiles believed to attack carbon are compared in Table V. The rate data show that Me_3NO is a strong nucleophile, second only to MeLi. The nucleophiles considered here for attack on the carbonyl carbon decrease in nucleophilic strength in the order MeLi > Me_3NO > $PhCH_2MgBr$ ≫ N_3^- > NCO^- > NCS^- > Cl^- > Br^- > I^-. Table V shows that the reactivity of the $M(CO)_6$ complexes toward these nucleophiles (except the halide ions) is W > Mo ≳ Cr, in accord with the highest positive charge on carbon being present in $W(CO)_6$. That Me_3NO is a strong nucleophile seems reasonable because of the high negative charge[25] on oxygen in $Me_3N^{\delta+} \rightarrow O^{\delta-}$. What is anomalous is that Me_3NO is both a good nucleophile and a good oxidizing reagent, for the reactions being discussed involve oxidation of CO to CO_2 with reduction of Me_3NO to Me_3N. Usually a good nucleophile is a good reducing agent[26] because both processes require the release of electrons by the reagent toward the substrate.

Acknowledgment. We wish to thank the United States-China Cooperative Science Program for the support of this collaborative research. The program is under the auspices of the U.S. National Science Foundation and the Chinese Academy of Sciences and Ministry of Education. D.L.K. thanks the graduate school at Northwestern University for a fellowship.

Registry No. $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; Me_3NO, 1184-78-7; PPh_3, 603-35-0.

Supplementary Material Available: Additional values of k_{obsd} for reaction 1 with changes in Me_3NO concentration at different temperatures in dichloromethane (3 pages). Ordering information is given on any current masthead page.

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