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Kinetic Studies of Carbonyl Substitution in Quinolinolatotetracarbonylmanganese(I) and Its Tricarbonyl Derivatives

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The rates of reactions of quinolinolatotetracarbonylmanganese(I), $Mn(CO)_4$(oxine), with the monodentate ligands C_5H_5N, 4-$CH_3C_5H_4N$, p-$CH_3C_6H_4NH_2$, p-$FC_6H_4NH_2$, $P(C_6H_5)_3$, and $As(C_6H_5)_3$ (L) in chloroform, 1,2-dichloroethane, benzene, and acetone were followed by visible spectroscopy and by gas evolution (volumetrically) at 0–24° C. All reactions are first-order in the concentration of $Mn(CO)_4$(oxine) and independent of the nature and concentration of L. A mechanism is proposed which involves dissociation of one of the mutually trans CO ligands. Apart from acetone, solvent exerts little influence on the rate. The rate constant, k, in chloroform at 23.9° C is 8.7×10^{-3} sec^{-1}, whereas $E_a = 18.6$–19.6 kcal/mol and $\Delta S^{\neq} = -4.9$ to 0.3 e.u.

The rates of reactions of $Mn(CO)_3L'$(oxine) with L' in chloroform to give $Mn(CO)_2L'_2$(oxine) were monitored by infrared spectroscopy in the $\nu_{C\equiv O}$ region; they decrease as a function of L' in the order $P(O\text{-}n\text{-}C_4H_9)_3 > P(OC_6H_5)_3 > P(n\text{-}C_4H_9)_3$. The reaction of the L' = $P(n\text{-}C_4H_9)_3$ compound is first-order in the concentration of the complex and essentially independent of the concentration of the phosphine; at 23.3° C, it is about 40 times slower than the reaction of $Mn(CO)_4$(oxine) with L.

The foregoing reactions are compared and contrasted with those of other manganese(I) and of chromium(0) carbonyl complexes containing "hard" donor atoms.

Introduction

Kinetic studies on substitution reactions of six-coordinate manganese(I) carbonyl complexes have received considerable attention.[1,2] However, these investigations have been limited to various pentacarbonyls of general formula $Mn(CO)_5X$ (X = monodentate, uninegative ligand) and to their substitution products.

In the preceding paper[3] we have described the synthesis and characterization of quinolinolatotetracarbonylmanganese(I), $Mn(CO)_4$(oxine),[4] and its tricarbonyl and dicarbonyl derivatives. A feature of interest in these complexes is the presence of the bidentate oxine ligand, which bonds to the metal through the "hard" oxygen and nitrogen atoms. In order to ascertain the effect of these two donors on the rate and mechanism of carbonyl substitution in $Mn(CO)_4$(oxine), and in order to compare these reactions with those of electronically related $Cr(CO)_4$(L–L) (L–L = 2,2′-bipyridine, o-phenanthroline, and their substituted analogs)[5,6] we undertook a kinetic investigation of replacement of carbon monoxide with monodentate ligands in $Mn(CO)_4$(oxine) and in some of its tricarbonyl derivatives. Reported here are our results.

Experimental

Materials

All manganese(I) carbonyl oxine complexes were prepared as reported in the preceding paper.[3] Ligands were purified as follows: *p*-fluoroaniline (bp 187° C) and tri-*n*-butylphosphine (bp 97–99° C, 6 mm) were distilled, stored under nitrogen, and used within 24 hr; reagent grade pyridine (bp 115° C) and 4-picoline (bp 143° C) were dried over BaO and fractionally distilled under nitrogen; triphenylphosphine was recrystallized from ethanol. Other ligands were used as received from various sources.[3]

Spectroscopic grade chloroform, 1,2-dichloroethane, and acetone were purchased from Matheson, Coleman and Bell and were used without further purification. Reagent grade benzene was dried over CaH_2 for 24 hr and distilled, bp 80° C.

For ^1H NMR measurements, $CDCl_3$ of greater than 99.5% purity was purchased from Volk Chemical Co. Deuteroacetone was furnished by Stohler Isotope Chemicals.

Kinetic Measurements

(a) By visible spectroscopy

Unless otherwise indicated, reactions of $Mn(CO)_4$(oxine) with various L to give $Mn(CO)_3L$(oxine) were followed by visible spectroscopy using a Cary 14 spectrophotometer. A solution of $Mn(CO)_4$(oxine) in a 0.1-cm constant temperature cell (Series 430, Scientific Glass Apparatus Co.) was placed in the sample compartment of the spectrophotometer and allowed to reach thermal equilibrium (0–24° C, > ±0.05° accuracy). An aliquot of thermostated ligand (L) solution was introduced into the sample cell by means of a spring injector syringe[7,8] to insure rapid mixing. The absorbance of the reaction mixture was then monitored at 450 mμ.

The reactions were followed to 85% completion, and t_∞ readings were taken after 10 half-lives. The complexes $Mn(CO)_4$(oxine) and each of $Mn(CO)_3L$ (oxine) were found to be stable toward visible light and to obey Beer's law. The nature of the reaction products was confirmed by comparison of the $\nu_{C\equiv O}$ infrared absorptions of the final solutions with those of authentic samples.

(b) Volumetrically (Carbon monoxide evolution)

Some reactions of $Mn(CO)_4$(oxine) with L to yield $Mn(CO)_3L$(oxine) were followed also by measuring the volume of liberated carbon monoxide. The apparatus used was similar to that described elsewhere[9,10] and incorporated a gas buret with a pressure-equalizing side arm. The buret was connected to a thermostated flask which contained a solution of Mn $(CO)_4$(oxine) ($\sim 8 \times 10^{-3} M$) under an atmosphere of nitrogen. A thermostated ligand (L) solution ($>4 \times 10^{-1} M$) was then syringed into the flask through a serum cap-fitted side arm. The amount of gas collected ($\gtrsim$ 20 ml) was found to be in good agreement with that calculated for the release of one mole of CO per mole of $Mn(CO)_4$(oxine).

(c) By infrared spectroscopy

Reactions of $Mn(CO)_3L'$(oxine) with L′ to give $Mn(CO)_2L'_2$(oxine) were monitored by infrared spectroscopy in the $\nu_{C\equiv O}$ region using a Perkin–Elmer Model 337 spectrophotometer operated at a slow scanning speed and calibrated with a polystyrene film.

Solutions of $Mn(CO)_4$(oxine) and L′ were thermostated separately at 18–25° C (±0.1°); after thermal equilibrium had been attained (*ca.* 20 min), 5 ml of the ligand (L′) solution was pipetted into the flask containing the tetracarbonyl complex. The resultant solution was shaken to ensure complete mixing, and aliquots were periodically syringed therefrom into a 0.1-mm KBr cell for infrared measurements.

Under the above conditions the reaction between $Mn(CO)_4$(oxine) and L′ to give $Mn(CO)_3L'$(oxine) requires approximately 7 min for completion; the formation of the dicarbonyl, $Mn(CO)_2L'_2$(oxine), which proceeds more slowly, was then followed. Generally, the disappearance of the highest frequency $\nu_{C\equiv O}$ band of $Mn(CO)_3L'$(oxine) (see ref. 3, Table II) was monitored; however, the appearance of the lower frequency $\nu_{C\equiv O}$ absorption of $Mn(CO)_2L'_2$(oxine) was also examined for comparison.

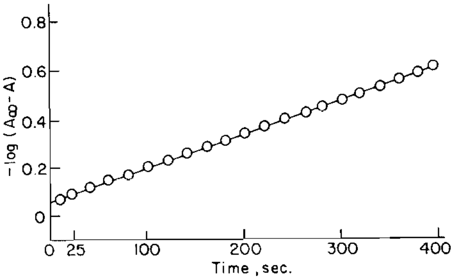


Figure 1. Plot of $-\log(A_\infty - A)$ *vs.* time for the reaction of $Mn(CO)_4$(oxine) with pyridine in chloroform at 13.8° C.

The reactions were followed to 85% completion with 10–15 measurements, and t_∞ readings were taken after 10 half-lives or longer. In all cases, the final $\nu_{C\equiv O}$ spectrum correponded to that of the appropriate authentic product.

(d) By ¹H NMR spectroscopy

Changes in the ¹H NMR spectra of solutions containing $Mn(CO)_4$(oxine) and L were investigated using a Varian Associates A-60A spectrometer equipped with variable-temperature accessories. No kinetic data were collected by this method, however.

Treatment of Data

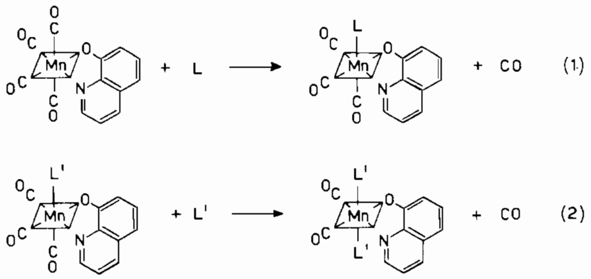
Using the spectroscopic data obtained at 450 mμ, linear plots were constructed of $-\log(A_\infty - A)$ *vs* time where A_∞ is the absorbance at the end of the reaction and A is the absorbance at any given time. A typical plot is shown in Figure 1. First-order rate constants, k, were calculated from the slopes of these lines; they are reproducible to ±3% or better.

Data from the infrared spectroscopic and gas volumetric kinetic experiments were treated similarly to furnish first-order rate constants, k.

A least-squares computer program was used to calculate values of the activation parameters and their standard deviations.

Results

Two general types of carbonyl substitution reaction were investigated in this work; they are shown in equations (1) and (2). The reactions in equation (1) were followed by visible spectroscopy and, less extensively, where specified, by gas evolution. Good agreement was observed between the rate constants, k, obtained by the two methods. For example, the reaction of $Mn(CO)_4$(oxine) with C_5H_5N in 1,2-dichloroethane



solution at 0° C gives $k = 1.83 \times 10^{-3}$ sec^{-1} when followed volumetrically, and $k = 1.67 \times 10^{-3}$ sec^{-1} when monitored spectrophotometrically.

Rate data on the reactions of Mn(CO)$_4$(oxine) with each of C_5H_5N, 4-$CH_3C_5H_4N$, p-$CH_3C_6H_4NH_2$, p-$FC_6H_4NH_2$, $P(C_6H_5)_3$, and $As(C_6H_5)_3$ in chloroform solution at 23.9° C are presented in Table I. The rates of the substitution are independent of the nature and concentration of the entering ligand, L, and follow the expression

$$-\frac{d[\mathrm{Mn(CO)_4(oxine)}]}{dt} = \frac{d[\mathrm{Mn(CO)_3L(oxine)}]}{dt} = k[\mathrm{Mn(CO)_4(oxine)}] \quad (3)$$

The rate constants, k, for the reactions of Mn(CO)$_4$ (oxine) with C_5H_5N and $As(C_6H_5)_3$ in chloroform at various temperatures from 9.8 to 23.9° C are given in Table II.

TABLE I. Rates of Reaction of Mn(CO)$_4$(oxine) with Various Ligands (L) in Chloroform at 23.9° C.
Mn(CO)$_4$(oxine) + L→Mn(CO)$_3$L(oxine) + CO

L	$\frac{[L]}{[Mn(CO)_4(oxine)]}$ [b]	$k \times 10^3$, sec^{-1}
C_5H_5N[a]	4.9	8.19
	12.8	8.20
4-$CH_3C_5H_4N$	6.54	8.80
	21.1	8.55
p-$CH_3C_6H_4NH_2$	4.46	8.63
	10.01	8.58
	24.55	8.64
p-$FC_6H_4NH_2$	4.54	8.85
	9.50	8.50
$P(C_6H_5)_3$	2.24	8.75
	2.80	8.66
	4.53	8.66
	5.73	8.56
	8.10	8.72
	23.7	8.86
$As(C_6H_5)_3$	5.29	8.94
	11.35	8.72
	27.29	8.65

[a] At 23.5° C. [b] Concentration of Mn(CO)$_4$(oxine) = 6.0–6.1 × 10^{-4} M.

TABLE II. Rates of Reaction of Mn(CO)$_4$(oxine) with Pyridine and Triphenylarsine (L) in Chloroform at Various Temperatures.
Mn(CO)$_4$(oxine) + L→Mn(CO)$_3$L(oxine) + CO

L	Temp, ° C	$k \times 10^3$, sec^{-1}
C_5H_5N	23.9	8.60
	23.5	8.20
	19.7	5.57
	19.4	4.43
	9.8	1.70
$As(C_6H_5)_3$	23.9	8.77
	19.5	5.76
	18.3	4.77
	11.5	2.25
	10.1	1.92

Rate data on the reactions of Mn(CO)$_4$(oxine) with C_5H_5N and $As(C_6H_5)_3$ in 1,2-dichloroethane, benzene, and acetone at several temperatures in the range 7.4–23.9° C are contained in Table III. Again, neither the nature nor the concentration of the incoming ligand affects the rate of the monosubstitution. Changes in the dielectric constant of the solvent[11] do not strictly parallel variations in the rate constants; thus the rates increase as a function of the medium in the order 1,2-dichloroethane ($\varepsilon = 10.4$) < benzene (2.28) < chloroform (3.73) < acetone (20.7), with the last-mentioned solvent having been examined only very cursorily.

Activation parameters for the reactions of Mn(CO)$_4$ (oxine) with C_5H_5N and $As(C_6H_5)_3$ in chloroform and 1,2-dichloroethane are listed in Table IV. These parameters appear to be invariant to both the solvent and the entering ligand, L.

Reactions represented by equation (2) were followed by infrared spectroscopy in the $\nu_{C\equiv O}$ region. The tricarbonyls Mn(CO)$_3$L'(oxine) form quite rapidly upon treatment of Mn(CO)$_4$(oxine) with L' (see Tables I–III); their substitution reactions with additional L' to afford Mn(CO)$_2$L'$_2$(oxine) were then monitored as described in the Experimental.

Changes in the infrared $\nu_{C\equiv O}$ bands as a function of time for the substitution using L' = P(O-n-$C_4H_9)_3$, $P(OC_6H_5)_3$, and P(n-$C_4H_9)_3$ are shown in Figures 2–4, respectively. These reactions were not investigated nearly in as much detail as those represented by equation (1). Nevertheless, several trends, mainly qualitative, are apparent. As may be seen in Figures 2–4, the rate of the substitution of CO in Mn(CO)$_3$ L'(oxine) by L' in chloroform solution at 23.3° C varies with the already bonded ligand (which is also the entering ligand) in the order P(O-n-$C_4H_9)_3$ > $P(OC_6H_5)_3$ > P(n-$C_4H_9)_3$. The reactions of Mn (CO)$_3$L'(oxine) with the two phosphites were examined only qualitatively; that with $P(OC_6H_5)_3$

TABLE III. Rates of Reaction of $Mn(CO)_4$(oxine) with Pyridine and Triphenylarsine (L) in 1,2-Dichloroethane, Benzene, and Acetone at Various Temperatures.

$Mn(CO)_4(oxine) + L \rightarrow Mn(CO)_3L(oxine) + CO$

Solvent	L	Temp, °C	$\frac{[L]}{[Mn(CO)_4(oxine)]}$	$k \times 10^3$, sec^{-1}
1,2-Dichloroethane	C_5H_5N	23.9	4.60	3.23
		23.9	2.12	3.18
		18.5	5.30	1.85
		18.0	5.80	1.68
		11.3	5.80	0.74
	$As(C_6H_5)_3$	23.9	4.8	3.37
		23.9	9.6	3.27
		17.8	9.2	1.29
		11.8	10.2	0.86
Benzene	C_5H_5N	23.9	3.1	3.91
		23.9	31.0	4.24
		18.5	20.5	2.27
		14.7	15.6	1.50
		10.5	12.6	1.07
	$As(C_6H_5)_3$	23.9	4.6	4.05
		23.9	10.8	3.87
Acetone	C_5H_5N	7.4	3.6	18.8
		7.4	24.1	18.6

TABLE IV. Activation Parameters for Reaction of $Mn(CO)_4$(oxine) with Various Ligands (L).
$Mn(CO)_4(oxine) + L \rightarrow Mn(CO)_3L(oxine) + CO$

Solvent	Dielectric constant[a]	L	E_a, kcal/mol	ΔS^{+}, e.u.
Chloroform	3.73	C_5H_5N	19.1 ± 1.2	−3.4 ± 4.3
		$As(C_6H_5)_3$	18.6 ± 0.3	−4.9 ± 1.1
1,2-Dichloroethane	10.4	C_5H_5N	19.6 ± 0.6	−3.8 ± 3.0
		$As(C_6H_5)_3$	18.6 ± 3.6	0.3 ± 6.1

[a] National Bureau of Standards, No. 514.

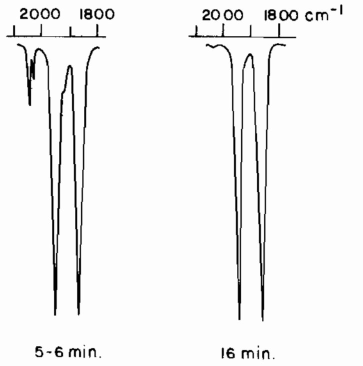


Figure 2. The infrared spectra in the $\nu_{C\equiv O}$ region of a reaction mixture of $Mn(CO)_3[P(O\text{-}n\text{-}C_4H_9)_3]$(oxine) and $P(O\text{-}n\text{-}C_4H_9)_3$ in chloroform at 23.3° C at two different time intervals.

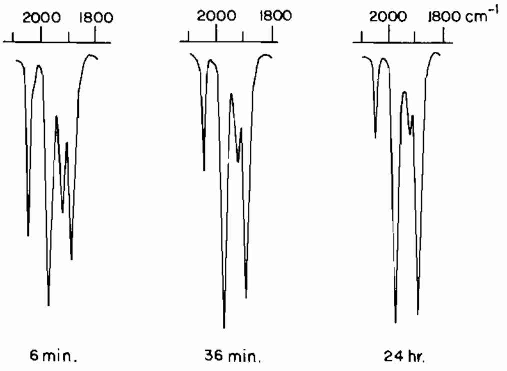


Figure 3. The infrared spectra in the $\nu_{C\equiv O}$ region of a reaction mixture of $Mn(CO)_3[P(OC_6H_5)_3]$(oxinc) and $P(OC_6H_5)_3$ in chloroform at 23.3° C at three different time intervals.

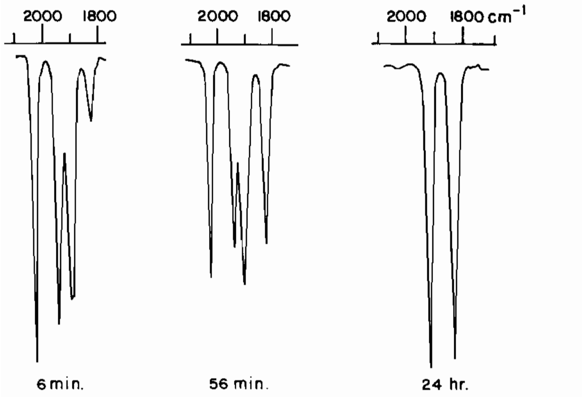


Figure 4. The infrared spectra in the $\nu_{C\equiv O}$ region of a reaction mixture of $Mn(CO)_3[P(n\text{-}C_4H_9)_3]$(oxine) and $P(n\text{-}C_4H_9)_3$ in chloroform at 23.3° C at three different time intervals.

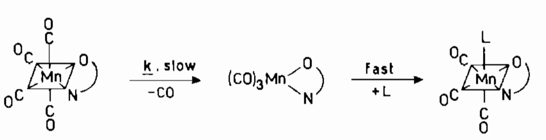
reaches an equilibrium shown in equation (4) under the experimental conditions employed herein.

$$Mn(CO)_3[P(OC_6H_5)_3](\text{oxine}) + P(OC_6H_5)_3 \rightleftharpoons Mn(CO)_2[P(OC_6H_5)_3]_2(\text{oxine}) + CO \quad (4)$$

The reaction between $Mn(CO)_3[P(n\text{-}C_4H_9)_3]$ (oxine) and $P(n\text{-}C_4H_9)_3$ was studied kinetically in chloroform solution at 23.3° C. Table V contains pertinent rate data. The substitution is first-order in the concentration of the tricarbonyl complex and appears to be essentially independent of the concentration of the phosphine ligand.

Discussion

Lack of dependence on the nature and concentration of the entering ligand, L, in the formation of $Mn(CO)_3$ L(oxine) from $Mn(CO)_4$(oxine) (equation (1)) supports a dissociative, S_N1, mechanism for the substitution. This mechanism is depicted in equation (5) (N–O represents oxine). The carbon monoxide lost is almost certainly one of the mutually trans carbonyls, which are bonded to the manganese more weakly than the carbonyls trans to the oxygen and nitrogen donors.



(5)

TABLE V. Rates of Reaction of $Mn(CO)_3[P(n\text{-}C_4H_9)_3]$ (oxine) with $P(n\text{-}C_4H_9)_3$ in Chloroform at 23.3°.

$Mn(CO)_3[P(n\text{-}C_4H_9)_3](\text{oxine}) + P(n\text{-}C_4H_9)_3 \rightarrow$
$Mn(CO)_2[P(n\text{-}C_4H_9)_3]_2(\text{oxine}) + CO$

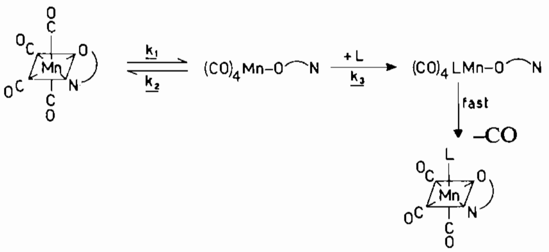
$\frac{[P(n\text{-}C_4H_9)_3]}{[Mn(CO)_3[P(n\text{-}C_4H_9)_3](\text{oxine})]}$ [a]	$k \times 10^4$, sec^{-1}
3.81	1.94
5.70	2.19
9.00	2.22

[a] Concentration of $Mn(CO)_3[P(n\text{-}C_4H_9)_3]$(oxine) ~ $2.1 \times 10^{-2}M$.

Apart from acetone, solvents with different dielectric constants do not significantly affect the rate (<3-fold increase from 1,2-dichloroethane to chloroform). Moreover, the observed minor variations in rate are not a function of increasing or decreasing dielectric constant. Small solvent effects and little correlation between rates and the dielectric constant of the solvent are typical features of substitution reactions of neutral metal carbonyl complexes.[1a] The reaction in acetone was not examined in as much detail as that in the other solvents; accordingly, little can be said to account for the observed faster rate of the substitution therein.

The calculated values of $\Delta S^{\ddagger}$ for the reactions of $Mn(CO)_4$(oxine) with $L = C_5H_5N$ and $As(C_6H_5)_3$ in chloroform and 1,2-dichloroethane lie in the range of –4.9 to 0.3 e.u. (Table IV). Entropies of activation for dissociative reactions of metal carbonyls are normally positive, but small negative values have been obtained.[1a] The enthalpies of activation for the reactions in question (18.0–19.0 kcal/mol) are also on the low side of the range reported for related S_N1 processes.[1a]

There is another mechanism, kinetically indistinguishable from that given in equation (5), which deserves close scrutiny. It is depicted in equation (6).



(6)

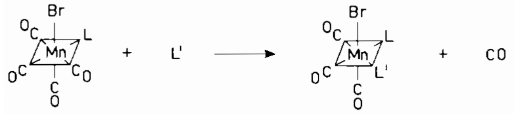
By assuming a steady-state concentration of the intermediate $(CO)_4Mn$–O–N and the condition that $k_2 \ll k_3[L]$, a rate law identical with that in equation (3) is obtained (with $k = k_1$).[12] However, in this pathway, intermediates containing monodentate oxine such as $(CO)_4LMn$–O–N might be expected to afford also $Mn(CO)_4L_2^+$ by the reaction with additional L. No cationic metal carbonyl species were detected by us in these reactions.

Several attempts were made at ascertaining whether the reactions of $Mn(CO)_4$(oxine) with L proceed through a detectable intermediate. Thus the entire visible spectral region was repeatedly scanned for the reaction mixtures at low temperatures. What appears to be an isosbestic point was observed at *ca.* 410 mμ. Similarly, ^1H NMR spectra of solutions containing $Mn(CO)_4$(oxine) and L were monitored at –25° C. Only the resonances characteristic of the reactants and products were noted. These observations are consistent with the mechanism in equation (5), but they do not by themselves militate against the mechanism in equation (6).

The replacement of the second CO in $Mn(CO)_4$ (oxine) (equation (2)) proceeds at a rate which is essentially independent of the concentration of L′ when L′ = $P(n\text{-}C_4H_9)_3$. A dissociative mechanism, similar to that in equation (5), is most likely the principal, if not the sole, pathway for the substitution. However, other mechanisms consistent with the observed first-order kinetics cannot be dismissed from the limited data available. It is further noteworthy that in chloroform solution at 23.3° C the replacement of the second CO in $Mn(CO)_4$(oxine) by $P(n\text{-}C_4H_9)_3$ proceeds some 40 times slower than the replacement of the first CO. Such a decrease in rates of substitution reactions of metal carbonyl complexes as carbon monoxide is progressively replaced by better σ-bonding and weaker π-bonding ligands has been frequently observed and discussed.[1, 13]

The rate of the formation of $Mn(CO)_2L'_2$(oxine) from $Mn(CO)_3L'$(oxine) and L′ decreases as a function of L′ in the order $P(O\text{-}n\text{-}C_4H_9)_3 > P(OC_6H_5)_3 > P(n\text{-}C_4H_9)_3$. The faster reaction of the phosphite complexes than of the $P(n\text{-}C_4H_9)_3$ complex is readily explainable. If all three reactions proceed by an S_N1 mechanism, as is likely the case, then the entering ligand, L′, has no effect on the rate. However, the L′ already present in the tricarbonyl complex will labilize the CO more effectively if it is a phosphite, a weaker σ-bonder but a stronger π-bonder,[14] rather than a tertiary phosphine. That the complex containing the more basic phosphite, $P(O\text{-}n\text{-}C_4H_9)_3$,[15] reacts faster than that containing $P(OC_6H_5)_3$ is not obvious and indicates that other factors may be also important.

It is of interest that the relative rates of the reaction,



(7)

which also proceeds by an S_N1 mechanism, vary with L in the order $P(n\text{-}C_4H_9)_3 > P(OC_6H_5)_3 > P(O\text{-}n\text{-}C_4H_9)_3$.[16] This reactivity sequence has been ascribed to steric effects associated with L, and is exactly the opposite of that noted above for $Mn(CO)_3L'$(oxine). However, these two opposite reactivity orders may be readily reconciled since the dissociating CO is *cis* to L in $Mn(CO)_4LBr$, but trans to L′ in $Mn(CO)_3L'$ (oxine). Thus steric properties of L′ are not expected to influence rates of the latter substitution.

We now want to compare the rates of carbonyl substitution reactions of several manganese(I) complexes containing "hard" donor ligands. In chloroform solutions at 22° C, $Mn(CO)_4$(oxine) is approximately 40 times as reactive as $Mn(CO)_5Cl$,[17] indicating that two "hard" atoms (N and O) labilize the CO with respect to dissociation substantially more than only one "hard" atom (Cl). The presence of two coordinated oxygens, as in $Mn(CO)_4$(hfac) and $Mn(CO)_4$(tfac),[18] increases the extent of carbonyl group labilization even more; at 15° C, these complexes react with various neutral ligands at a rate which is too rapid to measure by such techniques as visible and infrared spectroscopy, or gas evolution.[19] Similarly, the reaction of $Mn(CO)_4(C_5H_5N)Cl$ with C_5H_5N proceeds immeasurably fast at 22° C, since only $Mn(CO)_3(C_5H_5N)_2Cl$ is detected and isolated upon treatment of $Mn(CO)_5Cl$ with pyridine.[17] Thus experimental evidence points unequivocally to a remarkable lability of coordinated CO in complexes of the type $Mn(CO)_4$(X–L), where X and L are "hard" donor atoms.

The phenomenon of labilization of carbonyl groups by "hard" donor atoms was observed and discussed initially by Angelici[1a, 6] and more recently by Dobson.[20–22] A plausible explanation may be sought not only in terms of σ- and π-bonding effects but also, more importantly, through consideration of direct overlap of the filled σ_z bonding orbital of the donor X or Y and the π^* orbitals of the carbonyls cis to X and Y.[23] Such "direct donation" strengthens M–CO (*cis* to X or Y) bonding; calculations[20–23] show this donation to be appreciable when X and Y are "soft" atoms, including phosphorus, but not when they are "hard" atoms such as amine nitrogen, oxygen, or chlorine. As a result, M–CO (*cis* to X or Y) bonding in complexes containing *P*-donor atoms is strengthened relative to the bonding in complexes with *N*- and/or *O*-donor atoms.

Finally, we wish to point out that $Mn(CO)_4$(oxine) is considerably more reactive towards various ligands than are the complexes $Cr(CO)_4$(L–L) where L–L = 2,2′-bipyridine, *o*-phenanthroline, and their analogs[5, 6] Moreover, the enthalpies of activation for the substitution in $Cr(CO)_4$(L–L) (23–26 kcal/mol) are higher than those for the substitution in $Mn(CO)_4$(oxine) (18–19 kcal/mol). These differences are not unexpected, since the oxidation number of the chromium is lower than that of the manganese (0 *vs.* +1), and since oxine contains "harder" donor atoms (nitrogen and oxygen) than do the ligands L–L (2 nitrogens). As a result, the Cr–CO bonds should be stronger than the Mn–CO bonds. These expected relative bond strengths are confirmed by the values of both ΔH^{+}, given above, and $\nu_{C\equiv O}$, which are significantly higher for $Mn(CO)_4$(oxine) (2110, 2035, 1931, and 1916 cm^{-1} [3]) than for $Cr(CO)_4$(L–L) (*e.g.*, 2008, 1907, 1883, and 1831 cm^{-1} for $Cr(CO)_4$(phen)[6]).

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