in the spectra of the insertion products are probably due to the B mode. Two comparisons can be made. Since the carbonyl stretching frequencies for the $Cr(CO)_5SnCl_3^-$ and $W(CO)_5SnCl_3^-$ ions occur at higher wavenumbers than for $Cr(CO)_5SnI_2Cr(CO)_5^{2-}$ and the corresponding tungsten compound, the $SnCl_3^-$ group appears to be a better π acceptor than the $SnI_2M(CO)_5^-$ group as would be expected. Furthermore a comparison of the carbon stretching frequencies for the isoelectronic species $Cr(CO)_5SnX_3^-$ and $Cr(CO)_5InX_3^{2-}$ and $W(CO)_5SnX_3^-$ and $W(CO)_5InX_3^{2-}$ suggests that the SnX_3^- group is a better π acceptor than InX_3^{2-}. However, since the halogens employed in both cases differ, these conclusions may have to be qualified, although very little differences were noted in the carbonyl stretching frequencies of $Mn(CO)_5SnCl_3$ and $Mn(CO)_5SnBr_3$ and the corresponding rhenium compounds.[13]

The infrared spectra of the two products obtained from the dianions and sulfur dioxide contained, in addition to the above-listed carbonyl bands and bands due to the tetramethylammonium ion, three distinct bands at 1138 (m), 980 (m), and 504 (w) cm^{-1} and 1138 (m), 978 (m), and 504 (w) cm^{-1} for the chromium and tungsten derivatives, respectively. These bands are quite close to those observed in the spectrum of the complex $K_6[(CN)_5CoSO_2Co(CN)_5]$[14] at 1076 (s), 984 (s), and 533 (m) and 525 (m) cm^{-1} which are assigned to the asymmetric and symmetric S–O stretching frequencies and the SO_2 bending frequency, respectively. The observed spectra are indicative of bidentate bonding for the SO_2 group. The absence of a band in the 1300–1350-cm^{-1} region which has been assigned to monodentate SO_2 (and confirmed by X-ray studies in $Ru(NH_3)_5SO_2Br_2$[15]) further supports the assumed structure for the complex anions.

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Kinetic Studies of Group VI Metal Carbonyl Complexes. VI. Substitution Reactions of the Group VI Metal Hexacarbonyls.

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Hexacarbonyl complexes of the group VI transition metals react with phosphine and phosphite ligands, L, in decalin solvent according to the equation: $M(CO)_6 + L \rightarrow M(CO)_5L + CO$. The rate of reaction is governed by the two-term rate law: rate $= k_1[M(CO)_6] + k_2[L][M(CO)_6]$. SN1 and SN2 types of reaction mechanisms are proposed to account for the two terms. Positive ΔS_1^* values for the k_1 paths and negative ΔS_2^* values for the k_2 paths support the proposed mechanisms. The values of ΔH_1^* for the k_1 path decrease in the order: $Cr(CO)_6 \sim W(CO)_6 > Mo(CO)_6$. The magnitude of the second-order rate constants, k_2, was found to be a function of the basicity of the ligand, L, and increases as follows: $As(C_6H_5)_3 < P(OC_6H_5)_3 < P(C_6H_5)_3 < P(OCH_2)_3CC_2H_5 < P(OC_2H_5)_3 < P(n\text{-}C_4H_9)_3$. A comparison of k_2/k_1 ratios for the reaction of the hexacarbonyl complexes with $P(n\text{-}C_4H_9)_3$ suggests that the SN2 path becomes more preferred as the size of the metal atom increases from Cr to Mo to W.

Introduction

Recently several kinetic studies of the substitution and exchange reactions of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ have been reported. Pajaro, Calderazzo, and Ercoli[1] followed the rate of exchange of ^{14}CO with $Cr(CO)_6$ in the gas phase while Cetini and Gambino[2,3] carried out similar studies on the hexacarbonyl complexes of Mo and W. At the time that the present study was in progress Werner and Prinz[4,5] reported a kinetic study of the reactions of $M(CO)_6$ (where M = Cr, Mo, or W) with L (where L is a phosphine or amine) to form $M(CO)_5L$ using a mixture of *n*-decane and cyclohexane as the reaction solvent. Both the results from the ^{14}CO-exchange study and the study conducted in solution indicated that the hexacarbonyl complexes of the group VI metals react with L at a rate which is governed by a simple first-order rate law

$$\text{rate} = k[M(CO)_6] \qquad (1)$$

A more recent study of the reaction of $Mo(CO)_6$ with L conducted in these laboratories[6] indicated that $Mo(CO)_6$, with the proper choice of ligand and ligand concentration, reacted with phosphines and phosphites at a rate

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which was dependent upon the concentration and nature of the ligand used

$$\text{rate} = k_1[\text{M(CO)}_6] + k_2[\text{L}][\text{M(CO)}_6] \tag{2}$$

Since this ligand dependence was not detected in the previous studies, it was felt that a more complete study of substitution reactions of the group VI metal hexacarbonyl complexes was of interest.

Experimental Section

Purification of Materials.—The metal hexacarbonyls were very readily purified by sublimation under vacuum (~0.1 mm) between 40 and 60°. The reaction solvent, decalin, was purified by first refluxing over sodium metal for several hours and then fractionally distilling at reduced pressures. The bicyclic ligand 4-ethyl-3,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, $P(OCH_2)_3CC_2H_5$, was obtained by refluxing $P(OCH_3)_3$ with the appropriate triol and purified by sublimation under vacuum.[7] Triethyl phosphite, $P(OC_2H_5)_3$ (Matheson Coleman and Bell), and tri-*n*-butylphosphine (Aldrich Chemical Co.) were purified by fractional distillation at reduced pressures. Triphenylphosphine, $P(C_6H_5)_3$, triphenyl phosphite, $P(OC_6H_5)_3$, and triphenylarsine, $As(C_6H_5)_3$ (Eastman Chemicals), were used as obtained.

Determination of Reaction Rates.—The infrared spectrum of $M(CO)_6$, where M = Cr, Mo, or W, in the C–O stretching region consists essentially of one very intense absorption at about 1980 cm^{-1}. When $M(CO)_6$ reacts with phosphines and phosphites according to eq 3, this strong C–O absorption begins

$$\text{M(CO)}_6 + \text{L} \longrightarrow \text{M(CO)}_5\text{L} + \text{CO} \tag{3}$$

to disappear and is replaced by the two C–O absorptions of the reaction product, $M(CO)_5L$. Since there is no overlap of the product bands with the stretching absorption of $M(CO)_6$, the rates of reaction were determined by following the disappearance of the $M(CO)_6$ peak with time. The concentration of L for a particular run was essentially constant because its concentration was always greater than 15 times the concentration of $M(CO)_6$. Linear first-order plots of ln $(A - A_\infty)$, where A is the absorbance at any time t and A_∞ is the absorbance at infinite time, *vs.* time t had slopes which were the pseudo-first-order rate constants, k_{obsd}, for the reaction. These plots were linear to at least 80% reaction completion, and the average deviation of the rate constants for identical runs was normally less than 3% for the $Cr(CO)_6$ and $Mo(CO)_6$ reactions and less than 5% for the $W(CO)_6$ reactions.

The reaction rates were determined on a Beckman IR-8 infrared spectrophotometer using NaCl cells with 0.5-mm spacers. Since the reaction of $M(CO)_6$ with L proceeds only at relatively high temperatures (>100°), a constant-temperature oil bath (±0.05°) was used to thermally equilibrate the reaction vessels. At these temperatures the group VI metal hexacarbonyl complexes are quite volatile and had a tendency to sublime from the reaction solution. To eliminate this problem during a kinetic run, a reaction vessel was used that eliminated any gas phase above the reaction solution. It consisted of simply a 10-ml syringe equipped with a long syringe needle that was bent up above the surface of the thermostating oil so as to allow samples to be removed from the syringe while it was partially submerged in the constant-temperature oil bath. Although CO gas is one product of the reaction, it caused no problems because the small amounts liberated were completely soluble in the solvent.

A typical kinetic run was carried out in the following manner. The ligand, L, and $M(CO)_6$ were weighed out in a 10-ml volumetric flask and then diluted to 10 ml with decalin. The amount of $M(CO)_6$ used depended upon the reaction temperature. Enough $M(CO)_6$ (between 6×10^{-4} and 12×10^{-4} M) to allow the reaction solution to be thermally equilibrated in the oil bath for between 20 and 30 min and still have sufficient hexacarbonyl remaining to give an absorbance of at least 0.8 was employed. The syringes were filled with the solutions in a nitrogen-filled glove bag thus ensuring that the kinetic measurements were carried out under a nitrogen atmosphere. After the equilibration time, the absorbance of the reaction solution was measured at 5–15-min time intervals.

The product of the reaction of $M(CO)_6$ with L is $M(CO)_5L$. For the poorer nucleophiles such as $P(C_6H_5)_3$, $P(OC_6H_5)_3$, and $As(C_6H_5)_3$ this was the only product observed at the reaction temperatures. For $P(n\text{-}C_4H_9)_3$, a good nucleophile, a small amount of $M(CO)_4[P(n\text{-}C_4H_9)_3]_2$ was formed at the higher temperatures. It resulted from the reaction of $M(CO)_5[P(n\text{-}C_4H_9)_3]$ with excess ligand. Most of the complexes of the type $M(CO)_5L$ formed in this study had been prepared previously, and their infrared spectra are reported in the literature.[8,9]

Results

Hexacarbonyl complexes of the group VI metals react with ligands L at temperatures greater than 100° in a hydrocarbon solvent to yield $M(CO)_5L$ as the initial reaction product (eq 3). The data listed in Tables I–III show that the rate of reaction follows a two-term rate law (eq 3) over a wide range of concentrations of L. Values of k_1 and k_2 determined for the reaction of $M(CO)_6$ with various ligands are listed in Table IV. The rate constant, k_1, is independent of the nature of L while k_2 definitely depends upon L. The values of k_1 and k_2 were determined by using a nonlinear least-squares computer program.[10] This same program was also used to calculate the values of the entropies and enthalpies of activation and their standard deviations which are listed in Table V.

TABLE I

RATES OF REACTION OF $Cr(CO)_6$ WITH VARIOUS LIGANDS IN DECALIN AT 130.7°

[L], M	10^4k_{obsd}, sec^{-1}	[L], M	10^4k_{obsd}, sec^{-1}
$P(n\text{-}C_4H_9)_3$		$P(C_6H_5)_3$	
0.0168	1.38	0.0140	1.38
0.0719	1.41	0.0476	1.40
0.138	1.60	0.0927	1.51
0.376	1.66	0.200	1.45
0.696	1.98	0.444	1.56
0.0176	2.39[a]	$P(OC_2H_5)_3$	
0.0344	2.46[a]	0.0169	1.32
0.133	2.58[a]	0.0850	1.35
0.404	2.86[a]	0.247	1.53
0.909	3.55[a]	0.481	1.59
0.0157	6.75[b]	0.843	1.76
0.0368	6.81[b]		
0.125	6.90[b]		
0.396	7.77[b]		
0.917	8.93[b]		

[a] At 135.5°. [b] At 143.9°.

In the reaction of $M(CO)_6$ with L, $M(CO)_5L$ is the only reaction product formed at the temperatures used in this study for all ligands except $P(n\text{-}C_4H_9)_3$. With $P(n\text{-}C_4H_9)_3$ some $M(CO)_4L_2$ is formed in addition. If during a kinetic run the $M(CO)_5P(n\text{-}C_4H_9)_3$ formed

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TABLE II

RATES OF REACTION OF $Mo(CO)_6$ WITH VARIOUS LIGANDS IN DECALIN AT 112.0°

[L], M	10^4k_{obsd}, sec^{-1}
$P(n\text{-}C_4H_9)_3$	
0.0142	1.11[a]
0.0587	1.59[a]
0.128	2.48[a]
0.404	5.44[a]
0.805	9.34[a]
0.0159	1.59[b]
0.0533	2.14[b]
0.141	3.56[b]
0.454	8.00[b]
0.800	11.5[b]
0.0176	2.43
0.0489	3.24
0.149	5.47
0.408	10.5
0.828	18.9
0.0164	4.57[c]
0.583	6.13[c]
0.146	8.79[c]
0.469	18.2[c]
0.856	30.7[c]
$P(OC_2H_5)_3$	
0.0325	2.51
0.0625	2.66
0.183	3.52
0.529	5.32
1.058	8.46

[L], M	10^4k_{obsd}, sec^{-1}
$P(OCH_2)_3CC_2H_5$	
0.0345	2.26
0.195	2.70
0.357	3.61
0.682	4.61
0.922	5.42
1.01	5.49
$P(C_6H_5)_3$	
0.0214	2.06
0.0251	2.18
0.0333	2.23
0.100	2.30
0.114	2.37
0.206	2.58
0.440	2.82
$P(OC_6H_5)_3$	
0.0107	2.14
0.0450	2.19
0.188	2.47
0.631	3.04
0.814	3.27
$As(C_6H_5)_3$	
0.0107	2.14
0.0378	2.17
0.144	2.51
0.688	2.73
0.492	2.75

[a] At 103.4°. [b] At 106.6°. [c] At 116.4°.

TABLE III

RATES OF REACTION OF $W(CO)_6$ WITH VARIOUS LIGANDS IN DECALIN AT 165.7°

[L], M	10^4k_{obsd}, sec^{-1}
$P(n\text{-}C_4H_9)_3$	
0.00842	0.146[a]
0.0437	0.185[a]
0.115	0.327[a]
0.379	0.658[a]
0.896	1.37[a]
0.0157	0.398[b]
0.0568	0.698[b]
0.182	1.20[b]
0.453	2.34[b]
0.864	3.77[b]
0.0175	1.33
0.0752	1.76
0.151	2.20
0.478	4.63
0.836	7.02
0.0185	3.83[c]
0.0550	3.98[c]
0.282	7.83[c]
0.554	13.0[c]

[L], M	10^4k_{obsd}, sec^{-1}
$P(OC_2H_5)_3$	
0.0242	1.15
0.123	1.49
0.311	1.68
0.598	2.14
$P(OCH_2)_3CC_2H_5$	
0.0154	1.10
0.0661	1.22
0.244	1.42
0.459	1.80
0.876	2.49
$P(C_6H_5)_3$	
0.00966	1.11
0.0417	1.15
0.130	1.19
0.229	1.32
0.382	1.54

[a] At 145.9°. [b] At 155.5°. [c] At 175.4°.

TABLE IV

RATE CONSTANTS FOR THE REACTION OF $M(CO)_6$ WITH VARIOUS LIGANDS IN DECALIN

		10^4k_2, M^{-1} sec^{-1}		
L	ΔHNP[a]	$Cr(CO)_6$[b]	$Mo(CO)_6$[c]	$W(CO)_6$[d]
$P(n\text{-}C_4H_9)_3$	131	0.854	20.5	7.10
$P(OC_2H_5)_3$	520	0.450	6.69	1.70
$P(OCH_2)_3CC_2H_5$			3.56	1.48
$P(C_6H_5)_3$	573	0.431	1.77	0.888
$P(OC_6H_5)_3$	875		1.48	
$As(C_6H_5)_3$			1.03	

[a] ΔHNP is the potential at half-neutralization of the ligand. Low ΔHNP values indicate strong bases: C. A. Streuli, *Anal. Chem.*, **32,** 985 (1960). [b] At 130.7°; $k_1 = 1.38 \times 10^{-4}$ sec^{-1}. [c] At 112.0°; $k_1 = 2.13 \times 10^{-4}$ sec^{-1}. [d] At 165.7°; $k_1 = 1.15 \times 10^{-4}$ sec^{-1}.

TABLE V

ACTIVATION PARAMETERS FOR THE REACTION OF THE GROUP VI METAL HEXACARBONYLS WITH $P(n\text{-}C_4H_9)_3$ IN DECALIN

	ΔH_1*, kcal/mole	ΔS_1*, eu	ΔH_2*, kcal/mole	ΔS_2*, eu
$Cr(CO)_6$	40.2 ± 0.6	22.6 ± 1.5	25.5 ± 2.9	-14.6 ± 7.0
	38.7[a]	18.5[c]		
	38.1[b]	17.7[b]		
$Mo(CO)_6$	31.7 ± 1.4	6.7 ± 3.7	21.7 ± 1.3	-14.9 ± 3.4
	30.2[a]	−0.4[c]		
	30.2[b]	2.7[b]		
$W(CO)_6$	39.9 ± 1.6	13.8 ± 3.7	29.2 ± 1.6	-6.9 ± 3.8
	39.8[a]	11[c]		
	39.0[b]	11.6[b]		

[a] Data obtained from rates of ^{14}CO exchange in the gas phase.[1-3] [b] Results of Werner and Prinz.[5] [c] Calculated from data given in ref 1–3.

initially in the reaction is allowed to stand in the presence of excess L, it is converted to $M(CO)_4L_2$ at a rate which is considerably slower than the rate of reaction of $M(CO)_6$ with $P(n\text{-}C_4H_9)_3$. Therefore, during a typical kinetic run most of the $M(CO)_6$ is converted to $M(CO)_5L$ before any substantial amount of $M(CO)_4L_2$ is formed.

An attempt was made to study quantitatively the rate of reaction of $Mo(CO)_5[P(n\text{-}C_4H_9)_3]$ with $P(n\text{-}C_4H_9)_3$. Owing to the higher temperatures necessary for this reaction, the only moderate stability of the complex, and the extreme sensitivity of the reaction rates to minute traces of air and other impurities, this was impossible to do on a quantitative basis. However, qualitatively it was determined that the rate of this reaction followed a two-term rate law similar to eq 2. The value of k_1 was approximately one-fourth that obtained for the reaction of $Mo(CO)_6$ with L at the same temperature. The value of k_2 for the $Mo(CO)_5[P(n\text{-}C_4H_9)_3]$ reaction was also considerably smaller than that obtained for the $Mo(CO)_6$ reaction.

Discussion

The group VI metal hexacarbonyls react with phosphine and phosphite ligands at a rate which is governed by a two-term rate law (eq 2). Such a rate law indicates that the reaction occurs by two mechanisms. The first term, $k_1[M(CO)_6]$, which depends only on the concentration of $M(CO)_6$, suggests a simple dissociative (SN1) reaction mechanism which probably proceeds through a five-coordinated reaction intermediate (eq 4).

$$M(CO)_6 \xrightarrow[\text{slow}]{-CO} M(CO)_5 \xrightarrow[\text{fast}]{+L} M(CO)_5L \qquad (4)$$

This type of reaction mechanism is common to substitution reactions of most octahedral complexes and has been discussed in considerable detail in the literature.[11]

The enthalpies of activation, ΔH_1^*, decrease as follows: $Cr(CO)_6 \sim W(CO)_6 > Mo(CO)_6$. The positive values of the entropies of activation, ΔS_1^*, listed in Table V are consistent with an SN1 reaction mechanism. The enthalpies of activation for the first-order reaction path listed in Table V are within experimental error of the values obtained by other workers (Table V). Since there is good agreement between the values of ΔH_1^* determined for ^{14}CO exchange in the gas phase and those for substitution obtained here in a hydrocarbon solvent, it is suggested that very little solvent participation is involved in the rate-determining step of the reaction mechanism. This might be expected since decalin is a very nonpolar solvent and probably would not be expected to be capable of significantly assisting the dissociation of a CO group from the metal carbonyl complex.

Werner and Prinz, though they observed only a simple first-order rate law for the reaction of $M(CO)_6$ with L, determined first-order rate constants for the reaction of $M(CO)_6$ with $P(C_6H_5)_3$ in refluxing *n*-decane–cyclohexane mixtures. For example, at 111.3° they determined a value of $k = 2.63 \times 10^{-4}$ sec^{-1} for the reaction of $Mo(CO)_6$ with $P(C_6H_5)_3$. This compares favorably with a value of $k = 2.13 \times 10^{-4}$ sec^{-1} determined in this study for the same reaction at 112.0° using decalin as the solvent. This agreement indicates that the first-order rate law of Werner and Prinz does indeed correspond to the first term of the two-term rate law observed in this study. Values of ΔH_1^* and ΔS_1^* are also the same, within experimental error, for the two studies (Table V). The reasons that Werner and Prinz did not detect the second-order term are that they used relatively low concentrations of L and only L groups which are relatively poor nucleophiles were studied.

The second term of the two-term rate law, $k_2[L]\cdot[M(CO)_6]$, is perhaps best ascribed to a reaction mechanism which involves a nucleophilic attack by L upon the complex. This interpretation is consistent with the negative values of ΔS_2^* obtained for this term. Ligand attack could result in either a six- or seven-coordinated reaction intermediate or transition state. Seven-coordination would be involved if attack takes place at the central metal atom. On the other hand, the metal complex could retain its octahedral geometry if the ligand attack occurs at one of the carbonyl carbon atoms. Since both modes of ligand attack upon the metal complex would yield the same expression in the observed rate law and since the reaction intermediate or transition state is too short-lived to be observed by conventional methods, it is impossible to say with any certainty at what position in the metal complex the nucleophilic attack occurs. It should be noted, however, that seven-coordinated carbonyl complexes of Cr, Mo, and W in the +2 oxidation state are known[12] and that the stability of the Cr derivative is significantly lower than that of the analogous Mo and W complexes. On the other hand, attack at a carbonyl carbon presumably occurs in the reaction of $[Mn(CO)_4L_2]^+$ with $C_2H_5O^-$ to form $Mn(CO)_3L_2COOC_2H_5$.[13]

The nucleophilicity of L, as measured by k_2, increases with its basicity. The nucleophilic order and the basicities (given in parentheses as ΔHNP values;[14] low values indicate strong bases) of the ligands follow: $As(C_6H_5)_3 < P(OC_6H_5)_3$ (875) $< P(C_6H_5)_3$ (573) $< P(OCH_2)_3CC_2H_5 < P(OC_2H_5)_3$ (520) $< P(n\text{-}C_4H_9)_3$ (131). This same trend has been observed for k_2 in other kinetic studies of metal carbonyl complexes.[15–17]

The size of the central metal atom apparently plays a significant role in determining the tendency of the $M(CO)_6$ complexes to react by an SN2 mechanism as compared to SN1 reactivity. This can be inferred from a comparison of the ratio k_2/k_1 for $Cr(CO)_6$ (0.7), $Mo(CO)_6$ (9.6), and $W(CO)_6$ (34.8) for the reaction with the same ligand, $P(n\text{-}C_4H_9)_3$, at 112°. The radii of the zerovalent group VI metals increase in this same order. Thus as the size of the metal atom in the $M(CO)_6$ complexes increases, the complex has a greater tendency to undergo substitution by an SN2 mechanism.

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