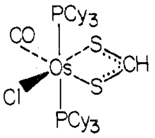
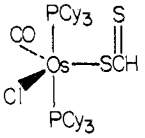
found for $Re(CO)_3(DPE)(HCS_2)$, $Mn(CO)_3(DPE)(HCS_2)$, and $Re(CO)_2[P(C_6H_5)_3]_2(HCS_2)$[14-16] with DPE = diphenylphosphinoethane. In the region 2550-2600 cm^{-1} a ν S-H was not observed. From these data it is suggested that the β complex has one of the following structures.





In the mass spectra (Table II) of these carbon disulfide complexes, there is a cluster with the lowest fragment ion having *m/e* 884 which is in agreement with the lowest fragment ion $^{184}OsH^{35}Cl(CO)(PCy_3)_2(C^{32}S_2)$. The relative abundances of the peaks in this cluster agree with the calculated ratios. The described complexes are diamagnetic (measured between room temperature and −150°) indicating a low spin d^6 configuration. Distinguishing between the possible structures of these complexes with X-ray structure determination meets with difficulties because suitable crystals have not yet been obtained.

Registry No. $OsH(CO)Cl(PCy_3)_2$, 31177-20-5; $OsH(CO)Cl(PCy_3)_2(SO_2)$, 40583-39-9; $OsH(CO)Cl(PCy_3)_2(CS_2)$, 40583-40-2; $Os(CO)Cl(PCy_3)_2(HCS_2)$, 40631-70-6.

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Effect of Pressure on the Rates of Substitution Reactions of Metal Carbonyls

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The kinetics and mechanisms of the substitution reactions of metal carbonyls have been intensively studied during the last decade. The field has been reviewed by Werner.[1] Depending on choice of reaction conditions and substituting ligand, both first- and second-order rate laws have been found. Usually the activation entropies are positive when the first-order rate law applies and negative for second order. Rate laws and activation entropies provide the principal evidence for assigning either the associative mechanism (1) or the dissociative mechanism (2).

$$M(CO)_n + L \xrightarrow{slow} M(CO)_nL \xrightarrow{fast} products \qquad (1)$$

$$M(CO)_n \xrightarrow{slow} CO + M(CO)_{n-1} \xrightarrow{L,\ fast} products \qquad (2)$$

In recent years, especially for organic reactions, the volume of activation, ΔV^*, has proved to be a valuable criterion of mechanism.[2,3] It would be desirable to establish that the method also has utility for the study of inorganic reactions by choosing a group for which a great deal of mechanistic evidence already exists. Application of the method to the first-order decomposition reactions of metal carbonyls is especially promising owing to the fact that reactants and products are neutral molecules; thus, there can be no question of electrostrictive effects which often cloud and sometimes totally obscure the interpretation of activation volumes.

Reagents. Nickel tetracarbonyl was obtained from Matheson Gas Products. Chromium, molybdenum, and tungsten hexacarbonyl were obtained from Strem Chemicals, Inc. Triethyl phosphite was prepared by the method of Ford-Moore and Perry.[4] Tri-*n*-butylphosphine was prepared by the method of Kauffman and Teter.[5] Triphenylphosphine was obtained from Eastman Organic Chemicals. Tetraethylammonium azide was prepared by neutralization of tetraethylammonium hydroxide with aqueous hydrazoic acid. The solution was then evaporated to dryness under a stream of air.

Rate of Reaction of Nickel Tetracarbonyl with Triethyl Phosphite. Reaction mixtures were prepared by quickly combining cold heptane solutions of triethyl phosphite and nickel carbonyl to form 2 ml of solution which was 0.03 *M* in carbonyl and 0.15 *M* in phosphite. The solution together with a small magnetic stirring bar was placed in a 10-ml gas buret which was filled with mercury and inverted over mercury in a slightly larger test tube. These operations were performed within 1 min at a temperature below 0°. The reaction cell was then pressurized at 0° for 90 min. After depressurization, the stirring bar was agitated with an external magnet to expel CO, the inner and outer levels of mercury were equalized, and the volume of gas in the buret was recorded. The volume of gas after 10 half-lives was also recorded, and values of $\ln (V_\infty/V_\infty - V_t)$ were plotted against t. The mean deviation from the mean was 1.5%.

Rates of Reaction of Chromium and Molybdenum Hexacarbonyl with Triphenylphosphine. Cyclohexane solutions of chromium hexacarbonyl (6×10^{-3} *M*) and triphenylphosphine (2.4×10^{-2} *M*) were allowed to react for 3.75 hr at 124.0°, and the decrease in absorbance at 1983 cm^{-1} was measured. Solutions having corresponding concentrations of molybdenum hexacarbonyl and triphenylphosphine in 2,2,4-trimethylpentane were allowed to react for 4.0 hr at 103.0°, and the band at 1980 cm^{-1} was observed. The mean deviation of the mean of rate constants was 2.5%.

Rate of Reaction of Tungsten Hexacarbonyl with Tri-*n*-butylphosphine. The reaction was carried out under pseudounimolecular conditions using cyclohexane solutions 0.03 *M* in carbonyl and 0.3 *M* in phosphine. The 4-ml samples were allowed to react at 120.0° for various times from 2.5 to 4.0 hr. The reaction was followed by measurement of the volume of carbon monoxide as described in the case of nickel tetracarbonyl. The mean deviation from the mean was 3.0%.

Rate of Reaction of Chromium Hexacarbonyl with Azide Ion. Acetone solutions of chromium hexacarbonyl (3.37×10^{-2} *M*) and tetraethylammonium azide (3.37×10^{-2} *M*) were allowed to react for 1.5 hr at 24.0°. Analysis was performed by the volumetric method developed for nickel

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tetracarbonyl. The mean deviation from the mean was 3.3%.

Calculation of Activation Volumes. The logarithm of the ratio of the rate constant at pressure to the rate constant at 1 atm (k_p/k_1) was plotted against pressure, and the best straight line was drawn through the origin and the other points. The slope was used to evaluate the activation volume according to the equation

$$RT(\delta \ln k/\delta P)_T = -\Delta V^*$$

In all cases where comparison was possible, either directly or by calculation using activation parameters, our values of k_1 agreed satisfactorily with those previously reported. For all reactions the pressures used were 1340, 680, 1020, and 1360 atm.

High-Pressure Apparatus. The apparatus has been described previously.[6] The activation volumes are shown in Table I. The reactions of nickel tetracarbonyl with triethyl phosphite and chromium and molybdenum hexacarbonyl with triphenylphosphine were carried out under conditions which have been previously reported to give first-order kinetics.[7-9] For the hexacarbonyls it was necessary to use a low concentration of phosphine in order to suppress the second-order term. Positive values in the vicinity of 10 ml/mol are appropriate for unimolecular decomposition reactions such as those of arenediazonium ions,[10] *tert*-alkylsulfonium ions,[11] alkylmercuric ions and carboxylate ions,[12] and peroxides.[13] By far the majority of these examples involve the cleavage of an ion into a neutral molecule and a smaller ion, and although the effects of electrostriction are absent in the first degree of approximation, they are perhaps not totally excluded. It is welcome, therefore, to have a new example in which all product and reactant particles are neutral.

In order to derive an estimate of the length of the breaking metal-to-carbon bond, we can model the reactant molecule as a cylinder which elongates in the direction of the bond axis. The activation volume divided by the cross-sectional area gives the increase in bond length at the transition state.[2] The diameter of the carbon monoxide molecule has been estimated at 3.16 or 3.80 Å depending on whether the van der Waals *b* constant or the gas viscosity provides the basis.[14] The average value, 3.48 Å, applied to the activation volume of nickel tetracarbonyl gives 1.4 Å for the elongation of the Ni–C bond. For molybdenum and chromium hexacarbonyl the figures are respectively 1.7 and 2.5 Å. At complete rupture the elongation would be equal to the sum of two van der Waals radii minus the M–C bond length and plus any change in the C–O bond length. Not all of the necessary data are available, but a reasonable approximation can be obtained by subtracting the C–O bond length from the van der Waals diameter of carbon monoxide. The result is 2.35 Å. Thus, we see that the bond is severely stretched in the transition state for nickel tetracarbonyl and essentially broken in that for chromium hexacarbonyl.

Table I. Volumes of Activation

Substrate	Ligand	Kinetic order	Solvent	T, °C	ΔV^* ml/mol
$Ni(CO)_4$	$(EtO)_3P$	First	Heptane	0.0	8 ± 1
$Mo(CO)_6$	Ph_3P	First	"Isooctane"	103.0	10 ± 1
$Cr(CO)_6$	Ph_3P	First	Cyclohexane	124.0	15 ± 1
$W(CO)_6$	Bu_3P	Second	Cyclohexane	120.0	−10 ± 2
$Cr(CO)_6$	N_3^-	Second	Acetone	24.0	0 ± 1

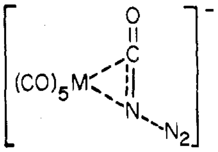
It has been previously noted that in closely related series of reactions having a wide range of rates the magnitude of the activation volume increased as the reactivity decreased.[6] The same phenomenon appears in the present series. The enthalpies of activation for the carbonyls of nickel,[15] molybdenum,[9] and chromium[9] are respectively 23, 30, and 39 kcal/mol. The relative reactivities of the group VI carbonyls have been explained as a consequence of the lanthanide contraction.[16]

As an example of a second-order process, the reaction of tungsten hexacarbonyl with tributylphosphine was selected for study. It belongs to a very rare charge-type since almost all organic bimolecular reactions involving neutral substrates and reagents yield ionic products. Since the reaction may be classified as a neutral displacement, we should expect an activation volume in the vicinity of −5 to −20 ml/mol as observed for several organic reactions of this type.[2,3] The measured value is −10 ml/mol. This result harmonizes with the associative mechanistic hypothesis.

Since the activation volumes for typical first- and second-order reactions of metal carbonyls conformed so well with existing evidence, we were encouraged to apply the method to the slightly bizarre second-order reaction with azide ion[17] as follows (3).

$$M(CO)_6 + N_3^- \rightarrow M(CO)_5NCO^- + N_2 \qquad (3)$$

The structure below has been proposed for the transition state.



If the reaction were dominated by bond making as in eq 1, we should expect a value of −10 ml/mol for the activation volume. The situation is complicated, however, by the disruption of the nucleophile which could be far advanced in the transition state. In view of these considerations, the range of possible values for ΔV^* should extend from −10 ml/mol to perhaps +10 ml/mol depending on the relative contributions of bond making and bond breaking. The experimental value is near zero which indicates that the effects of the two processes are balanced with neither one very close to inception or completion.

Registry No. $Ni(CO)_4$, 13463-39-3; $Mo(CO)_6$, 13939-06-5; $Cr(CO)_6$, 13007-92-6; $W(CO)_6$, 14040-11-0; $(EtO)_3P$, 122-52-1; Ph_3P, 603-35-0; Bu_3P, 998-40-3; $(Et_4N)N_3$, 993-20-4.

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