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Rates of Oxidative Elimination Reactions of Tungsten and Molybdenum Carbonyls with Mercuric Halides

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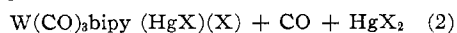
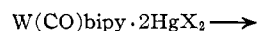
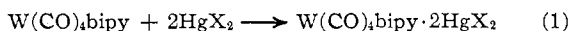
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Kinetic data have been obtained for the oxidative elimination reactions of $M(\text{CO})_4\text{L}_2$ ($M = \text{Mo}, \text{W}$; $\text{L}_2 = 2,2'$ -bipyridine, 1,10-phenanthroline) with mercuric halides which yield $M(\text{CO})_3\text{L}_2(\text{HgX})(\text{X})$ and CO . Both acetone and 1,2-dichloroethane were used as solvents. In acetone the reaction involves the initial rapid formation of $M(\text{CO})_4\text{L}_2 \cdot 2\text{HgX}_2$ which decomposes in the rate-determining step to yield the final product. Equilibrium constants for the formation of the intermediate have been calculated for the tungsten systems using both HgCl_2 and HgBr_2 . For both compounds studied the equilibrium constant is larger for HgBr_2 than for HgCl_2 . No intermediate is observed for the reactions of the molybdenum compounds, but the kinetic data are consistent with the mechanism proposed for the tungsten systems. In 1,2-dichloroethane the kinetic data indicate the presence of both $M(\text{CO})_4\text{L}_2 \cdot \text{HgX}_2$ and $M(\text{CO})_4\text{L}_2 \cdot 2\text{HgX}_2$ as intermediates.

Introduction

There has been considerable interest recently in the oxidative elimination reactions of transition metal carbonyl complexes with electrophilic reagents. These reactions are characterized by expulsion of one carbonyl ligand and its replacement by two univalent ligands, thus increasing the coordination number of the metal by 1 and the oxidation state by 2 units. Much of the work carried out has been concerned with the reactions of group IV and mercuric halides with metal carbonyls which yield compounds containing metal-metal bonds. In particular $M(\text{CO})_4\text{L}_2$ ($M = \text{Mo}, \text{W}$; $\text{L}_2 =$ bidentate ligand),¹⁻⁴ $\text{Fe}(\text{CO})_5$,^{5,6} $\text{C}_5\text{H}_5\text{-Co}(\text{CO})_2$,⁷ and $\text{C}_5\text{H}_5\text{Rh}(\text{CO})[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$ ⁸ have been found to undergo oxidative elimination reactions with these metal halides as well as with other electrophilic reagents such as halogens and alkyl halides. Most of the work reported in this field has been of a preparative nature. In this paper we describe the results of a kinetic study made in order to elucidate the mechanisms of oxidative elimination reactions.

Recently a study of the reactions of $M(\text{CO})_4\text{bipy}$ ($M = \text{MO}, \text{W}$; $\text{bipy} = 2,2'$ -bipyridine) with mercuric halides was reported.¹ The compound $\text{W}(\text{CO})_4\text{bipy}$ was found to react with HgX_2 to yield a 1:2 adduct, $\text{W}(\text{CO})_4\text{bipy} \cdot 2\text{HgX}_2$. On standing, this yellow solid dissolved with evolution of CO to yield red $\text{W}(\text{CO})_3\text{bipy}(\text{HgX})(\text{X})$ which was formulated as a seven-coordinate derivative of $\text{W}(\text{II})$. The reactions involved are represented by eq 1 and 2. The analogous molyb-



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(4) M. H. B. Stiddard, *J. Chem. Soc.*, 4712 (1962).

(5) J. Lewis and S. B. Wild, *ibid.*, A, 69 (1966).

(6) R. Kummer and W. A. G. Graham, *Inorg. Chem.*, **7**, 1208 (1968).

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denum complex reacted with HgX_2 to give $\text{Mo}(\text{CO})_3\text{-bipy}(\text{HgX})(\text{X})$, with no intermediate species observed. Since these reactions involve a metal carbonyl derivative acting as a base, they present an opportunity to gain knowledge about trends in metal basicity⁹ within a group and also information on relative electrophilicity of various mercuric halides. With this in mind, we have carried out a kinetic study of these reactions and the analogous reactions of $M(\text{CO})_4\text{phen}$ ($M = \text{Mo}, \text{W}$; $\text{phen} = 1,10\text{-phenanthroline}$) using both HgCl_2 and HgBr_2 . Equilibrium constants for the formation of the 1:2 adducts of the tungsten complexes have been calculated and the kinetic data are interpreted in terms of a reasonable mechanism.

Experimental Section

Materials.—The compounds $M(\text{CO})_4\text{L}_2$ ($M = \text{Mo}, \text{W}$; $\text{L}_2 = \text{bipy}, \text{phen}$) were prepared by methods described in the literature.^{4,10} The compounds were identified by their ir spectra. Analytical grade HgCl_2 and HgBr_2 were purchased from Mallinckrodt Chemical Works. Reagent grade acetone and 1,2-dichloroethane were used in the kinetic runs.

Kinetics.—Reaction rates were studied by following changes in the visible spectra of reaction mixtures. Reactions of $\text{W}(\text{CO})_4\text{bipy}$ and $\text{W}(\text{CO})_4\text{phen}$ were monitored at 390 and 400 nm, respectively, whereas reactions of $\text{Mo}(\text{CO})_4\text{bipy}$ and $\text{Mo}(\text{CO})_4\text{-phen}$ were followed at 470 nm. A Cary 14 recording spectrophotometer thermostated at 25° was used to follow the spectral changes. Rates were measured under pseudo-first-order conditions with the mercuric halide in excess and plots of $\log(A - A_\infty)$ vs. time show excellent linearity for at least 2 half-lives. In most cases, rate constants were reproducible within $\pm 5\%$.

Measurement of Equilibrium Constants.—Molar extinction coefficients were measured at 400 and 470 nm for $\text{W}(\text{CO})_4\text{phen}$ and $\text{W}(\text{CO})_4\text{phen} \cdot 2\text{HgX}_2$ and at 390 and 470 nm for $\text{W}(\text{CO})_4\text{-bipy}$ and $\text{W}(\text{CO})_4\text{bipy} \cdot 2\text{HgX}_2$. The 1:2 adducts were formed *in situ* by using a large enough concentration of mercuric halide to convert all of the starting material to the adduct. The absorbances of the solution were then rapidly measured before the adduct had time to react. For the measurement of equilibrium constants, concentrations of mercuric halide were such that significant amounts of both adduct and starting material were present in solution. Solutions of HgX_2 and W -

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$(\text{CO})_4\text{L}_2$ were thermostated at 0° and mixed, and the absorbances at the two aforementioned wavelengths were rapidly measured using a Beckman DU-2 spectrophotometer. By solving the resulting set of two simultaneous equations in two unknowns, the concentrations of $\text{W}(\text{CO})_4\text{L}_2$ and $\text{W}(\text{CO})_4\text{L}_2 \cdot 2\text{HgX}_2$ were calculated for a given concentration of HgX_2 . This in turn permitted estimates of the equilibrium constants for adduct formation in accordance with the equations



Preparation of 1:2 Adducts.—These compounds were prepared by the method previously described¹ for $\text{W}(\text{CO})_4\text{bipy} \cdot 2\text{HgX}_2$. A typical procedure involved the addition of 3 g of HgX_2 to a solution of 0.5 g of complex in 10–15 ml of acetone. Upon vigorous stirring, the yellow 1:2 adducts precipitated. The adducts were quickly separated by filtration, washed twice with 5-ml portions of CH_2Cl_2 , and dried *in vacuo*. The compounds were identified by their ir spectra in the carbonyl region which are almost identical with the values of CO stretching frequencies (in cm^{-1}) of 2075 (w), 1985 (s), 1950 (m), and 1935 (s) reported¹ for $\text{W}(\text{CO})_4\text{bipy} \cdot 2\text{HgCl}_2$; for $\text{W}(\text{CO})_4\text{phen} \cdot 2\text{HgCl}_2$, ν_{CO} 2070 (w), 1985 (s), 1950 (m), 1925 (s); for $\text{W}(\text{CO})_4\text{bipy} \cdot 2\text{HgBr}_2$, ν_{CO} 2080 (w), 1990 (s), 1950 (m), 1925 (s); for $\text{W}(\text{CO})_4\text{phen} \cdot 2\text{HgBr}_2$, ν_{CO} 2075 (w), 1985 (s), 1950 (m), 1930 (s).

Results

Reactions of $\text{W}(\text{CO})_4\text{L}_2$.—All reactions were carried out at 25° in either acetone or 1,2-dichloroethane. The compounds $\text{W}(\text{CO})_4\text{phen}$ and $\text{W}(\text{CO})_4\text{bipy}$ were allowed to react with both HgCl_2 and HgBr_2 . Typical spectral changes observed for these reactions at high concentrations of mercuric halide in acetone are shown in Figure 1. Consistent with the earlier report¹ on

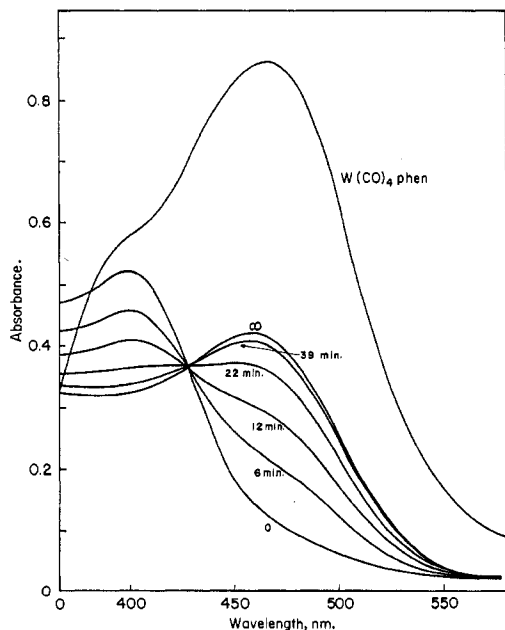


Figure 1.—Spectral changes for the reaction of $\text{W}(\text{CO})_4\text{phen}$ with HgCl_2 in acetone at 25° .

these systems, the spectra clearly show the presence of a rapidly formed intermediate which then reacts to yield a final product. At lower concentrations of mercuric halide, the isosbestic point evident in Figure 1 was not observed in the spectral changes. The decay of the

intermediate was monitored kinetically and the dependence of the observed rate constant on the mercuric halide concentration was studied. Plots of the observed rate constant *vs.* concentration of HgCl_2 for the two systems studied are shown in Figure 2. Limiting rates

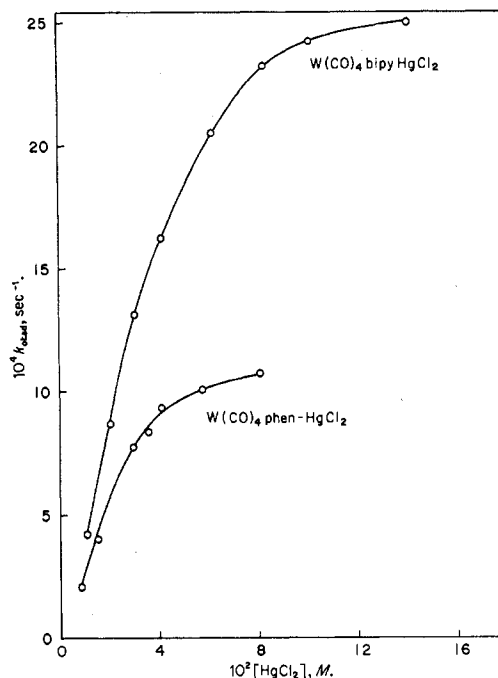


Figure 2.—Plots of k_{obsd} *vs.* $[\text{HgCl}_2]$ for the reaction of $\text{W}(\text{CO})_4\text{L}_2$ with HgCl_2 in acetone at 25° .

only were determined for the reactions of the two compounds studied with mercuric bromide. At 25° and $[\text{HgBr}_2] = 13.1 \times 10^{-2} \text{ M}$, $k_{\text{obsd}} = 1.80 \times 10^{-3} \text{ sec}^{-1}$ for $\text{W}(\text{CO})_4\text{bipy}$ and $k_{\text{obsd}} = 0.81 \times 10^{-3} \text{ sec}^{-1}$ for $\text{W}(\text{CO})_4\text{phen}$.

The spectral changes for the reactions of the tungsten complexes in dichloroethane were very similar to those observed in acetone. At high concentrations of mercuric halide, however, the isosbestic point was not as sharp as that for the reactions in acetone, indicating the presence of more than two species in solution. The dependence of the observed rate constant on the mercuric halide concentration was markedly different than in acetone and Figure 3 shows the dependence for the reactions with mercuric chloride. The study of the reactions with mercuric bromide was limited by the low solubility of the reagent in dichloroethane, and as a result the decrease of the observed rate constant with increasing concentration of mercuric bromide was less clear than for mercuric chloride. Table I gives the rate data for the $\text{W}(\text{CO})_4\text{L}_2\text{--HgBr}_2$ systems.

Reactions of $\text{Mo}(\text{CO})_4\text{L}_2$.—The spectral changes observed for the reaction of $\text{Mo}(\text{CO})_4\text{phen}$ with HgCl_2 in acetone are shown in Figure 4. Consistent with the previous study¹ of these reactions, no intermediate was observed spectrally. Plots of the observed rate constant *vs.* the square of the mercuric halide concentration for the $\text{Mo}(\text{CO})_4\text{phen--HgX}_2$ systems are linear, as is represented in Figure 5. The data for the Mo-

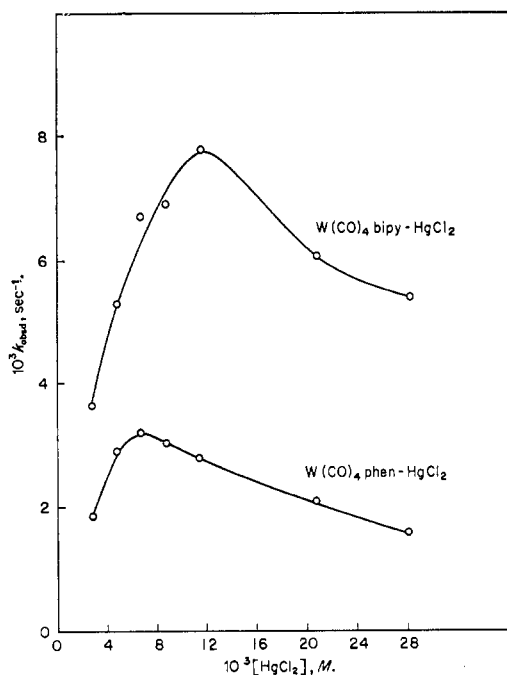


Figure 3.—Plots of k_{obsd} vs. $[\text{HgCl}_2]$ for the reaction of $\text{W}(\text{CO})_4\text{L}_2$ with HgCl_2 in dichloroethane at 25° .

TABLE I
OBSERVED RATE CONSTANTS FOR THE
REACTION OF $\text{W}(\text{CO})_4\text{L}_2 + \text{HgX}_2$

System	Solvent ^a	$10^3[\text{HgX}_2], M$	$10^4 k_{\text{obsd}}, \text{sec}^{-1}$
$\text{W}(\text{CO})_4\text{bipy-HgCl}_2$	Acetone	10.5	4.15
$\text{W}(\text{CO})_4\text{bipy-HgCl}_2$	Acetone	40.6	16.2
$\text{W}(\text{CO})_4\text{bipy-HgCl}_2$	Acetone	82.2	23.2
$\text{W}(\text{CO})_4\text{bipy-HgCl}_2$	Acetone	140	25.5
$\text{W}(\text{CO})_4\text{phen-HgCl}_2$	Acetone	7.8	2.00
$\text{W}(\text{CO})_4\text{phen-HgCl}_2$	Acetone	28.6	7.66
$\text{W}(\text{CO})_4\text{phen-HgCl}_2$	Acetone	56.7	9.97
$\text{W}(\text{CO})_4\text{phen-HgCl}_2$	Acetone	80.0	10.7
$\text{W}(\text{CO})_4\text{bipy-HgCl}_2$	DCE	2.80	36.5
$\text{W}(\text{CO})_4\text{bipy-HgCl}_2$	DCE	11.3	77.9
$\text{W}(\text{CO})_4\text{bipy-HgCl}_2$	DCE	20.7	60.4
$\text{W}(\text{CO})_4\text{bipy-HgCl}_2$	DCE	28.0	54.2
$\text{W}(\text{CO})_4\text{phen-HgCl}_2$	DCE	2.80	18.5
$\text{W}(\text{CO})_4\text{phen-HgCl}_2$	DCE	6.60	31.7
$\text{W}(\text{CO})_4\text{phen-HgCl}_2$	DCE	20.7	20.8
$\text{W}(\text{CO})_4\text{phen-HgCl}_2$	DCE	28.0	15.6
$\text{W}(\text{CO})_4\text{bipy-HgBr}_2$	DCE	9.70	3.87
$\text{W}(\text{CO})_4\text{bipy-HgBr}_2$	DCE	15.2	5.42
$\text{W}(\text{CO})_4\text{bipy-HgBr}_2$	DCE	18.9	7.17
$\text{W}(\text{CO})_4\text{bipy-HgBr}_2$	DCE	26.4	9.30
$\text{W}(\text{CO})_4\text{phen-HgBr}_2$	DCE	9.70	2.50
$\text{W}(\text{CO})_4\text{phen-HgBr}_2$	DCE	15.2	3.28
$\text{W}(\text{CO})_4\text{phen-HgBr}_2$	DCE	18.9	3.73
$\text{W}(\text{CO})_4\text{phen-HgBr}_2$	DCE	26.4	3.56

^a DCE = 1,2-dichloroethane.

$(\text{CO})_4\text{bipy-HgCl}_2$ system were very similar to those for the $\text{Mo}(\text{CO})_4\text{phen-HgX}_2$ systems and the values of the observed rate constants are given in Table II. It should be noted that a positive intercept was observed in the plots of k_{obsd} vs. the square of the mercuric halide concentration for all of these reactions.

In dichloroethane, the spectral changes for the reactions were very similar to those in acetone. Figure 6 shows a plot of the observed rate constant vs. the square of the mercuric halide concentration for the $\text{Mo}(\text{CO})_4\text{phen-HgX}_2$ systems.

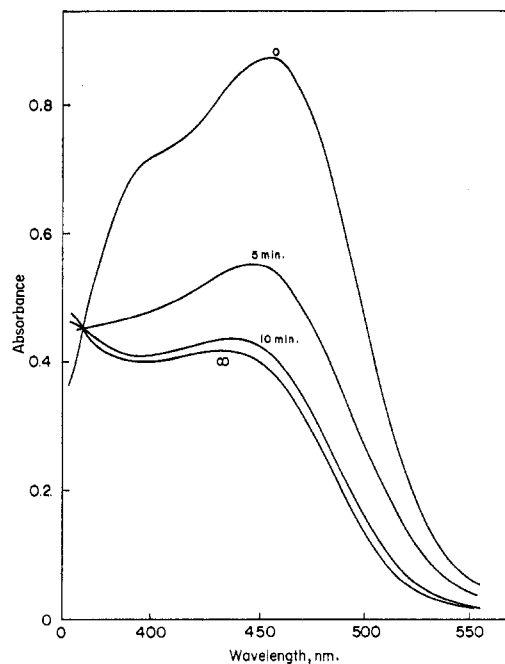


Figure 4.—Spectral changes for the reaction of $\text{Mo}(\text{CO})_4\text{phen}$ with HgCl_2 in acetone at 25° .

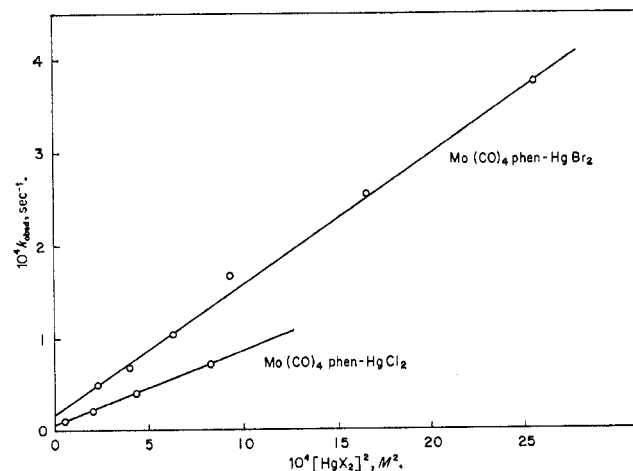


Figure 5.—Plots of k_{obsd} vs. $[\text{HgX}_2]^2$ for the reaction of $\text{Mo}(\text{CO})_4\text{phen}$ with HgX_2 in acetone at 25° .

phen-HgX_2 systems. The data for the $\text{Mo}(\text{CO})_4\text{bipy-HgX}_2$ reactions were similar to those shown in Figure 6 and the data obtained are presented in Table II. For the reactions with mercuric chloride the dependence on reagent concentration was between first and second order, whereas the reactions with mercuric bromide showed a linear dependence on reagent concentration. Positive intercepts were observed for these systems as was the case for the same reactions in acetone.

Discussion

Reactions of $\text{W}(\text{CO})_4\text{L}_2$.—The kinetic data for these reactions in acetone show that a limiting rate is reached at high concentrations of mercuric halide. This behavior is consistent with a rapid preequilibrium to form an intermediate which then reacts in a rate-determining step yielding the final product. This observation is in keeping with the work previously done on these sys-

TABLE II
OBSERVED RATE CONSTANTS FOR THE
REACTION OF $\text{Mo}(\text{CO})_4\text{L}_2 + \text{HgX}_2$ AT 25°

System	Solvent ^a	$10^2[\text{HgX}_2], M$	$10^2k_{\text{obsd}}, \text{sec}^{-1}$
$\text{Mo}(\text{CO})_4\text{bipy-HgCl}_2$	Acetone	7.8	0.72
$\text{Mo}(\text{CO})_4\text{bipy-HgCl}_2$	Acetone	13.9	1.88
$\text{Mo}(\text{CO})_4\text{bipy-HgCl}_2$	Acetone	20.6	3.56
$\text{Mo}(\text{CO})_4\text{bipy-HgCl}_2$	Acetone	28.6	6.72
$\text{Mo}(\text{CO})_4\text{phen-HgCl}_2$	Acetone	7.8	0.70
$\text{Mo}(\text{CO})_4\text{phen-HgCl}_2$	Acetone	13.9	1.83
$\text{Mo}(\text{CO})_4\text{phen-HgCl}_2$	Acetone	20.6	3.84
$\text{Mo}(\text{CO})_4\text{phen-HgCl}_2$	Acetone	28.6	7.07
$\text{Mo}(\text{CO})_4\text{bipy-HgCl}_2$	DCE	0.97	1.83
$\text{Mo}(\text{CO})_4\text{bipy-HgCl}_2$	DCE	1.94	4.62
$\text{Mo}(\text{CO})_4\text{bipy-HgCl}_2$	DCE	3.62	11.2
$\text{Mo}(\text{CO})_4\text{bipy-HgCl}_2$	DCE	4.84	16.8
$\text{Mo}(\text{CO})_4\text{phen-HgCl}_2$	DCE	0.97	1.55
$\text{Mo}(\text{CO})_4\text{phen-HgCl}_2$	DCE	1.94	3.74
$\text{Mo}(\text{CO})_4\text{phen-HgCl}_2$	DCE	2.90	6.46
$\text{Mo}(\text{CO})_4\text{phen-HgCl}_2$	DCE	6.00	18.2
$\text{Mo}(\text{CO})_4\text{phen-HgCl}_2$	DCE	7.00	22.4
$\text{Mo}(\text{CO})_4\text{bipy-HgBr}_2$	DCE	3.06	0.83
$\text{Mo}(\text{CO})_4\text{bipy-HgBr}_2$	DCE	6.12	2.27
$\text{Mo}(\text{CO})_4\text{bipy-HgBr}_2$	DCE	9.18	4.34
$\text{Mo}(\text{CO})_4\text{bipy-HgBr}_2$	DCE	12.3	7.34
$\text{Mo}(\text{CO})_4\text{bipy-HgBr}_2$	DCE	16.9	12.7
$\text{Mo}(\text{CO})_4\text{phen-HgBr}_2$	DCE	3.06	0.82
$\text{Mo}(\text{CO})_4\text{phen-HgBr}_2$	DCE	6.12	2.10
$\text{Mo}(\text{CO})_4\text{phen-HgBr}_2$	DCE	9.18	4.17
$\text{Mo}(\text{CO})_4\text{phen-HgBr}_2$	DCE	15.3	9.55
$\text{Mo}(\text{CO})_4\text{phen-HgBr}_2$	DCE	16.9	11.8
$\text{Mo}(\text{CO})_4\text{phen-HgBr}_2$	Acetone	15.0	4.7
$\text{Mo}(\text{CO})_4\text{phen-HgBr}_2$	Acetone	20.0	6.6
$\text{Mo}(\text{CO})_4\text{phen-HgBr}_2$	Acetone	25.0	10.3
$\text{Mo}(\text{CO})_4\text{phen-HgBr}_2$	Acetone	30.4	16.7
$\text{Mo}(\text{CO})_4\text{phen-HgBr}_2$	Acetone	40.5	25.5
$\text{Mo}(\text{CO})_4\text{phen-HgBr}_2$	Acetone	50.6	37.4

^a DCE = 1,2-dichloroethane.

tems,¹ since $\text{W}(\text{CO})_4\text{L}_2 \cdot 2\text{HgX}_2$ was isolated as an intermediate (eq 1) and was then found to decompose (eq 2) with evolution of CO forming $\text{W}(\text{CO})_3\text{L}_2(\text{HgX})(\text{X})$. Likewise, the spectral changes associated with these reactions in acetone are consistent with such a process. At high concentrations of mercuric halide, an excellent isobestic point is present in the spectral changes that occur during reaction (Figure 1). This indicates that at these conditions virtually all of the $\text{W}(\text{CO})_4\text{L}_2$ has been converted to an intermediate and this corresponds to the reaction taking place at the limiting rates shown in Figure 2.

The fact that the 1:2 adduct was isolated as an intermediate does not ensure that this compound was the spectrally observed species. Since 1:1 adducts are common between transition metal complexes and mercuric halides⁹ and since the 1:2 adduct was no doubt formed by a two-step equilibrium, it was necessary to determine the nature of the reacting intermediate in solution. To accomplish this, equilibrium constants for the formation of the intermediate were determined at different concentrations of mercuric halide. If the 1:1 adduct were the spectrally observed species, then the equilibrium involved is that represented by (3) and the equilibrium constant is given by

$$K_1 = \frac{[\text{W}(\text{CO})_4\text{L}_2 \cdot \text{HgX}_2]}{[\text{W}(\text{CO})_4\text{L}_2][\text{HgX}_2]} \quad (5)$$

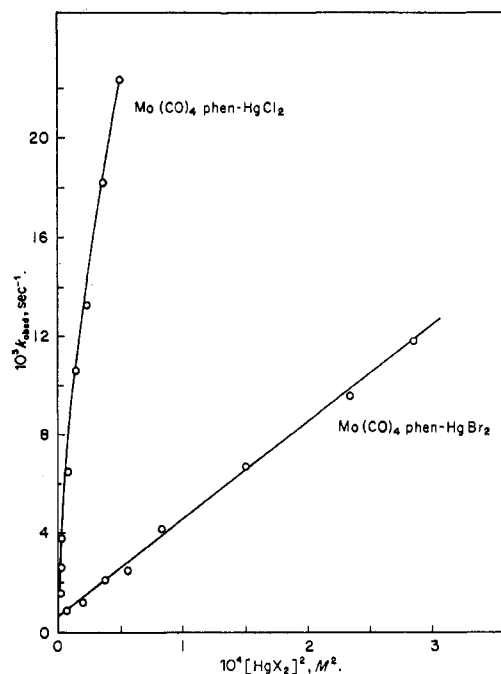


Figure 6.—Plots of k_{obsd} vs. $[\text{HgX}_2]^2$ for the reaction of $\text{Mo}(\text{CO})_4\text{phen}$ with HgX_2 in dichloroethane at 25°.

If, however, the observed intermediate is the 1:2 adduct, then the overall equilibrium is represented by (4) and the equilibrium constant is given by

$$K_1K_2 = \frac{[\text{W}(\text{CO})_4\text{L}_2 \cdot 2\text{HgX}_2]}{[\text{W}(\text{CO})_4\text{L}_2][\text{HgX}_2]^2} \quad (6)$$

The correct expression for the equilibrium constant should not vary for different concentrations of mercuric halide. Table III gives the calculated equilibrium con-

TABLE III
EQUILIBRIUM CONSTANTS FOR THE ADDUCT FORMATION
BETWEEN $\text{W}(\text{CO})_4\text{phen}$ AND HgCl_2 IN ACETONE AT 0°

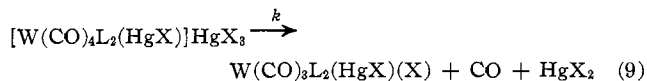
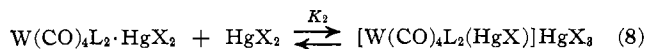
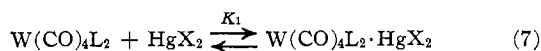
$10^2[\text{HgCl}_2], M$	K_1, M^{-1}	K_1K_2, M^{-2}
4.10	51.7	1158
6.20	69.6	1127
8.00	94.9	1178

^a See eq 5. ^b See eq 6.

stants for the $\text{W}(\text{CO})_4\text{phen-HgCl}_2$ system in acetone at three different concentrations of mercuric chloride and from these data it is evident that the observed intermediate is the 1:2 adduct. Similar behavior was observed in the other three systems studied.

The structure of the 1:2 adduct remains somewhat in doubt, although evidence has been cited¹ in support of its formulation as an ionic compound, $[\text{W}(\text{CO})_4\text{L}_2(\text{HgX})]\text{HgX}_3$. Also $[\text{Os}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{HgX})]\text{HgX}_3$ was isolated as the product from the reaction of $\text{Os}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]_2$ and HgX_2 .¹¹ Similarly the reaction of $\text{C}_6\text{H}_5\text{Rh}(\text{CO})[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$ with Cl_2 yielded $[\text{C}_6\text{H}_5\text{Rh}(\text{CO})[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]\text{Cl}]\text{Cl}$ which decomposed on heating to form $\text{C}_6\text{H}_5\text{Rh}[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]\text{Cl}_2$ and CO .⁸ This latter reaction is very analogous to the work described in this paper.

A reasonable mechanism for these reactions in acetone is represented by reaction scheme (7)–(9). Equations



10 and 11 give two forms of the equation for the observed rate constant derived from the above mechanism.

$$k_{\text{obsd}} = \frac{kK_1K_2[\text{HgX}_2]^2}{1 + K_1K_2[\text{HgX}_2]^2} \quad (10)$$

$$\frac{1}{k_{\text{obsd}}} = \left(\frac{1}{[\text{HgX}_2]^2} \right) \left(\frac{1}{kK_1K_2} \right) + \frac{1}{k} \quad (11)$$

Expression 11 predicts that a plot of $1/k_{\text{obsd}}$ vs. $1/[\text{HgX}_2]^2$ should be linear if the mechanism is correct and Figure 7 shows this plot for the reactions of $\text{W}(\text{CO})_4$ -

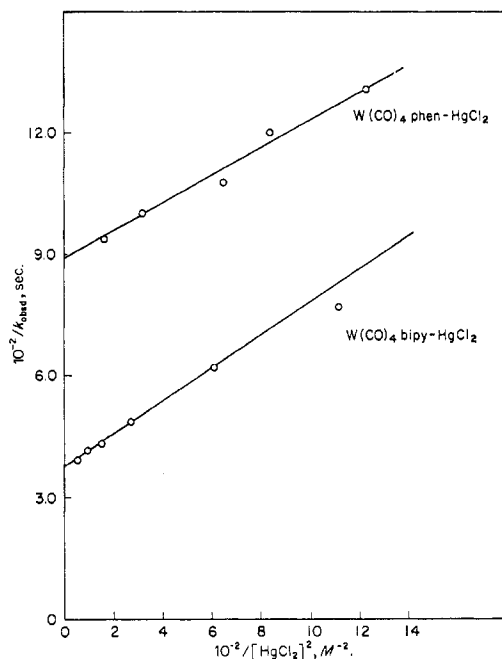
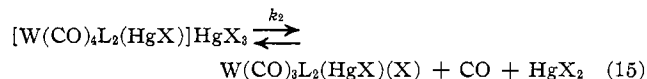
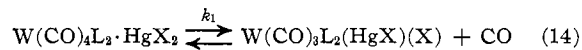
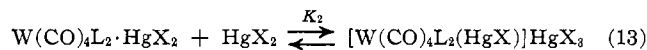
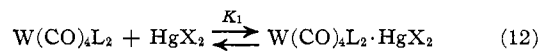


Figure 7.—Plots of $1/k_{\text{obsd}}$ vs. $1/[\text{HgCl}_2]^2$ for the reaction of $\text{W}(\text{CO})_4\text{L}_2$ with HgCl_2 in acetone at 25° .

phen and $\text{W}(\text{CO})_4\text{bipy}$ with HgCl_2 . At the high concentrations of mercuric halide shown in Figure 7, the plots show good linearity, but at low concentrations of HgX_2 (not included in Figure 7), significant deviation is observed. This deviation at low mercuric halide concentration may be due to reaction of the 1:1 adduct $\text{W}(\text{CO})_4\text{L}_2 \cdot \text{HgX}_2$ to form the final product without adding a second mole of HgX_2 . The kinetic data obtained in dichloroethane lend credence to this argument.

In dichloroethane, the observed rate constant reaches a maximum at a certain concentration of mercuric halide and then falls off as the HgX_2 concentration is increased. This behavior is reasonable if it is assumed that two intermediates are reacting to form the final

product and the revised mechanism becomes that represented by the scheme



Assuming that $\text{W}(\text{CO})_4\text{L}_2 \cdot \text{HgX}_2$ is the more prevalent reactive species at low concentrations of HgX_2 and assuming that $k_1 > k_2$, then the observed rate profile (Figure 3) can be qualitatively explained. Equation 16 gives the expression for the observed rate constant as derived from the above mechanism. Since the values of K_1 and K_2 are not known, it is not possible to make a graphical check on this mechanism. However, the

$$k_{\text{obsd}} = \frac{k_1K_1[\text{HgX}_2] + k_2K_1K_2[\text{HgX}_2]^2}{1 + K_1[\text{HgX}_2] + K_1K_2[\text{HgX}_2]^2} \quad (16)$$

equation does accommodate the observed kinetic behavior.

If the 1:1 adduct is assumed to be a nonionic species, then the difference in the kinetic behavior in the solvents acetone and dichloroethane may be due to the greater stability of the 1:1 complex in the less polar solvent. In the same way the more polar acetone stabilizes the ionic 1:2 adduct and suppresses the formation of the 1:1 intermediate, except at low concentrations of mercuric halide.

Equilibrium constants for the formation of the 1:2 adducts in acetone have been calculated, since these species are the predominant intermediates in that solvent. Table IV contains the equilibrium constants

TABLE IV
EQUILIBRIUM CONSTANTS FOR THE ADDUCT FORMATION
BETWEEN $\text{W}(\text{CO})_4\text{L}_2$ AND HgX_2 IN ACETONE AT 0°

System	$K_1K_2,^a$ M^{-2}	System	$K_1K_2,^a$ M^{-2}
$\text{W}(\text{CO})_4\text{bipy-HgCl}_2$	539	$\text{W}(\text{CO})_4\text{bipy-HgBr}_2$	3300
$\text{W}(\text{CO})_4\text{phen-HgCl}_2$	1150	$\text{W}(\text{CO})_4\text{phen-HgBr}_2$	5210

^a See eq 6.

obtained for the four systems studied. The values are the result of averaging three determinations. It is evident that the 1:2 adduct is formed more favorably with mercuric bromide than with mercuric chloride for both $\text{W}(\text{CO})_4\text{bipy}$ and $\text{W}(\text{CO})_4\text{phen}$. This result is not expected on the basis of inductive and steric considerations which predict HgCl_2 to be the more electrophilic reagent. However, a consideration of relative Lewis acid strengths of HgX_2 need not apply because the species formed are not simple acid-base adducts but are salts of the type $[\text{W}(\text{CO})_4\text{L}_2(\text{HgX})]\text{HgX}_3$. Alternatively one may suggest that the soft¹² Lewis bases, $\text{W}(\text{CO})_4\text{L}_2$, may form more stable products with the softer Lewis acid HgBr_2 in preference to HgCl_2 .

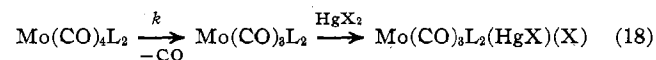
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Reactions of $\text{Mo}(\text{CO})_4\text{L}_2$.—No intermediate was observed spectrally in the reactions of the molybdenum complexes with mercuric halides. This result is consistent with the previous study¹ of these reactions where no intermediate could be isolated. In acetone the observed rate constant shows a linear dependence on the square of the mercuric halide concentration for the three systems studied. The mechanism proposed above for the tungsten systems in acetone is applicable to these reactions if it is assumed that the equilibrium constant for the formation of the 1:2 adduct is small. If $K_1K_2[\text{HgX}_2]^2 \ll 1$, then expression 10 reduces to expression 17 and this equation is consistent with the observed kinetics. The assumption that K_1K_2 is

$$k_{\text{obsd}} = kK_1K_2[\text{HgX}_2]^2 \quad (17)$$

much less for molybdenum than for tungsten is reasonable, since the magnitude of this equilibrium constant is a measure of the basicity of the metal complex and it is known that basicity generally increases going down a given group.⁹ The slopes of the plots in Figure 5 correspond to the value of kK_1K_2 in the postulated mechanism. Since a limiting rate is never reached for the molybdenum systems, it was not possible to calculate separately values for k and K_1K_2 . The products of the rate and equilibrium constants for the three systems studied are as follows: $\text{Mo}(\text{CO})_4\text{bipy}-\text{HgCl}_2$, $kK_1K_2 = 7.85 \text{ sec}^{-1} M^{-2}$; $\text{Mo}(\text{CO})_4\text{phen}-\text{HgCl}_2$, $kK_1K_2 = 8.33 \text{ sec}^{-1} M^{-2}$; $\text{Mo}(\text{CO})_4\text{phen}-\text{HgBr}_2$, $kK_1K_2 = 13.4 \text{ sec}^{-1} M^{-2}$. If the value of k is about the same (or less) for HgBr_2 than for HgCl_2 , as was the case for the tungsten systems, then K_1K_2 must be larger for HgBr_2 than for HgCl_2 . This result is consistent with the data obtained for the tungsten systems where HgBr_2 was the better electrophile.

The positive intercepts for the lines in Figure 5 are rather puzzling. The intercepts could correspond to reaction of $\text{Mo}(\text{CO})_4\text{L}_2$ by a dissociative path with HgX_2 to yield the product directly without the formation of an intermediate adduct (eq 18). The values of the inter-



cepts, however, are higher than the rate constants calcu-

lated for this type of mechanism for the reaction of $\text{Mo}(\text{CO})_4\text{bipy}$ with phosphines.¹³ It is possible that reaction of the 1:1 adduct is responsible for the positive intercepts.

In dichloroethane the oxidative elimination reactions of $\text{Mo}(\text{CO})_4\text{L}_2$ showed different kinetic behavior depending on whether HgCl_2 or HgBr_2 was the electrophile. The rates of reaction with HgCl_2 did not show a linear dependence on either the first power or the square of the mercuric chloride concentration. The dependence was instead intermediate between the two extremes. This behavior indicates some reaction of both 1:1 and 1:2 adduct intermediates in this solvent and is consistent with the behavior found for the tungsten systems in dichloroethane.

The observed rate constant for the reactions of $\text{Mo}(\text{CO})_4\text{L}_2$ with HgBr_2 in dichloroethane shows a linear dependence on the square of the mercuric bromide concentration. This is in contrast to the reactions of mercuric chloride with the same compounds in this solvent and indicates that HgBr_2 stabilizes the 1:2 adduct to a greater extent than does HgCl_2 .

This work indicates that the reactions of both the tungsten and molybdenum complexes with mercuric halides proceed through intermediates which are formulated as adducts of the metal complex and the electrophile.

The formation of these adducts is a consequence of donation of electrons from the basic metal complex to the electrophilic mercuric halide. This flow of electron density away from the metal complex results in the weakening of the M-CO bond and makes loss of CO more facile. This result is similar to the observation that carbon monoxide exchange reactions of some iron carbonyls are acid catalyzed.¹⁴

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