THE KINETICS AND MECHANSIM OF THE REACTION OF IRON PENTACARBONYL WITH MERCURIC HALIDES
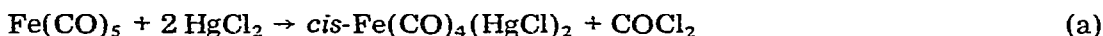
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Summary

The reaction of $Fe(CO)_5$ with $HgCl_2$ proceeds via the consecutive reactions

$$Fe(CO)_5 + 2\,HgCl_2 \rightarrow cis\text{-}Fe(CO)_4(HgCl)_2 + COCl_2 \qquad (a)$$

$$cis\text{-}Fe(CO)_4(HgCl)_2 + 2\,HgCl_2 \rightarrow cis\text{-}Fe(CO)_4(HgCl \cdot HgCl_2)_2 \qquad (b)$$

a and b. The kinetics and mechanism of the two processes have been tsudied. They have been found to obey the rate laws:

$$-d[Fe(CO)_5]/dt = k_a[Fe(CO)_5][HgCl_2]^2$$

$$-d[cis\text{-}Fe(CO)_4(HgCl)_2]/dt = k_b[cis\text{-}Fe(CO)_4(HgCl)_2][HgCl_2]^2$$

The mechanism for process a is inferred to be similar to that observed for other oxidative addition—elimination reactions, involving the successive formation of 1/1 and 1/2 "adducts" of $Fe(CO)_5$ and $HgCl_2$, and other rapid steps. Analogies between this mechanism and those of reactions involving the fixation of molecular nitrogen are discussed. The mechanism of reaction b, and activation parameters for each path are presented and discussed.

Introduction

Oxidative elimination reactions of metal carbonyls and derivatives, which involve the replacement of a carbonyl by two univalent ligands (eq. 1), with the attendant increase in the coordination number and the formal oxidation state of the metal, have been studied for a wide variety of electrophilic reagents (TX), including $R_xSnX_{(4-x)}$ [1], X_2 [2], and HgX_2 [3] (X = Cl, Br, I). The kinetics and mechanism of these reactions have also been the subject of considerable

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interest [4—7]. An unusual, related reaction is that of iron pentacarbonyl with mercuric halides [8] (eq. 2), in which an "internal" oxidation of CO to afford COCl$_2$ is inferred.

$$Fe(CO)_5 \div 2\,HgCl_2 \rightarrow cis\text{-}Fe^{II}(CO)_4(HgCl)_2 + COCl_2 . \tag{2}$$

The transformation of a coordinated ligand such as is observed in eq. 2 is of particular interest in view of the closely-related reaction 3, in which coordinated

$$trans\text{-}(diphos)_2W(N_2)_2 + 2\,HX \rightarrow (diphos)_2W^{II}(X)_2(N_2H_2) + N_2 \tag{3}$$
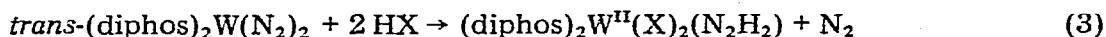
molecular nitrogen is "fixed" [9]. In each of the processes 2 and 3, a coordinated ligand is transformed during an addition—elimination reaction. Moreover, CO and N$_2$ are isoelectronic, coordinated in the same manner (end-on) and have similar electronic distributions, in which the atom coordinated to the metal bears a more positive charge than does the "terminal" atom [10].

In view of the great theoretical and practical interest in reactions such as 3, as well as interest in the mechanism of oxidative addition—elimination reactions 1 in general, a study of the kinetics and mechanism of 2 was dictated. The results of that study are the subject of this report.

Experimental

General. Reaction rates, and all infrared spectra were obtained employing a Perkin—Elmer Model 621 grating spectrophotometer. Individual spectra were calibrated against a band of water vapor at 1869.4 cm^{-1} [11]. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Preparation and purification of materials. The rate of the reaction of Fe(CO)$_5$ with HgCl$_2$ was found to be very sensitive to the purity of the iron pentacarbonyl (Apache Chemical Company, Rockford, Illinois). Thus, Fe(CO)$_5$ was rigorously purified by trap-to-trap distillation under high vacuum (five times), and was stored under nitrogen in the cold in a foil-wrapped container. Mercuric chloride (Fisher Scientific) was twice recrystallized from absolute ethanol, dried, and then stored in a brown vial in a desiccator. The HgCl$_2$ was occasionally redried under high vacuum. Mercuric bromide and mercuric iodide (Fisher) were purified and handled similarly. Spectrophotometric grade acetone (Fisher) was purified through use of established procedures [12—15], but it was found that reaction rates obtained employing this highly purified acetone did not differ · significantly from those obtained employing the spectrophotmetric grade acetone. The latter was therefore employed in the remaining kinetics runs.

Determination of reaction rates. Initial reaction rates were determined under pseudo first-order reaction conditions (at least a thirty-fold excess of mercuric halide) through observation of the decrease in intensity of the A_2'' carbonyl stretching band of Fe(CO)$_5$ at 1995 cm^{-1} [16]. Solutions of Fe(CO)$_5$ and HgCl$_2$ in acetone were found to react with the NaCl cell windows and with the metal parts of the observation cells. It thus was necessary to construct special cells which eliminated contact of the solutions with NaCl and all metals. These cells (Fig. 1) employed Irtran-2 windows, 1 mm Teflon spacers and Kel-F hubs. The hubs were constructed so as to form a tight seal with the cell body. Due to the relative incompressibility of Teflon it was necessary to place Parafilm sheets
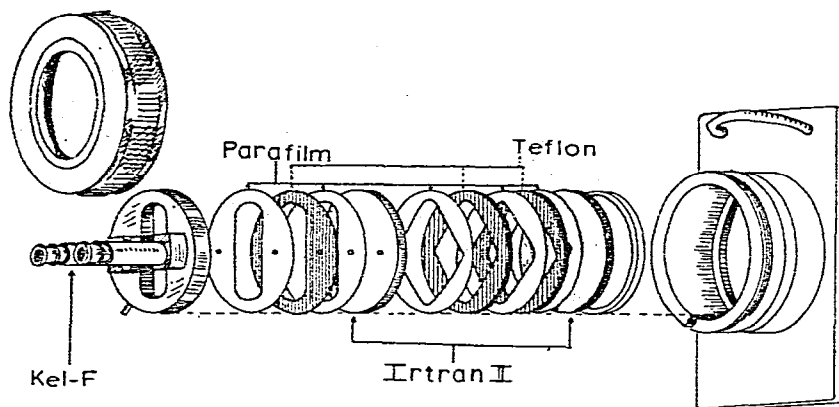
Fig. 1. Infrared cell constructed to allow solution contact only with unreactive surfaces.

on either side of the spacers to insure a leak-proof seal.

To avoid the use of metal needles for sampling, a modified reaction flask was employed. Teflon tubing (0.022 mm id, Hamilton), of sufficient length to reach the bottom of a 25 ml volumetric flask, was inserted through a rubber septum. The outside end of the tubing was fitted to a Kel-F Luer hub (Hamilton) to which a Delrin valve (Ace Glass) was attached. An all-glass Luer syringe (2 ml) was then employed for sample removal.

Preparation of reaction solutions. The folowing procedure was employed: Mercuric chloride was weighed into a 25 ml volumetric flask under a nitrogen atmosphere. About 20 ml of acetone was then added, and the flask was then sealed, and placed in a constant temperature bath (Haake Model ED circulator). After the flask had attained the reaction temperature, the volume was brought to the mark by injection of acetone through the septum employing a needle and syringe. Iron pentacarbonyl (to make the solution ca. 1.5×10^{-3} M) was then added in the same manner, and the resulting solution was well-mixed. A volume of nitrogen equal to that of each sample removed was added to the reaction vessel during sampling.

Plots of $\ln(A_t - A_\infty)$ vs. time (where A_t and A_∞ are absorbances of the solution at time t and at infinite time, respectively) exhibited curvature after about thirty per cent of reaction completion (vide infra), and thus initial slopes were employed in the determination of the rate of disappearance of Fe(CO)$_5$. The rate of appearance of the final reaction product, Fe(CO)$_4$-(HgCl · HgCl$_2$)$_2$ was also monitored, at 2094 cm^{-1}. After an initial induction period which corresponded to the conversion of Fe(CO)$_5$ to *cis*-Fe(CO)$_4$(HgCl)$_2$ plots of $\ln(A_t - A_\infty)$ vs. time were linear to three or more half-lives.

Identification of reaction products. Scans of the carbonyl stretching region of the infrared spectrum (2200—1900 cm^{-1}) during the course of the reaction indicated the presence of the reported reaction product, *cis*-Fe(CO)$_4$(HgCl)$_2$ [17]. The complex was isolated as follows: Reaction of Fe(CO)$_5$ with excess HgCl$_2$ in acetone at 55°C was monitored in the carbonyl stretching region until Fe(CO)$_5$ had reacted completely. Solvent was then removed under vacuum, the residue was washed with water and n-hexane, and the yellow, crystalline residue was dried in vacuo. Anal. found: C, 7.46; Fe, 8.79; Cl, 10.88. C$_4$Cl$_2$-

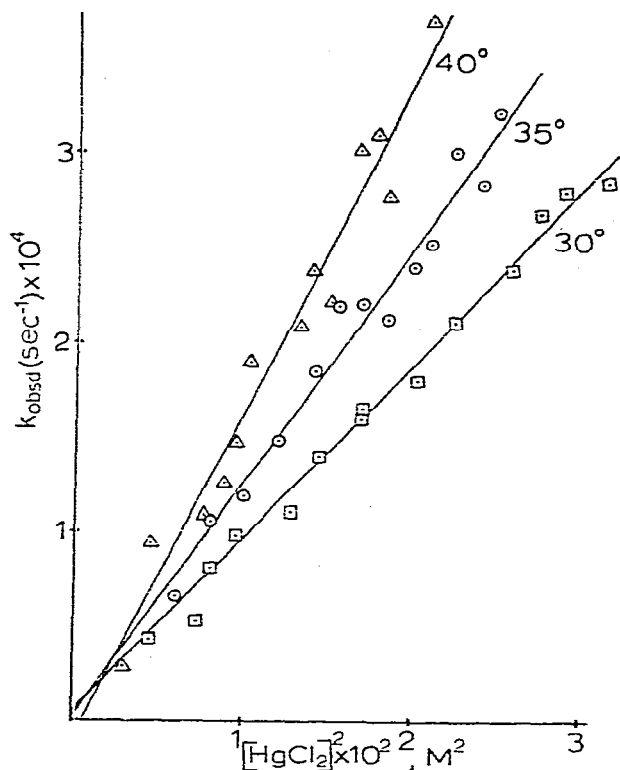Fig. 2. Plots of k_{obsd} vs. $[HgCl_2]^2$ for reaction of iron pentacarbonyl with mercuric chloride to afford *cis*-Fe(CO)$_4$(HgCl)$_2$.

$FeHg_2O_4$ calcd.: C, 7.51; Fe, 8.72; Cl, 11.08%. The carbonyl stretching spectra of this product in acetone, and as a nujol mull are given in Table 1.

If reaction of Fe(CO)$_5$ with excess mercuric chloride is followed in the infrared and a similar workup is carried out after seven or eight reaction half-lives, or if *cis*-Fe(CO)$_4$(HgCl)$_2$, prepared as described above is allowed to react further with excess HgCl$_2$, a second product, an air-stable, red-brown powder

TABLE 1

CARBONYL STRETCHING FREQUENCIES OF PRODUCTS OBTAINED THROUGH REACTION OF IRON PENTACARBONYL WITH MERCURIC CHLORIDE

Compound	Medium	$\nu(CO)$ (cm^{-1})
cis-Fe(CO)$_4$(HgCl)$_2$	Nujol mull	2095(sh), 2087ms, 2032(sh), 2008s, 1980(sh)
	Acetone solution	2089ms, 2075s, 2046(sh), 2015vs, 1995(sh)
cis-Fe(CO)$_4$(HgCl · HgCl$_2$)$_2$	Nujol mull	2109n.s, 2077ms, 2050s, 2040s, 2015(sh)
	Acetone solution	2090m., 2076(sh), 2020s, 2000(sh)

which elemental analysis analysis indicates to be $Fe(CO)_4(HgCl \cdot HgCl_2)_2$ is obtained. Anal. found (two separate samples): C, 4.41; 4.21; Cl, 16.70; Fe, 4.65, 4.90; Hg, 67.86, 67.77. $C_4Cl_6FeHg_4O_4$ calcd.: C, 4.06; Cl, 17.98; Fe, 4.72; Hg, 67.82%. The infrared spectra (carbonyl stretching region) for $Fe(CO)_4(HgCl \cdot HgCl_2)_2$ in acetone and as a nujol mull are given in Table 1.

Electrolytic properties of both products were studied employing a Beckman Model RC 16B2 conductivity bridge with dip-type platinum electrode. For 10^{-3} M solutions in nitrobenzene at $24°C$ both products are non-electrolytes.

The formation of phosgene gas as a reaction product was not observed directly; reasons for failure to observe $COCl_2$ have been discussed [8]. However, the effluent gas for reaction of $Fe(CO)_5$ and $HgCl_2$ in ethanol and acetone was found by qualitative and infrared analysis to contain CO, HCl and CO_2. The latter two substances are the products expected upon hydrolysis of $COCl_2$, which could occur in the presence of traces of water present in those solvents [8].

Treatment of data. Values of the pseudo first-order rate constants, k_{obsd}, and the rate constants themselves were calculated employing a linear least-squares computer program on an IBM 360 model 50 computer of the North Texas State University computing center. The limits of error cited for data in Tables 2—4 are given in parentheses, and are one standard deviation. Rate constants which differed from the mean by more than two standard deviations were rejected.

TABLE 2

RATES OF REACTION OF IRON PENTACARBONYL WITH MERCURIC CHLORIDE IN ACETONE AT VARIOUS TEMPERATURES

| $[HgCl_2]$ (M)	$10^4 \, k_{obsd}$ (sec^{-1})	$[HgCl_2]$ (M)	$10^4 \, k_{obsd}$ (sec^{-1})
T 30.00(5)° C		*T 35.00(5) ° C*	
0.0662	0.428(21)	0.1305	2.20(8)
0.0727	0.559(23)	0.1348	2.12(6)
0.0897	0.812(18)	0.1416	2.39(5)
0.0979	0.983(9)	0.1451	2.51(3)
0.1131	1.10(1)	0.1498	3.00(2)
0.1202	1.40(4)	0.1552	2.82(1)
0.1299	1.59(5)	0.1583	3.20(12)
0.1308	1.64(5)		
0.1421	1.80(4)	*T 40.00(5) ° C*	
0.1497	2.11(5)	0.0543	0.281(5)
0.1606	2.38(5)	0.0678	0.941(68)
0.1657	2.67(7)	0.0876	1.08(5)
0.1698	2.78(2)	0.0938	1.25(11)
0.1778	2.84(6)	0.0976	1.47(5)
		0.1016	1.90(7)
T 35.00(5) ° C		0.1151	2.09(4)
0.0775	0.655(13)	0.1182	2.38(12)
0.0894	1.10(6)	0.1222	2.22(5)
0.1000	1.18(2)	0.1294	3.01(20)
0.1099	1.48(3)	0.1333	3.09(8)
0.1191	1.85(5)	0.1358	2.76(5)
0.1249	2.19(6)	0.1449	3.68(15)

TABLE 3

RATES OF REACTION OF *cis*-Fe(CO)$_4$(HgCl)$_2$ WITH MERCURIC CHLORIDE IN ACETONE AT VARIOUS TEMPERATURES

[HgCl$_2$] (M)	$10^4 \, k_{obsd}$ (sec^{-1})	[HgCl$_2$] (M)	$10^4 \, k_{obsd}$ (sec^{-1})
T 35.00(5) °C		T 45.00(5) °C	
0.0994	0.671(13)	0.1550	2.61(5)
0.0950	0.702(19)	0.1612	2.37(8)
0.1001	0.891(13)	0.1673	2.67(8)
0.1049	0.910(25)	0.1733	3.19(6)
0.1139	1.01(2)	0.1896	3.63(9)
0.1140	1.25(1)		
0.1182	1.35(2)	T 55.00(5) °C	
0.1225	1.46(3)	0.0549	0.387(4)
0.1265	1.41(1)	0.0632	0.561(9)
0.1304	1.69(6)	0.0707	0.584(4)
0.1341	1.59(4)	0.0775	0.777(7)
0.1414	1.94(3)	0.0836	0.761(12)
0.1484	1.96(3)	0.0894	0.992(13)
0.1549	2.10(3)	0.0948	0.966(10)
0.1613	2.35(4)	0.1021	1.22(1)
0.1673	2.38(4)	0.1095	1.52(1)
		0.1140	2.05(2)
T 45.00(5) °C		0.1328	2.00(2)
0.1000	1.05(1)	0.1342	2.18(1)
0.1095	1.16(1)	0.1448	2.39(3)
0.1182	1.38(2)	0.1483	2.47(3)
0.1266	1.63(2)	0.1516	2.84(5)
0.1341	1.73(1)	0.1580	2.97(11)
0.1414	2.23(2)	0.1643	3.22(5)
0.1483	2.30(5)	0.1643	3.23(5)
		0.1703	3.46(10)
		0.1845	3.96(6)

TABLE 4

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR REACTIONS OF IRON PENTA-CARBONYL WITH MERCURIC CHLORIDE IN ACETONE AT VARIOUS TEMPERATURES

Fe(CO)$_5$ + 2 HgCl$_2$
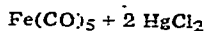
T (°C)	$10^2 \, k_1k_3k_5/k_2(k_4 + k_5)$ (M^{-2} sec^{-1})	ΔH^* (kcal/mole)	ΔS^* (cal/deg-mole)
30.00(5)	0.91(2)		
35.00(5)	1.24(7)	11.6(8)	−29.7(14)
40.00(5)	1.75(11)		

cis-Fe(CO)$_4$(HgCl)$_2$ + 2 HgCl$_2$

T (°C)	$10^2 \, k_6k_8/k_7$ (M^{-2} sec^{-1})	ΔH^* (kcal/mole)	ΔS^* (cal/deg-mole)
35.00(5)	0.90(4)		
45.00(5)	1.01(6)	2.01(2)	−61.5(10)
55.00(5)	1.17(2)		

Results and discussion

Rate data, and the identification of the reaction products indicate the overall reaction to be reactions 2 and 4. While cis-$Fe(CO)_4(HgCl)_2$ is a well-character-

$$cis\text{-}Fe(CO)_4(HgCl)_2 + 2\,HgCl_2 \rightleftharpoons cis\text{-}Fe(CO)_4(HgCl \cdot HgCl_2)_2 \qquad (4)$$

ized compound whose spectral [17] and structural [18] characteristics have been determined, cis-$Fe(CO)_4(HgCl \cdot HgCl_2)_2$ had not been reported.

The similarity of the carbonyl stretching spectra of this complex and that of the parent cis-$Fe(CO)_4(HgCl)_2$ (Table 1) indicates that the non-electrolyte $Fe(CO)_4(HgCl \cdot HgCl_2)_2$ also exhibits cis stereochemistry. The carbonyl stretching spectra for the two products show an average shift of ca. 35 cm^{-1} to higher energies of the bands for cis-$Fe(CO)_4(HgCl \cdot HgCl_2)_2$, consistent with electron-withdrawal from Fe as $HgCl_2$ is complexed, presumably to HgCl.

A comparison of the carbonyl stretching spectra for this complex as a nujol mull and in acetone solution (Table 1) suggests that in the absence of excess $HgCl_2$ the complex dissociates to afford cis-$Fe(CO)_4(HgCl)_2$. Thus interconversion of the two reaction products is reversible.

Plots of $\ln(A_t - A_\infty)$ vs. time for reaction of $Fe(CO)_5$ with excess $HgCl_2$ in acetone exhibit non-linearity, indicative of the formation of at least two absorbing species, and consistent with the isolation of the two products, cis-$Fe(CO)_4(HgCl)_2$ and cis-$Fe(CO)_4(HgCl \cdot HgCl_2)_2$. Thus the initial linear portions of these plots (over the first thirty per cent of the reactions) measure the rate of disappearance of $Fe(CO)_5$ to form cis-$Fe(CO)_4(HgCl)_2$, while the subsequent linearity of the plots, over three or more half-lives, measure the rate of conversion of that species to cis-$Fe(CO)_4(HgCl \cdot HgCl_2)_2$ after disappearance of $Fe(CO)_5$. It was found that more convenient to study the latter process at a wavelength at which $Fe(CO)_4(HgCl)_2$ and the product exhibit maximum spectral differences, at 2094 cm^{-1}. Values of k_{obsd} at various concentrations of $HgCl_2$ at several reaction temperatures for reactions of both $Fe(CO)_5$ and $Fe(CO)_4(HgCl)_2$ with $HgCl_2$ are presented in Tables 2 and 3, respectively.
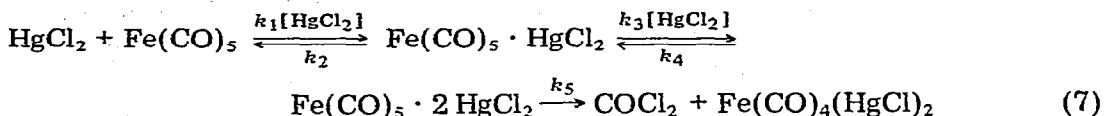
For reaction of $Fe(CO)_5$ according to eq. 2, plots of log k_{obsd} vs. log $[HgCl_2]$ are linear with slope of 2, indicative of the rate law shown in eq. 5. Plots of

$$k_{obsd} = k[HgCl_2]^2 \qquad (5)$$

k_{obsd} vs. $[HgCl]^2$ are illustrated in Fig. 2. The data support an overall rate law, 6.

$$-d[Fe(CO)_5]/dt = k[Fe(CO)_5][HgCl_2]^2 \qquad (6)$$

This type of rate behavior has been observed previously for oxidative elimination reactions of $(o$-phen$)Mo(CO)_4$ with $HgCl_2$ (o-phen = o-phenanthroline) [6,7], of $(dipy)W(CO)_4$ with $RSnCl_3$ and R_2SnCl_2 (dipy = 2,2'-dipyridyl; R = alkyl, aryl) [4] and for reaction of $Fe(CO)_5$ with I_2, which affords cis-$Fe(CO)_4$-I_2 [5]. It is consistent with a mechanism involving reversible addition of $HgCl_2$ to form a 1/1 "adduct", addition of a second mole of $HgCl_2$ to form a 1/2 "adduct", and other steps which lead to the observed products (eq. 7).

$$HgCl_2 + Fe(CO)_5 \underset{k_2}{\overset{k_1[HgCl_2]}{\rightleftharpoons}} Fe(CO)_5 \cdot HgCl_2 \underset{k_4}{\overset{k_3[HgCl_2]}{\rightleftharpoons}}$$

$$Fe(CO)_5 \cdot 2\,HgCl_2 \overset{k_5}{\longrightarrow} COCl_2 + Fe(CO)_4(HgCl)_2 \qquad (7)$$

Employing the steady-state approximation for the concentration of the 1/1 and 1/2 "adducts", the rate law:

$$-d[Fe(CO)_5]/dt = k_1 k_3 k_5 [Fe(CO)_5][HgCl_2]^2/(k_2(k_4 + k_5) + k_3 k_5 [HgCl_2]) \quad (8)$$

is obtained. When $k_2(k_4 + k_5) \gg k_3 k_5 [L]$, most likely to be observed at low $[HgCl_2]$, this equation becomes:

$$-d[Fe(CO)_5]/dt = (k_1 k_2 k_5/k_2(k_4 + k_5))[Fe(CO)_5][HgCl_2]^2 \quad (9)$$

which is consistent with the observed rate law 6.

The rate constants $k_1 k_3 k_5/(k_2(k_4 + k_5))$ and activation parameters obtained from data at three temperatures are exhibited in Table 4. It is of interest to note that a negative entropy of activation is expected in that the processes governed by k_1 and k_3 are expected to involve more bond-making than bond-breaking in the transition state, while that governed by k_2 is expected to involve more bond-breaking. Thus, a negative contribution to the observed entropy of each term in ΔS^*_{obsd} is expected. The observed value ($\Delta S^*_{obsd} = -29.7 \pm 1.7$ cal/deg-mole) is in agreement with this expectation.

Support for mechanism 7 also comes from results of other studies in which both 1/1 and 1/2 "adducts" have been isolated. Of particular interest are the results of Kemmitt and coworkers [19], who have studied reactions of substituted iron carbonyls with mercuric halides. They formulate 1/1 adducts of the type $Fe(CO)_3L_2 \cdot HgX_2$ (L = PPh_3, $AsPh_3$, $SbPh_3$, X = Cl, Br) as metal donor complexes, $L_2(CO)_3Fe{\rightarrow}HgX_2$, which would be analogous to the structure of $(\pi\text{-}C_5H_5)(CO)_2Co{\rightarrow}HgCl_2$, which was determined by X-ray structural study [20]. In the case of an isolated 1/2 adduct, conductivity and infrared studies on $Fe(CO)_3L_2 \cdot 2 HgX_2$ (L = $P(OC_6H_5)_3$; X = Cl, Br) led to their formulation as non-ionic six-coordinate metal donor complexes containing one mole of mercuric halide in the lattice [16]. A recent X-ray crystallographic study of $(\pi\text{-}C_6H_3(CH_3)_3)Mo(CO)_3 \cdot 2 HgCl_2$ has revealed this complex to be, in fact, a 2/4 "adduct" [21], in which the seven-coordinate Mo atoms are bridged by a Hg—Cl network. If $Fe(CO)_5 \cdot 2 HgCl_2$ were to possess an analogous structure (Fig. 3), molecular models suggest the possibility that molecular vibrations could bring the two chlorines nearest a carbonyl carbon to within bonding distance, and thus afford the observed phosgene product. The failure to observe phosgene as a product of the decomposition of $[(\pi\text{-}C_6H_3(CH_3)_3Mo(CO)_3]_2(HgCl_2)_4$ could be attributable to the greater electron density at the carbonyl carbons in that complex, as is indicated by comparison of the carbonyl stretching frequencies for the two complexes [3].

The limited solubilities of $HgBr_2$ and HgI_2 and the products of their reactions with $Fe(CO)_5$ in acetone precluded the acquisition of rate data; however, it was possible to determine that the rates of reaction of $Fe(CO)_5$ with HgX_2 varied in the order Br > Cl > I.

The isolation of a second reaction product, which data indicate to be cis-$Fe(CO)_4(HgCl \cdot HgCl_2)_2$ (vide supra), supports further reaction of cis-$Fe(CO)_4$-$(HgCl)_2$ with mercuric chloride according to eq. 4. Reaction 4 has not been observed previously, probably because of differing conditions (large excess of $HgCl_2$ employed in this study), and the greater solubility of $Fe(CO)_4(HgCl \cdot HgCl_2)_2$; the cis-$Fe(CO)_4(HgCl)_2$ product is usually obtained as a precipitate from the reaction solution [5].
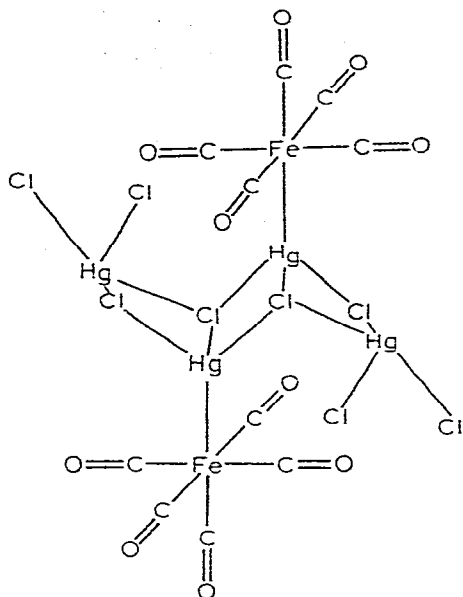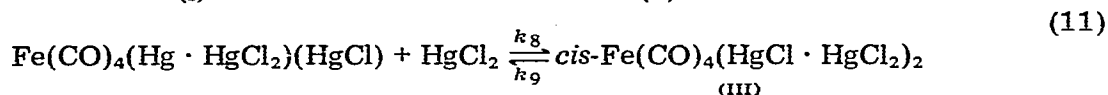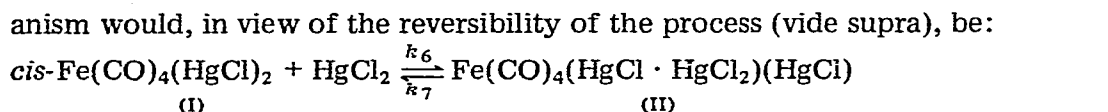
Fig. 3. Possible structure of 1/2 adduct, $Fe(CO)_5 \cdot 2 HgCl_2$.

Rate data for eq. 5 (Table 3) support the rate law 10 for which a likely mech-

$$d[Fe(CO)_4(HgCl \cdot HgCl_2)_2]/dt = k'[Fe(CO)_4(HgCl)_2][HgCl_2]^2 \tag{10}$$

anism would, in view of the reversibility of the process (vide supra), be:

$$cis\text{-}Fe(CO)_4(HgCl)_2 + HgCl_2 \underset{k_7}{\overset{k_6}{\rightleftharpoons}} Fe(CO)_4(HgCl \cdot HgCl_2)(HgCl)$$
$$\text{(I)} \qquad\qquad\qquad\qquad \text{(II)}$$

$$\tag{11}$$

$$Fe(CO)_4(Hg \cdot HgCl_2)(HgCl) + HgCl_2 \underset{k_9}{\overset{k_8}{\rightleftharpoons}} cis\text{-}Fe(CO)_4(HgCl \cdot HgCl_2)_2$$
$$\text{(III)}$$

Assuming a steady-state concentration of compound II, the rate law 12 is

$$d[III]/dt = \frac{k_6k_8[I][HgCl_2]^2 - k_6k_9[III]}{k_7 + k_8[HgCl_2]} \tag{12}$$
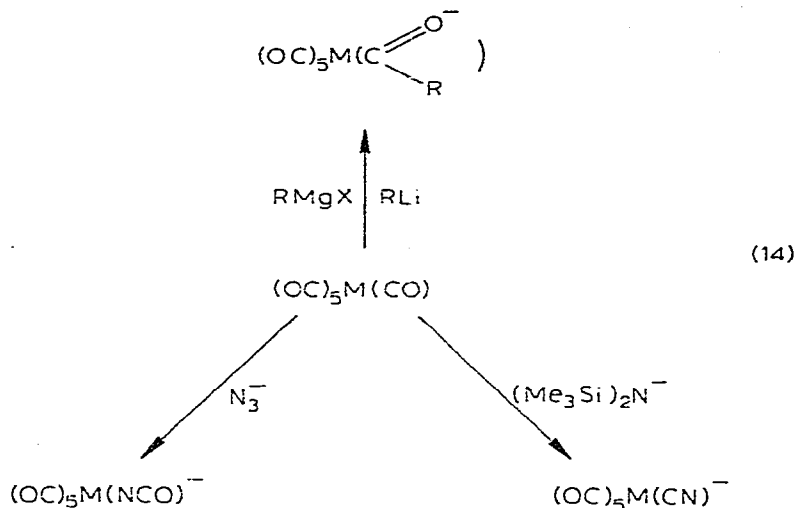
obtained. In the limits $k_6k_8[I][HgCl_2]^2 \gg k_6k_9[III]$, and $k_7 \gg k_8[HgCl_2]$, eq. 12 affords eq. 13, equivalent to eq. 11.

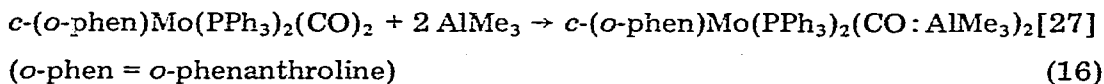$$d[III]/dt = k_6k_8/k_7[Fe(CO)_4(HgCl)_2][HgCl_2]^2 \tag{13}$$

The entropy of activation for the overall process 11 is observed to be highly negative ($-61.5(10)$ cal/deg-mole) as is to be expected.

Some general comments are appropriate before comparison of the series of "nitrogen fixation" reactions studied by Chatt and coworkers and typified by 3 to the present results. It has been observed that both carbon and oxygen can function as reactive sites in metal carbonyls and derivatives under the proper conditions, depending upon the relative charges placed upon the C and O through interaction with the metal atom. In metal carbonyls in which high carbonyl stretching frequencies indicate a relatively positive metal, and, consequently,

a positive carbon [22], that carbon is susceptible to attack by nucleophilic reagents such as carbanions derived from organolithiums [23] and Grignard reagents [24] azides [25] and the bis(trimethylsilyl)amide anion [26], e.g.:

$$(OC)_5M(C \overset{\displaystyle O^-}{\underset{\displaystyle R}{<}} \quad)$$

$$\Big\uparrow \; RMgX \; \Big| \; RLi$$

$$(OC)_5M(CO)$$

(14)

$$N_3^- \swarrow \qquad \searrow (Me_3Si)_2N^-$$

$$(OC)_5M(NCO)^- \qquad\qquad (OC)_5M(CN)^-$$

On the other hand, in complexes in which lower $\nu(CO)$ indicate a relatively negative carbonyl oxygen, interaction by electron-deficient species such as trimethylaluminum can occur at that atom, e.g.:

c-(o-phen)Mo(PPh$_3$)$_2$(CO)$_2$ + 2 AlMe$_3$ → c-(o-phen)Mo(PPh$_3$)$_2$(CO : AlMe$_3$)$_2$[27]

(o-phen = o-phenanthroline)   (16)

Such interactions have been studied in detail, and reviewed by Shriver [28].

In the present system, the inference of a phosgene reaction product, and relatively high carbonyl stretching frequencies observed in Fe(CO)$_5$ and presumably present in Fe(CO)$_5$ · 2 HgCl *, based upon comparison of those in the corresponding Fe(CO)$_3$L$_2$ and Fe(CO)$_3$L$_2$ · 2 HgX$_2$ complexes [19], dictate interaction at carbon. The failure to observe oxidative addition—elimination products for reactions of L$_2$Fe(CO)$_3$ complexes, and the isolation of 1/2 adducts for other highly substituted metal carbonyls such as (π-(CH$_3$)$_3$C$_6$H$_3$)-Mo(CO)$_3$ [3,19] are consistent with this premise.

However, considerable metallic electron density is present in the highly-substituted $trans$-(diphos)$_2$W(N$_2$)$_2$, as is supported by the observation of a relatively low N—N stretching frequency in this complex [29], and synthetic results which demonstrate the terminal nitrogen to be a reactive site for electron-deficient species [30]. Thus the terminal nitrogen is the probable site of attack by H$^+$ of strong acids [9,10].

Thus can be seen analogies in reactions of metal carbonyls, and in complexes containing coordinated dinitrogen. It is also evident that coordinated CO exhibits versatile reactivity via associative paths, although, in contrast, recent evidence suggests that the ligand-dependent path observed in ligand-exchange

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* A (OC)$_5$Fe→HgCl$_2$ interaction in the "adducts" would be expected to remove electron density from the iron atom.

reactions of metal carbonyls, e.g.:

$$M(CO)_x + L \rightarrow M(CO)_{x-1}(L) + CO \tag{17}$$

is largely a dissociative (I_d) [31] process [32,33].

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