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Kinetic Studies of Group VII Metal Carbonyls. I. Substitution Reactions of Tetracarbonyl Halide Dimers of Rhenium

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The tetracarbonyl halide dimers of rhenium, $[Re(CO)_4X]_2$, where X = Cl, Br, or I, undergo substitution reaction with various reagents L, where L = $P(C_6H_5)_3$, pyridine, γ-picoline, or α-chloropyridine, to yield the compounds $Re(CO)_4XL$. The reactions are first order in both the metal carbonyl and the ligand concentrations. For the same reagent the rates decrease with changes in halogen Cl > Br > I, and for the same metal carbonyl the rates decrease with changes in reagent in the order γ-pic > py > $P(C_6H_5)_3$ > α-Clpy. The synthesis and properties of the monosubstituted compounds, $Re(CO)_4XL$, are reported.

Introduction

Several kinetic studies have been reported on isotopic exchange of carbon monoxide[1] and substitution reactions of $Mn(CO)_5X$[2] and its derivatives;[3] these reactions were found to be first order, being zero order in carbon monoxide or any other entering ligand and first order in manganese carbonyl complexes. Analogous studies have not yet been carried out with rhenium carbonyl halides.

It is known that rhenium pentacarbonyl halides, $Re(CO)_5X$, react at relatively high temperatures with several monodentate ligands having phosphorus, nitrogen, or oxygen as donor atom, yielding the disubstituted compounds $Re(CO)_3XL_2$.[4] Disubstituted derivatives can also be obtained from the dimeric tetracarbonyl halides $[Re(CO)_4X]_2$, as, for example, the reaction between pyridine and $[Re(CO)_4I]_2$ gave the compound $Re(CO)_3(py)_2I$.[5] A monosubstituted derivative, $Re(CO)_4BrP(C_6H_5)_3$, was obtained only recently in the reaction between $Re(CO)_5Br$ and triphenylphosphine.[6]

We have now found that under relatively mild conditions it is possible to prepare the monosubstituted derivatives of the rhenium tetracarbonyl halides according to the reaction

$$[Re(CO)_4X]_2 + 2L \longrightarrow 2Re(CO)_4XL \qquad (1)$$

In this paper we report kinetic data on reaction 1 with several ligands as well as the syntheses and full characterization of some of these monosubstituted products.

We propose to report later the kinetics and mechanism both of the reaction between the monosubstituted rhenium carbonyl halides and a variety of ligands and of the dimerization reaction

$$2Re(CO)_5X \longrightarrow [Re(CO)_4X]_2 + 2CO \qquad (2)$$

Experimental Section

Compounds and Solvents.—The compounds $[Re(CO)_4I]_2$, $[Re(CO)_4Br]_2$, and $[Re(CO)_4Cl]_2$ were prepared according to the procedure in the literature.[5] The compounds were identified by carbon and halogen analyses and by their infrared spectra. Pyridine, γ-picoline, and α-chloropyridine (British Drug Houses) were distilled before use. Triphenylphosphine (Eastman Organic Chemicals Drug Houses Ltd.) was used as obtained without further purification. Carbon tetrachloride (Analar, British Drug Houses Ltd.) was also used as obtained. The *s*-tetrachloroethane was shaken with concentrated H_2SO_4, washed with water, dried over $CaCl_2$, and distilled.

General Procedure for the Synthesis of $Re(CO)_4XL$ (X = Cl, Br, I; L = Triphenylphosphine, Pyridine, γ-Picoline).—$[Re(CO)_4X]_2$ (0.00035 mole) and *ca.* 0.0008 mole of ligand dissolved in 80 ml of carbon tetrachloride were allowed to react at room temperature. The progress of the reaction was monitored by infrared spectroscopy. When no more dimeric rhenium tetracarbonyl halide could be detected, the solution was concentrated under reduced pressure and the product was precipitated by adding *n*-pentane. The white crystalline compound was collected on a filter, washed with *n*-pentane, and dried under high vacuum. Purification was effected by recrystallization from carbon tetrachloride. The yields are about 60–80%. All the compounds are slightly soluble in carbon tetrachloride, chloroform, *s*-tetrachloroethane, and benzene, but they are insoluble in aliphatic hydrocarbons. Elemental analyses and other data on the complexes are given in Table I.

Table I

$Re(CO)_4XL$ Complexes

				Analyses, %			
Complex	Mp, °C[a]		Mol wt[b]	C	H	N	Halogen
$Re(CO)_4IP(C_6H_5)_3$	147	Calcd	687	38.44	2.20		18.46
		Found	702	39.1	2.38		18.1
$Re(CO)_4BrP(C_6H_5)_3$	151	Calcd	640	41.26	2.36		12.48
		Found	630	42.11	2.58		12.08
$Re(CO)_4ClP(C_6H_5)_3$	143	Calcd	596	44.33	2.54		5.95
		Found	582	44.9	2.73		5.82
$Re(CO)_4I(py)$	118	Calcd	504	21.44	1.00	2.80	25.10
		Found	522	21.85	1.02	2.7	24.61
$Re(CO)_4Br(py)$	128	Calcd	457	23.64	1.10	3.06	17.48
		Found	492	23.84	1.25	3.50	17.20
$Re(CO)_4Cl(py)$	122	Calcd	413	26.18	1.22	3.39	8.60
		Found	500	26.54	1.35	3.60	8.30
$Re(CO)_4I(\gamma\text{-pic})$	103	Calcd	518	23.17	1.36	2.70	24.49
		Found	580	23.50	1.44	3.05	24.20
$Re(CO)_4Br(\gamma\text{-pic})$	212	Calcd	471	25.48	1.50	2.97	16.96
		Found	530	25.80	1.68	3.07	17.10
$Re(CO)_4Cl(\gamma\text{-pic})$	206	Calcd	427	28.13	1.66	3.28	8.31
		Found	500	27.70	1.50	3.00	8.02

[a] Determined with a melting-point block and uncorrected. [b] Osmometry (5×10^{-4} *M* solution in benzene) with a Mechrolab Model 301-A instrument.

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Determination of Rates.—The rates were determined by following the disappearance of the strong higher frequency carbonyl absorption of $[Re(CO)_4X]_2$ as it reacted with L to form $Re(CO)_4XL$. All the kinetic studies were carried out under pseudo-first-order conditions, using at least a tenfold excess of reagent. A Perkin-Elmer Model 621 spectrophotometer was used to follow the product absorptions in the carbonyl stretching region. Because of the low solubility of $[Re(CO)_4X]_2$, infrared cells of 1-mm thickness were required to give satisfactory absorption intensities. An aluminum foil wrapped round-bottom flask containing the solution of metal carbonyl (concentration range 0.00011–0.00055 M) and one containing the solution of the ligand L (concentration range 0.008–0.12 M) were thermostated in a constant-temperature bath. At zero time the ligand solution was poured into the foil-wrapped flask and mixed well. Samples of the solution were periodically withdrawn with a syringe from the thermostated vessel and the spectrum was quickly measured. For the reactions with $k_{obsd} > 100\ sec^{-1}$, the reaction mixture was kept in a thermostated Perkin-Elmer 1-mm infrared cell, and the change in transmittance with time was recorded. Usually about twenty measurements were made during a period of three half-lives. All reactions proceed to completion. Good linear plots were obtained from the data by plotting log (log T_∞/T) *vs.* time, where T is the transmittance at time t and T_∞ is the transmittance of the base line. A 10% or better precision is obtained for the values of the rate constants. Uncertainties in values of ΔH^* are estimated to be ±1 kcal/mole and in ΔS^* ±2 eu. It was also determined that in the solvents used, the variations of the absorption intensities with changes in concentration of $[Re(CO)_4X]_2$ follow the Lambert–Beer law.

Results

The products of the reaction of $[Re(CO)_4X]_2$ with L (where L = triphenylphosphine, pyridine, γ-picoline, or α-chloropyridine) are *cis*-$Re(CO)_4XL$. Most compounds were isolated and characterized by means of analyses, molecular weights, and infrared spectra. The reaction of rhenium tetracarbonyl halides with an excess of ligand was followed by observing the changes in the infrared spectrum of the solution. The bands due to the C–O stretching frequencies of the starting material were replaced by bands of $Re(CO)_4XL$. Because reactions other than reaction 1 take place, the reactions of $[Re(CO)_4Cl]_2$ and $[Re(CO)_4Br]_2$ with α-chloropyridine were not amenable to quantitative treatment.

The estimated second-order rate constants for reaction 1 in the solvents carbon tetrachloride and s-tetrachloroethane are given in Table II. Plots of some of the experimental rate constants, k_{obsd}, *vs.* ligand concentrations are shown in Figure 1. Table III gives the activation parameters calculated from the rate constants determined at two or three different temperatures. In the case of $[Re(CO)_4Br]_2$ and $[Re(CO)_4Cl]_2$, reaction 1 is very fast so that it could be carried out only with triphenylphosphine at temperatures higher than room temperature. However, since the reactions are fast, the kinetic data at 40° with these two substrates could be detected only in a small range of ligand concentrations (0.005–0.04 M).

TABLE II

RATE CONSTANTS FOR THE REACTION $[Re(CO)_4X]_2 + 2L \rightarrow 2Re(CO)_4XL$ IN CCl_4 SOLUTION[a]

$[Re(CO)_4X]_2$	L	t, °C	10^3k, $M^{-1}\ sec^{-1}$
$[Re(CO)_4I]_2$	α-Clpy	40	1.1
		25	0.39
	$P(C_6H_5)_3$	55	15
		40	5.3
		25	1.6
	py	40	17
		25	5.3
		25[b]	3.1
	γ-pic	25	11
$[Re(CO)_4Br]_2$	$P(C_6H_5)_3$	40	91
		25	25
	py	25	75
	γ-pic	25	140
$[Re(CO)_4Cl]_2$	$P(C_6H_5)_3$	40	150
		25	54
	py	25	130
	γ-pic	25	310

[a] Supplementary material (specific kinetic data used to estimate values in this table) has been deposited as Document No. 9109 with the ADI, Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35-mm microfilm. Advance payment is required. Make checks payable to: Chief, Photoduplication Service, Library of Congress. [b] s-Tetrachloroethane as the solvent.

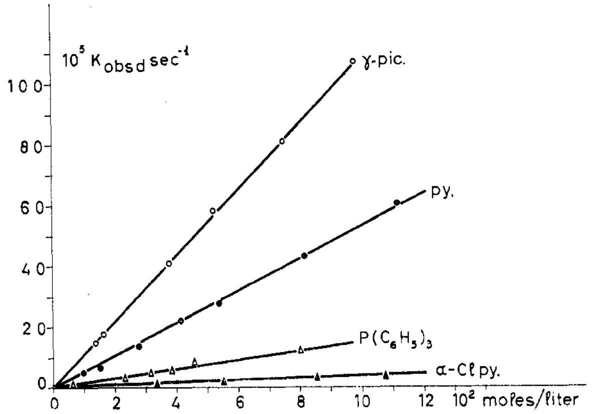


Figure 1.—Plot of k_{obsd} for the reaction of $[Re(CO)_4I]_2$ with different ligands at 25° in carbon tetrachloride.

TABLE III

ACTIVATION PARAMETERS FOR THE REACTION $[Re(CO)_4X]_2 + 2L \rightarrow 2Re(CO)_4XL$ IN CCl_4 SOLUTION

$[Re(CO)_4X]_2$	L	ΔH^*, kcal/mole	ΔS^*, eu
$[Re(CO)_4I]_2$	α-Clpy	13	−30
	$P(C_6H_5)_3$	15	−21
	py	14	−22
$[Re(CO)_4Br]_2$	$P(C_6H_5)_3$	16	−12
$[Re(CO)_4Cl]_2$	$P(C_6H_5)_3$	13	−21

The infrared spectrum in the carbonyl region of the reaction mixture at infinite time was in good agreement with that of the expected monosubstituted product previously prepared. The infrared spectra in the carbonyl stretching region of the reaction products are shown in Table IV. In Table V kinetic data for the reaction of $[Re(CO)_4I]_2$ with various reagents and their relative basicities are reported. Solvents such as acetone, nitromethane, and nitrobenzene gave very poor resolutions of the higher strong carbonyl absorption of $[Re(CO)_4X]_2$, so that the reaction could not be followed in these solvents.

TABLE IV[a,b]

Compound	Solvent[c]	Carbonyl stretching frequencies, cm^{-1}			
$Re(CO)_4IP(C_6H_5)_3$	A	2101 m	2018 s	2001 vs	1948 s
$Re(CO)_4BrP(C_6H_5)_3$	A	2107 m	2020 s	2003 vs	1947 s
$Re(CO)_4ClP(C_6H_5)_3$	A	2106 m	2018 s	2002 vs	1945 s
$Re(CO)_4I(py)$	A	2105 m	2005 vs		1938 s
	B	2108 m	2012 vs	1997 sh	1941 s
$Re(CO)_4Br(py)$	A	2110 m	2008 vs		1936 s
	B	2113 m	2012 vs	1996 sh	1932 s
$Re(CO)_4Cl(py)$	A	2111 m	2009 vs		1934 s
	B	2114 m	2015 vs	1997 sh	1928 s
$Re(CO)_4I(\gamma\text{-pic})$	A	2105 m	2009 vs		1938 s
	B	2107 m	2010 vs	1995 sh	1939 s
$Re(CO)_4Br(\gamma\text{-pic})$	A	2110 m	2008 vs		1935 s
	B	2111 m	2013 vs	1995 sh	1936 s
$Re(CO)_4Cl(\gamma\text{-pic})$	A	2111 m	2009 vs		1931 s
	B	2113 m	2013 vs	1995 sh	1923 s

[a] All spectra recorded on a Perkin-Elmer Model 621 spectrophotometer. [b] Abbreviations: vs, very strong; s, strong; m, medium; sh, shoulder. [c] A, carbon tetrachloride; B, *s*-tetrachlorethane.

TABLE V

RATE CONSTANTS FOR THE REACTION $[Re(CO)_4I]_2 + 2L \rightarrow 2Re(CO)_4IL$ IN CCl_4 SOLUTION AT 25°

L	k, M^{-1} sec^{-1}	ΔHNP[a]
α-Chloropyridine	3.9×10^{-4}	630
$P(C_6H_5)_3$	1.6×10^{-3}	573
Pyridine	5.3×10^{-3}	286
γ-Picoline	1.1×10^{-2}	220

[a] Difference in half-neutralization potential between L and N,N′-diphenylguanidine in nitromethane. The smaller ΔHNP, the more basic L. C. A. Streuli, *Anal. Chem.*, **31**, 1652 (1959); W. A. Henderson, Jr., and C. A. Streuli, *J. Am. Chem. Soc.*, **82**, 5791 (1960); C. A. Streuli, *Anal. Chem.*, **32**, 985 (1960).

Discussion

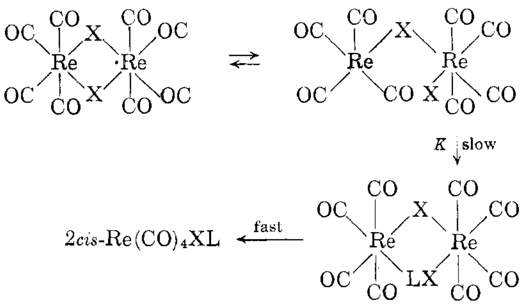
The structures of the compounds $[M(CO)_4X]_2$, where M = Mn, Tc, or Re and X = Cl, Br, or I, have been investigated recently.[7] The infrared spectrum in the carbonyl stretching region suggests either a D_{2h} (halogen bridging) or a C_{2h} (metal–metal bond) structure for the derivative $[M(CO)_4X]_2$. The infrared spectrum in the carbonyl bending region of $[Mn(CO)_4I]_2$ strongly suggests the D_{2h} structure. In the absence of any real evidence, we assume for the $[Re(CO)_4I]_2$ a structure similar to that of the analogous Mn(I) complexes with bridging halogens.

Reaction 1 follows the second-order rate law

$$\text{rate} = k[[Re(CO)_4X]_2][L] \qquad (3)$$

which is consistent with a bimolecular reaction. This could be explained by assuming that a rapid preequilibrium exists in solution between the dibridged form and a single bridged species. The nucleophilic attack may then occur on the vacant coordination position as is shown in Scheme I. Providing no rearrangement takes place, this sequence of reactions yields *cis*-$Re(CO)_4LX$ as is found experimentally. An alternative mechanism involves the formation of an activated complex in which the central atom has a higher coordination number. This first step should be followed by further rapid reaction to give the final product. It is pertinent to note that seven-coordinated rhenium complexes have been recently isolated.[8]

SCHEME I



The data reported in Table II show that the rates of reaction of $[Re(CO)_4X]_2$ decrease for changes in X in the order Cl > Br > I. The effect of different halogens in a bridged system on its extent of reaction was investigated by Chatt and Venanzi.[9] They studied the reaction of binuclear halogen-bridged complexes of platinum with monoamines and found that the equilibrium appears to lie increasingly in favor of the bridged complex as chlorine is replaced by bromine and bromine by iodine. Also this suggests that the iodo-bridged compound is more stable and may react less readily than the chloro compound, if the reactions occur through the second proposed mechanism. However, regardless of which of the two mechanisms is operating, the reactivity order of reaction 1 with changes in X can be explained on the basis of the different electronegativity of the halide ion. The more electronegative halide ion will induce the less electron density on the rhenium, making it more sensitive to nucleophilic attack. The second-order rate constants of reaction 1 decrease with changes in reagent in the order: γ-pic > py > $P(C_6H_5)_3$ > α-ClPy. The linear free energy relationship between the rate of reaction and the basicity of the ligand reported in Figure 2 shows that the decrease in rate constants parallels the decrease in basicity of the ligands. It may be pointed out also that $P(C_6H_5)_3$ appears to be a better nucleophile than is expected from its basicity. This result does agree

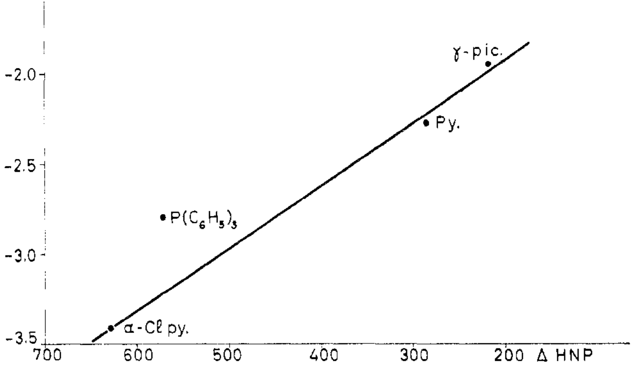


Figure 2.—The linear free energy relationship of the rate of reaction with the basicity of the nucleophile for the reaction of $[Re(CO)_4I]_2$ with different reagents at 25° in carbon tetrachloride. See footnote *a* of Table V for the definition of ΔHNP.

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with the previously reported results for carbonyl systems[10] which suggest that the ligands having phosphorus as donor atom react better than the ligands of the same basicity having nitrogen as donor atom. Such a behavior could be explained on the basis of the polarizability of the ligand atom, which will affect its nucleophilic strength toward these substrates. In fact, the metal in our system is of the class b[11] or soft acid type,[12] and it therefore will react with a P atom ligand easier than with a N atom ligand.

The activation parameters for reaction 1 are given in Table III: negative entropies of activation are in agreement with a bimolecular process in which there is considerable bond formation with the entering reagent in the transition state. The nature of the solvent appears to have little effect on the rate of reaction 1: this has been observed also for several other bimolecular reactions[13] in which the carbonyl derivatives of the transition metal are involved.

Finally, the carbonyl stretching frequencies of the isolated compounds are collected in Table IV. The four absorption bands observed in the range 2150–1900 cm^{-1} strongly support a *cis* structure; in fact, *cis*-$Re(CO)_4XL$ has C_s symmetry, which gives rise to four stretching frequencies ($3\ A' + A''$). The $A'(1)$ mode can be assigned to the band at lowest frequency, the $A'(3)$ mode to the band at highest frequency, and the $A'(2)$ and A'' modes to the bands at intermediate frequency.

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A Study of the Orthotungstate Condensation in Fused Equimolar Sodium Nitrate–Potassium Nitrate Solvent

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An electrochemical study of the orthotungstate condensation to ditungstate in an equimolar sodium nitrate–potassium nitrate solvent is reported. Selected values of the equilibrium constant for the reaction $2WO_4^{2-} \rightleftarrows W_2O_7^{2-} + O^{2-}$ at several temperatures are: 589°K, 3.3×10^{-3}; 621°K, 7.6×10^{-3}; 643°K, 1.8×10^{-2}. The values of the thermodynamic quantities $\Delta H°$ and $\Delta S°$ for this condensation are, respectively, 21.0 ± 0.3 kcal and 24.8 ± 0.4 eu.

Introduction

In aqueous solutions many oxy anions, such as silicate, are capable of condensing to form polyanionic species when the acidity of the solution is increased. Although phosphate oxy anions behave somewhat differently in aqueous solutions, polyphosphates being depolymerized at low pH values, Audrieth and co-workers[1] have pointed out that reactions analogous to the pH-dependent condensation of silicates occur with phosphates in certain high-temperature, solid-state processes. In general, condensed oxy anions can be considered acidic in terms of the Lux–Flood concept of acidity wherein an acid is defined as an oxide ion acceptor.

The group VIb oxides—CrO_3, MoO_3, and WO_3—have been shown to have acidic character when dissolved in a molten salt such as potassium nitrate.[2] This is in keeping with the infinite chain structure attributed to these oxides in the solid states.[3–5] Also the simplest condensed chromate, dichromate, has been shown to have acidic properties in fused alkali nitrate melts.[6] Presumably, then, it would be expected that in molten nitrates or similar high-temperature melts, the ortho oxy anions CrO_4^{2-}, MoO_4^{2-}, and WO_4^{2-} would tend to condense stepwise as the acidity of the melt were increased. However, potentiometric titrations in molten potassium nitrate[2] indicate that the species in equilibrium with the orthotungstate ion is tungstic oxide, WO_3, successive neutralization steps not being evident in the titration curves. This apparent absence of intermediate condensed species is unexpected in light of the relatively stable nature of dichromate in nitrate melts. This paper is a report of an investigation of the possibility of existence of ditungstate species in alkali nitrate melts.

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