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Kinetic Studies of Group VII Metals Carbonyls-IV-Dimerisation and Substitution Reactions of Mn(I) and Re(I) Pentacarbonyl Halides.

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Received April 8, 1967

Carbon monoxide replacements on rhenium pentacarbonyl halides with different neutral, mono- and bidentate entering groups are reported. The reactions proceed by a dissociation pathway, and the rate constants change with the nature of the halogen in the order Cl>Br>I. The dependence of the rate constants on the temperature has also been determined. For these reactions a mechanism is proposed which involves as a rate-determining step the formation of a five-coordinated intermediate, Re(CO)₄X, followed by a rapid reaction with the reagent ligand. The rates of formation of the rhenium and manganese dimeric, halogen-bridged tetracarbonyl compounds from the parent pentacarbonyl halides have also been determined. In these reactions an equilibrium is reached, which favours the monomeric form. The mechanism appears to be rather complicated and the dimerisation probably occurs through the same five-coordinated intermediate, M(CO)₄X. The rate of dimerisation in n-heptane varies in the order: Cl>Br>I and, for a given halide, Mn>Re.

Introduction

The carbonyls of rhenium are chemically similar to those of its congener manganese but few kinetic studies of substitution reactions of manganese and rhenium decacarbonyls have been reported and some of these are conflicting. For example, under drastic conditions, $Mn_2(CO)_{10}$ was reported to react with some phosphines, to yield the paramagnetic monomers $Mn(CO)_4L$,[1] and it has been proposed[2] that, the reaction of $Mn_2(CO)_{10}$ with triphenylphosphine and iodine involves homolytic Mn-Mn bond fission as the primary step, to form a pair of manganese pentacarbonyl radicals, $2Mn(CO)_5$, trapped in a solvent cage.[3,4] These radical-pairs can then recombine, decompose, undergo CO substitution by neutral ligands or be oxidised by O_2 or I_2. Wawersik and Basolo,[5] however, by reacting $Mn_2(CO)_{10}$ with $P(C_6H_5)_3$ (L) under preparative conditions have observed the formation of the monosubstituted, $(CO)_5Mn$-$Mn(CO)_4L$ and disubstituted derivatives, through a mechanism which involves the metal-CO cleavage as primary step. Similarly, $Re_2(CO)_{10}$ during its substitution reactions with $P(C_6H_5)_3$, gives the metal-metal bonded dimer $[Re(CO)_4L]_2$[6].

The rhenium carbonyl halides react with donors as do their manganese analogues. Thus, on heating their pentacarbonyl halides with suitable bases, disubstituted compounds of composition $Re(CO)_3XL_2$ are formed.[7-10] Only in one case was the monosubstituted rhenium compound obtained.[11] Thermal decomposition of the pentacarbonyl halides of Mn and Re in inert solvents results in the formation of the dimeric, halogen-bridged tetracarbonyl compounds, $[M(CO)_4X]_2$. These compounds react under rather mild conditions with a series of bases to yield the disubstituted tricarbonyl derivatives, $M(CO)_3XL_2$.[7,12] At the low concentrations required by the kinetic conditions, the monosubstituted $M(CO)_4XL$ have been obtained by treating $Mn(CO)_5X$[13] and $[Re(CO)_4X]_2$[14] with neutral ligands L.

The following is a schematic representation of the reactions known for manganese and rhenium derivatives:

$$\begin{array}{lr} M(CO)_5X \xrightarrow[\text{I}]{(+L,—CO)} M(CO)_4XL \xrightarrow[\text{II}]{(+L',—CO)} M(CO)_3XLL' & \\ (—CO)\quad \text{III} \qquad \text{IV} \quad (+L) & (1) \\ \qquad [M(CO)_4X]_2 & \end{array}$$

From a kinetic point of view, only in certain cases do rhenium carbonyl halides behave in a different way from their manganese analogues. We now intend to summarize briefly the kinetic studies so far reported in the literature.

The monomeric manganese carbonyl derivatives studied until now react at rates that are independent of

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the nature and concentration of the entering groups, but markedly dependent on the nature of the coordinated ligands.

The manganese pentacarbonyl halides, $Mn(CO)_5X$, undergo CO exchange[15] and CO substitution reactions[13] by a dissociative pathway, the reaction rates being first order in the complex and independent of the concentration of the entering group. In these systems, all five CO groups exchange at roughly the same rate.[16] Also in the reactions of monosubstituted manganese pentacarbonyl halides, $Mn(CO)_4XL$, with neutral ligands, L′, to form $Mn(CO)_3XLL'$, the reaction rates were found to be independent of the nature and concentration of the entering group. A steric acceleration associated with the bulkiness of the coordinated ligand L was found, as expected, for a dissociative mechanism.[17] In contrast to the results for $Mn(CO)_4XL$, the cleavage of halogen-bridged carbonyl compounds of Mn(I), $[Mn(CO)_4X]_2$, by pyridine derivatives has been found to follow a two-term rate law. The proposed mechanism required a rapid pre-equilibrium between the starting compound and partially labilized complex still reminescent of its original parent. This, in turn, slowly collapses to a reactive five-coordinate intermediate (k_1) and undergoes a concomitant nucleophilic attck of the entering group (k_2).[18] Thus, in the case of the dimer, the life of the intermediate is sufficiently long to allow it to react in a bimolecular way with the entering group. This behaviour is somewhat similar to that exhibited by the analogous rhenium derivatives (see below).

As far as rhenium carbonyls are concerned, kinetic studies have been made of carbon monoxide substitution for reaction (II) of scheme (1). Thus, in the CO substitution of $Re(CO)_4XL$ it appears that both S_N1 and S_N2 mechanisms may occur.[19,20] The rate constants for the dissociative process decrease with increasing atomic number of the halide X and decrease with changes in L from amine to phosphine bases, that is to say the «harder» the coordinated ligand L the more labile become the remaining «soft» CO groups.[19] The reaction of the halogen-bridged tetracarbonyl rhenium dimer to form $Re(CO)_4XL$ (reaction IV of scheme (1)) is of the second order and the proposed mechanism is analogous to that of the corresponding manganese compound. The reactivity order of $[Re(CO)_4X]_2$ is: Cl > Br > I, *i.e.*, the more electronegative the halide, the more sensitive is the central metal to nucleophilic attack.[14]

Generally speaking, manganese carbonyl dimers undergo metal-halide cleavage (via k_1) faster than the corresponding rhenium compounds, indicating that the metal-halide bond is stronger in the latter case and the Re-X bond strength varies as if M is a class (b) metal, *i.e.*, I > Br > Cl. For the k_2 term, the reactivity order is Re > Mn, suggesting that the nucleophilic displacement is facilitated by the larger rhenium atom. As far as the reactivity order of the entering group is concerned, a combination of the polarizability and basicity of the donor atom accounts for its nucleophilicity.

In order to complete the kinetic investigations on the reactions of the above scheme, we have examined the CO substitution reactions of $Re(CO)_5X$ with neutral monodentate and bidentate ligands, and the dimerisation in solution of both rhenium and manganese pentacarbonyl halides. In particular, it was hoped to clarify the sequence of the reactions which lead to the $M(CO)_3XLL'$, starting from $M(CO)_5X$ compounds.

Kinetic data are reported for the dimerisation reaction and for the substitution reaction:

$$2\,M(CO)_5X \rightarrow [M(CO)_4X]_2 + 2\,CO \qquad (2)$$

$$Re(CO)_5X + L\text{—}L \rightarrow Re(CO)_3X(L\text{—}L) + 2\,CO \qquad (3)$$

Furthermore, reaction (3) has been carried out by using monodentate ligand, and the final products were $Re(CO)_4XL$ or $Re(CO)_3XL_2$.

Experimental Section

Preparation and purification of materials. The 1,2-bis(diphenylphosphino)ethane was prepared according the procedure of Chatt and Hart.[21] The reagents o-phenylenebisdimethylarsine (Aldrich Chem. Co.), α,α′-bipyridyl (Fischer Scientific Co.), triphenylphosphine (Eastman Organic Chemicals Drug Houses Ltd.) were used as obtained without further purification. All the solvents were distilled under nitrogen. n-Heptane and thiophene free benzene were refluxed over sodium wire and then distilled.

Decacarbonylmanganese was prepared by the method of Calderazzo.[22] The compounds $Re(CO)_5X$ and $Mn(CO)_5X$ (X = Cl, Br and I) were prepared according to Kirkham *et al.*[23] $[Re(CO)_4Cl]_2$ was prepared following Abel *et al.*[7] Tetracarbonyl halide dimers of Mn(I), $[Mn(CO)_4X]_2$ (X = Cl, Br or I) were prepared according to a slightly modified literature procedure.[17] The complexes $Re(CO)_3X(L\text{-}L)$ (where L-L = 1,2-bis(diphenylphosphino)ethane, α,α′-bipyridyl and o-phenylenebisdimethylarsine), were obtained from rhenium pentacarbonl halides and the desired ligand as described in the literature.[7,23] The compounds $Re(CO)_4XP(C_6H_5)_3$ were prepared by treating tetracarbonyl halide dimers of rhenium with triphenylphosphine.[14] The compounds $Re(CO)_3X(py)_2$ were prepared as reported in the literature.[19] The identity and purity of all these compounds were confirmed by their carbon, hydrogen and nitrogen analysis. The I.R. spectra of these compounds in the C-O stretching region are given in Table I.

Kinetics. Two different experimental techniques were used in an attempt to investigate the kinetics of the reactions. The methods used were those described previously, which involve measuring changes during the reaction of (i), the infrared spectra in the C-O stretching region,[14] (ii) the visible and/or ultraviolet absorption spectra.[24] The reactions were followed spectrophoto-

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metrically by using a Perkin-Elmer Model 621 recording apparatus and an Optica CF-4 spectrophotometer, (450-300 mμ).

Table I. Carbonyl Stretching Frequencies, cm^{-1}, of Rhenium and Manganese Carbonyl Derivatives in CCl_4 Solution

Compound					Ref.
$Re(CO)_5Cl$	2151	2044	2013	1979	
$Re(CO)_5Br$	2149	2044	2014	1983	
$Re(CO)_5I$	2144	2039	2011	1986	
$[Re(CO)_4Cl]_2$	2114	2031	1998	1960	
$Re(CO)_4ClP(C_6H_5)_3$	2106	2018	2002	1945	
$Re(CO)_4Cl$(Diphos.)	2103	2016	2002	1939	
$Re(CO)_4Cl$(Diars.)	2101	2010	2000	1938	
$Re(CO)_4BrP(C_6H_5)_3$	2107	2020	2003	1947	
$Re(CO)_3Cl(py)_2$	2029	1931	1883		
$Re(CO)_3Cl$(Bipy)	2025	1923	1896*		
$Re(CO)_3Cl$(Diphos.)	2031	1954	1902*		(20)
$Re(CO)_3Cl$(Diars.)	2031	1953	1899*		
$Re(CO)_3Br(py)_2$	2027	1933	1887		
$Re(CO)_3Br$(Bipy)	2025	1926	1898*		
$Re(CO)_3I$(Bipy)	2024	1925	1899*		(19)
$Mn(CO)_5Cl$	2138	2054	2022	1999	(27)
$Mn(CO)_5Br$	2133	2050	2019	2001	(27)
$Mn(CO)_5I$	2125	2044	2016	2003	(27)
$[Mn(CO)_4Cl]_2$	2104	2045	2012	1975	
$[Mn(CO)_4Br]_2$	2098	2041	2012	1975	
$[Mn(CO)_4I]_2$	2087	2033	2008	1974	

All spectra recorded on a Perkin Elmer Model 621 Spectrophotometer. * Recorded in $CHCl_3$ solution.

Results and Discussion

Kinetics data for reactions (3) in different solvent are presented in Table II and IV. Table III, gives the activation parameters calculated from the rate constants determined at three different temperatures. For comparative purposes, the values relative to those for the reactions of $Mn(CO)_5X$ compounds are also given.

Table II. Reactions in CCl_4:
$Re(CO)_5X + L\text{-}L \rightarrow Re(CO)_3X(L\text{-}L) + 2\ CO$

Compound	L-L	Entering group concn. 10^2M	Temp., °C	$10^5 \times k_{obs}$ sec^{-1}	$10^5 \times k_{obs}$ sec^{-1} av.
$Re(CO)_5Cl$	bipyridyl	1.40	50	9.97	
»	»	6.50	»	10.21	9.92
»	»	14.00	»	9.59	
»	»	1.40	60	41.45	42.46
»	»	14.00	»	43.37	
»	»	1.45	65	88.8	85.4
»	»	14.50	»	82.4	
$Re(CO)_5Br$	»	1.50	50	1.64	1.87
»	»	14.40	»	2.10	
»	»	1.50	60	6.98	7.19
»	»	15.50	»	7.40	
»	»	1.50	65	15.2	15.2
$Re(CO)_5I$	»	1.50	60	0.99	0.94
»	»	15.00	»	0.88	
»	»	1.50	65	2.08	2.21
»	»	14.50	»	2.35	
»	»	2.80	70	3.28	3.31
»	»	14.80	»	3.35	
$Re(CO)_5Cl$	diphosphine	1.40	50	10.36	10.36
»	»	1.40*	»	6.74	6.86
»	»	14.40*	»	6.98	
»	»	1.40*	60	30.2	27.8
»	»	15.00*	»	25.59	
»	»	1.65*	65	58.3	59.4
»	»	14.40*	»	60.6	
»	diarsine	1.0	50	10.1	10.1

* Solvent = benzene.

Table III. Activation parameters for dissociative reactions of rhenium[a] and manganese[b] pentacarbonyl halides

Compound	ΔH^+ Kcal/mole		ΔS^+ e.u./mole	
	M=Re	M=Mn	M=Re	M=Mn
$M(CO)_5Cl$	30.5 ± 0.1 (30.4 ± 1)[c]	27.5	17.5 ± 0.3 (16.2 ± 3)[c]	15.7
$M(CO)_5Br$	29.45 ± 1.8	29.8	10.7 ± 5.4	18.9
$M(CO)_5I$	27.9 ± 5.6	32.2	2.2 ± 16.8	20.7

[a] Data in carbon tetrachloride (see Table II). [b] Values in chloroform from reference (13). [c] Data for the reaction of $Re(CO)_5Cl$ with P-P in benzene (Table II). The limits of error are standard deviations.

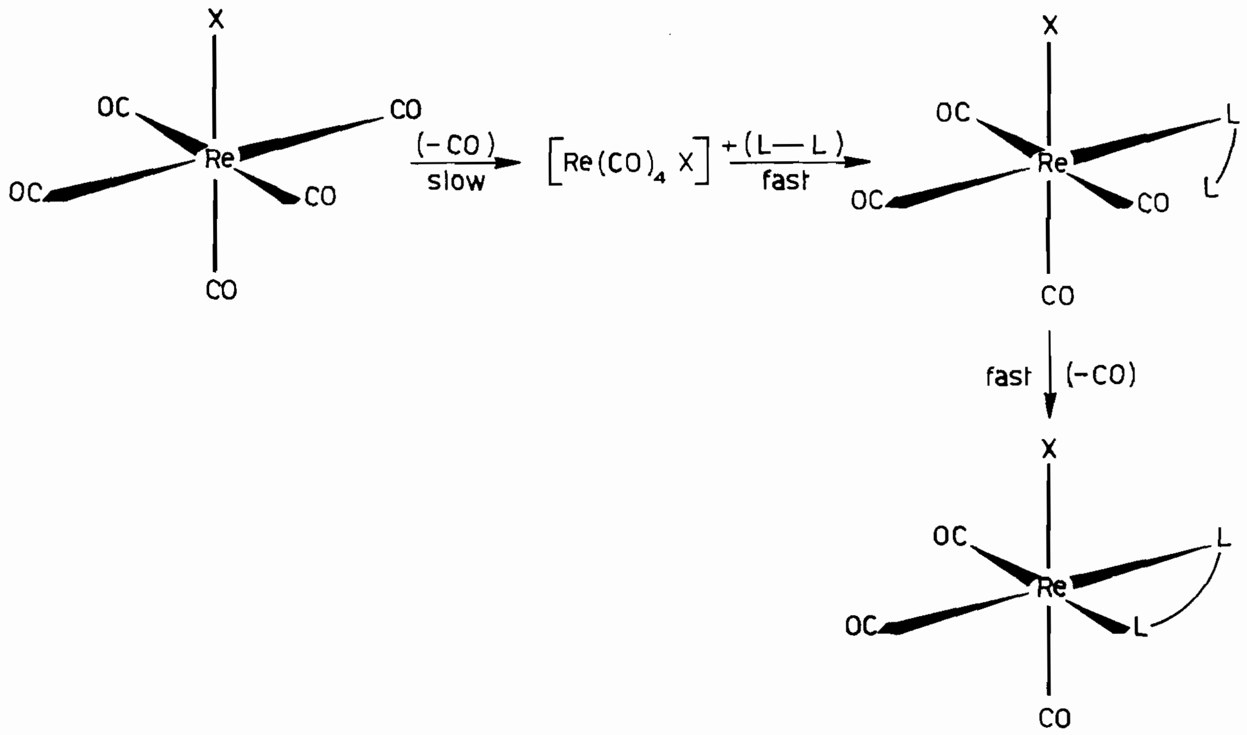
Rate data demonstrate that the rate of substitution is not dependent on the ligand and the reactions follow the first order rate law:

$$-d[\text{complex}]/dt = k[\text{complex}]$$

Furthermore, spectrophotometric and kinetic evidence clearly indicates that the subsequent replacement of the second carbon monoxide is very rapid. Thus, the rate determining step is the dissociation of carbon monoxide from $Re(CO)_5X$ and in some cases followed by the fast entry of L-L and rapid chelation, such a process accounts for the positive values of the activation entropies (Table IV) and is also in accord with the mechanism proposed for the carbon monoxide substitution by neutral ligands L in the analogous manganese derivatives, $Mn(CO)_5X$.[13] At this point it is pertinent to note that when the bidentate ligand is diphosphine or diarsine, we have spectrophotometric evidence (the IR spectra is reported in Table I) for the compound $Re(CO)_4X$(L-L). Nevertheless, the final product is the chelated derivative, $Re(CO)_3X$ (L-L). Although these reactions have been carried out in different solvents, in view of the smallness of the effect of the solvent upon the reactivity of these substrates in non-polar solvents, the comparison of the rate data can be made. Thus, manganese and rhenium pentacarbonyl halides both undergo a dissociative mechanism, with the manganese derivatives reacting (k_1) about one hundred times faster than corresponding rhenium compounds.

Table IV. Values of k_1 for the reactions in CCl_4 of some rhenium carbonyl derivatives with different monodentate ligand (Δ concn. ≃ 10) at 60°C

Reaction	$10^5 \times k_1$ sec^{-1}
$Re(CO)_5Cl + P(C_6H_5)_3 \longrightarrow Re(CO)_4ClP(C_6H_5)_3$	36
$Re(CO)_5Cl + py \longrightarrow Re(CO)_3Cl(py)_2$	42
$Re(CO)_5Br + P(C_6H_5)_3 \longrightarrow Re(CO)_4BrP(C_6H_5)_3$	7
$Re(CO)_5Br + py \longrightarrow Re(CO)_3Br(py)_2$	7



The positive values of activation entropy suggest in both cases a dissociative process, where some degrees of freedom are gained in the transition state. It is also observed in general that the second order rate constants are greater for Re compounds whereas for the dissociative processes the reverse order is observed.

As shown in Table II and IV, the replacement of carbon monoxide from rhenium pentacarbonyl halides proceeds by a dissociative mechanism and the first order rate constants decrease in the order Cl > Br > I. This is the same as the reactivity order found for the first-order CO substitution of the $Mn(CO)_5X$ compounds[13,15] and is expected on the basis of the greater Mn-C bond strength resulting from the presence of the more polarizable and less electronegative I^- relative to the Cl^-.* Consequently, the back donation Mn-CO in the latter case will be enhanced. The effect of the electronegativity of X upon the properties of the $M(CO)_5X$ derivatives is reflected, consistently, even in the CO stretching frequencies, which decrease in the order Cl > Br > I, although there is still some discussion about the significance of these frequencies.** The M-C double bonding, therefore increases in the reverse order, in agreement with infrared evidence.[26]

As far as the dimerization of $M(CO)_5X$ to form the halogen-bridged tetracarbonyl compounds, $[M(CO)_4X]_2$, is concerned, (2), data in Table V indicate that (i) the reaction rates decrease with increasing substrate concentration; (ii) the rate of dimerisation decreases with the nature of the coordinate halide, in the order Cl > Br > I, and (iii) the rates of dimerisation of rhenium pentacarbonyl halides are always slower than those of their manganese analogues.

Table V. Dimerisation reactions of rhenium and manganese carbonyl derivatives: $2M(CO)_5X \rightarrow [M(CO)_4X]_2 + 2CO$

Compound	Concn. $10^3 M$	Solvent	Temperature	$10^5 \times k_{obs}$ sec^{-1}
$Re(CO)_5Cl$	1.0	CCl_4	60	7.06
»	1.5	»	»	3.34
»	1.41	n-C_7H_{16}	»	10.47
»	2.46	»	»	8.20
$Mn(CO)_5Cl$	1.25	»	50	384 *
$Mn(CO)_5Br$	1.16	»	»	40.5 *
»	1.63	»	»	32.6 *
»	1.89	»	»	29.4 *
»	2.32	»	»	24.6 *
»	3.82	»	»	19.7 *
$Mn(CO)_5I$	1.087	»	50	1.141
»	2.857	»	»	1.416
»	2.174	»	60	2.06
»	3.10	»	»	1.06
»	0.66	»	80	39.8 *
» **	1.02	»	»	10.2 *
»	1.15	»	»	13.5 *
»	2.11	»	»	9.2 *

* Data obtained by visible and ultraviolet spectroscopy. ** In the presence of $[Mn(CO)_4I]_2$ (2.2×10^{-4} M).

It should be pointed out that each reaction was treated as a first order process, allowing for the existence of the equilibrium (the A_∞ used to calculate k_{obs} was estimated from the spectrum of an authentic sample of the dimer). Under these conditions, the plots of $\ln(A_\infty - A_t)$ *vs.* time remained linear for approximately one half-life. Thus, rate data reported in Table V are

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(*) *It should be noted, however, that the orders of activations enthalpies* and entropies are in apposite directions: Cl > Br > I for the rhenium compounds, I > Br > Cl for the manganese compounds, suggesting that steric and/or solvation factors may be responsible for this behavior.

(**) For a discussion concerning the reliability of the C-O stretching frequency shifts as a measure of the π-bonding abilities of ligands in substituted metal carbonyl complexes, see also reference (25).

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rimental limitations, the range of concentration of the extrapolated values. Unfortunately, because of expe- complex eamined was rather small, and this has prevented an extensive kinetic analysis (activation parameters, solvent-effect etc.) and has not allowed us to define confidently the general rate law for the dimerisation. Undoubtedly, an equilibrium involving the concentration of CO in solution is important, and the reactions should really be studied under conditions where the CO concentration is known.

Although no conclusive mechanistic evidence exists, we tentatively suggest that the species responsible for the dimerisation may be the labile, five-coordinated $M(CO)_4X$, formed by the loss of one CO group in a dissociative path.

In accord with such an hypothesis, the apparent rate of dimerisation for $M(CO)_5X$ compounds varies in the order $Cl > Br > I$, with the rhenium complex always less reactive than the manganese analogue. This is the same qualitative order as found for the dissociative processes of these substrates (see above). One can say that rhenium and manganese pentacarbonyl halides tend to dissociate to the same labile $M(CO)_4X$ intermediate which then may either dimerise or, in the presence of a suitable reagent L, yield $M(CO)_4XL$ derivatives.

In conclusion, looking at the above scheme (1) where the reaction of the dimers $[M(CO)_4X]_2$ with L is generally faster than that of $M(CO)_5X$ with L to give the same product $M(CO)_4XL$, it is very hard to say which of the two possible ways of obtaining the rhenium and manganese tetracarbonyl halide derivatives from $M(CO)_5X$ compounds is to be preferred. Depending on the experimental conditions (concn. of the reagents, solvent and temperature), and on the nature of the coordinated ligands, either reaction path may be followed.

Acknowledgments. We would like to thank the C.N.R. (Rome) and the N.A.T.O. for the financial support of this work.