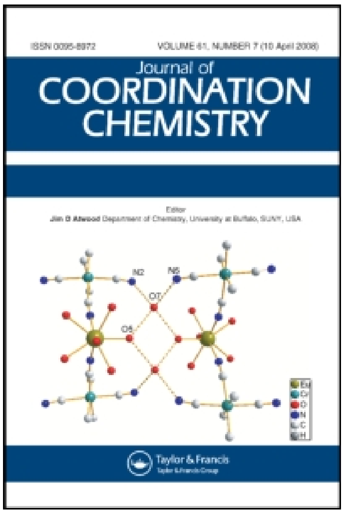

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OCTAHEDRAL METAL CARBONYLS. XXVIII.[1]
KINETICS AND MECHANISM OF OXIDATIVE ELIMINATION REACTIONS OF SUBSTITUTED GROUP VI-B METAL CARBONYLS WITH TIN- AND GERMANIUM-CONTAINING OXIDIZING AGENTS

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The kinetics and mechanism of reactions of (2,2′-dipyridyl)W$(CO)_4$ with $SnCl_4$, $(C_6H_5)SnCl_3$, $(n\text{-}C_4H_9)SnCl_3$ and $(C_6H_5)_2SnCl_2$, and of (*o*-phenanthroline)Mo$(CO)_4$ with GeI_4 have been investigated employing stopped flow and conventional kinetic techniques. The oxidizing agent-dependent rate laws are encompassed in a mechanism which involves reversible addition of two successive molecules of the oxidant to the substrate, followed by other, rapid, steps. For the reaction of $(C_6H_5)_2SnCl_2$ with (dipy)W$(CO)_4$ at 95–115°, a parallel reaction path probably involving rate-determining dissociation of CO was also observed. Rates were found to be very sensitive to the nature of the substituents bonded to the Group IV-A metal, being greatest for electron-withdrawing substituents. Different rate laws were observed for reactions which yielded products of different stereochemistries.

INTRODUCTION

Oxidative elimination reactions of metal carbonyls or derivatives involve replacement of one carbonyl by two formally one electron donating groups derived from the oxidizing agent,

$$M(CO)_n + TX \rightarrow M(CO)_{n-1}(T)(X) + CO \quad (X = Cl, Br, I) \qquad (1)$$

In these reactions, the formal oxidation state of the metal is increased by two, and its coordination number is increased by one. Thus, for derivatives of the Group VI–B metals (Mo, W), six-coordinate M(O) substrates yield seven-coordinate M(II) products, e.g.,

$$\underset{(a)}{cis\text{-}L_2M(CO)_4} + TX \rightarrow \underset{(b)}{L_2M^{II}(CO)_3(T)(X)} + CO \qquad (II)$$

Only for L_2 = 2, 2′-dipyridyl (dipy) and *o*-phenanthroline (phen) and $TX = HgCl_2$ and $HgBr_2$ have the kinetics and mechanism of reaction (II) been investigated,[2,3] despite the fact that preparative studies for reactions of such substrates with a variety of oxidizing agents have been reported. Versatile series of oxidants include the Group IV-A halides and their organic derivatives, ($TX = R_nM'X_{4-n}$; R = alkyl, aryl; M' = Sn, Ge; X = Cl, Br, I; n = 0–2), which have been extensively studied by Kummer and Graham[4] and by others.[5] These are of especial interest in that these oxidants yield two stereochemically different products (II-b), depending upon the identity of M', R and X. The structures of representative complexes of the two geometries, which approximate the capped octahedron and the capped trigonal prism, have been determined through use of X-ray crystallographic methods.[6–8]

To assist in the development of an understanding of the systematics of the kinetics and mechanism of oxidative elimination reactions, and to probe the question as to whether or not the formation of the two isomeric products is kinetically controlled, studies of the kinetics of reactions of *cis*-$L_2M(CO)_4$ substrates with various Group IV-A oxidizing agents have been undertaken. The present report describes kinetic studies of reactions which yield a single isomeric product, of (dipy)W$(CO)_4$ with $(C_6H_5)SnCl_3$, $(n\text{-}C_4H_9)SnCl_3$ and $(C_6H_5)_2SnCl_2$, and of (phen)Mo$(CO)_4$ with GeI_4.

EXPERIMENTAL SECTION

General

The preparation of all substrates, and reactions employed in product identification were carried out

**

under an atmosphere of prepurified nitrogen. Infrared spectra were recorded on a Perkin Elmer Model 621 grating spectrophotometer, and were calibrated against a band of water vapor at 1869.4 cm^{-1}.[9]

Preparation and purification of chemicals

The substrate (dipy)$W(CO)_4$ was prepared through use of the method of Stiddard, using xylene as the refluxing solvent.[10] (Phen)$Mo(CO)_4$ was synthesized through use of the method of Angelici and Graham.[11] Toluene was twice distilled from sodium, while chlorobenzene and 1,2-dichloroethane were distilled from P_2O_5. All manipulations involved in the purification of the oxidizing agents were carried out in a nitrogen-flushed glove bag. Germanium tetraiodide (99.999%, Alfa Inorganics) was further purified according to the method of Foster and Williston.[12] Tin tetrachloride and *n*-butyltin trichloride (Alfa) and phenyltin trichloride (Columbia Organic Chemicals) were distilled under reduced pressure (*c.* 0.1 torr), while diphenyltin dichloride (ROC/RIC) was twice recrystallized from petroleum ether (boiling range 35–60°), was dried under a stream of nitrogen, and was then stored in a dessicator until use.

Determination of reaction rates

The systems studied exhibited a wide range of reactivity, thus necessitating several different methods of study. The fastest reactions (for $SnCl_4$, $(C_6H_5)SnCl_3$ and GeI_4) were studied at $25.0 \pm 0.1°$ employing an Aminco-Morrow stopped flow system coupled to a Bausch and Lomb high intensity monochromator. The cell temperature was maintained through use of an external circulating bath and was monitored employing an iron-constantan thermocouple attached directly to the cell window. Data were taken from traces of per cent transmittance *vs.* time at 500 nm through use of a storage oscilloscope and polaroid camera or (for the slower reactions) a Sargent Model MR external recorder. The other reactions were monitored on a Beckman DU-2 direct reading spectrophotometer (at 500 nm) employing manual sampling techniques.[13]

Pseudo first order reaction conditions were employed for all runs through use of at least twenty-fold excesses of oxidizing agent. Where plots of ln $(A_t - A_\infty)$ *vs.* *t* were not linear over two or more half-lives (for $(C_6H_5)_2SnCl_2$ and GeI_4, where some product decomposition was observed for the t_∞ solutions), pseudo first-order rate constants were obtained through use of Guggenheim's method[14] from data taken over four or five half lives. These plots were typically linear to two or more half lives. Values of k_{obsd} and of the first, second and third order rate constants were calculated employing a non-linear least squares computer program. Values of k_{obsd} which deviated from the mean by more than two standard deviations were rejected.

Identification of reaction products

The products of the reactions of (dipy)$W(CO)_4$ with the tin-containing oxidizing agents had previously been prepared by Kummer and Graham[4] under somewhat different conditions than those employed in kinetic runs. Accordingly, these reactions (except for $SnCl_4$) were rerun under kinetic conditions employing 12–20-fold excesses of the appropriate oxidizing agent. The residues after solvent removal were dissolved in dichloromethane, and their carbonyl stretching spectra were recorded and compared to those reported in that solvent by Kummer and Graham.[4] In every case these spectra indicated the products obtained to be identical to those reported by those workers, *i.e.*, the capped octahedral isomers were obtained exclusively.[4,6] While (phen)$Mo(CO)_3(I)(GeI_3)$ had not previously been prepared, the very similar (dipy)$Mo(CO)_3(I)(GeI_3)$ has been, and its infrared spectrum has been exhibited.[4] Infrared[4] and X-ray[8] evidence indicate this to be the capped trigonal prismatic isomer. The phen complex was prepared under kinetic conditions employing a ten-fold excess of GeI_4. After workup (see above), its carbonyl stretching spectrum in dichloromethane was found to be almost identical to that reported for the dipy analogue (ν_{CO}: 1939 (very strong), 1975 (medium strong), 2034 (strong) cm^{-1}).

RESULTS AND DISCUSSION

Rate (k_{obsd}) data for the oxidative elimination reactions of metal carbonyl substrates with $(C_6H_5)SnCl_3$, $(n\text{-}C_4H_9)SnCl_3$, $(C_6H_5)_2SnCl_2$ and GeI_4 are presented in Table I. For $SnCl_4$ the reaction was found to be too fast for study by stopped flow methods. The other tin-containing oxidizing agents all yield linear plots of k_{obsd} *vs.* $[R_nSnCl_{4-n}]^2$ over the entire range of concentra-

TABLE I

Pseudo first order rate constants (k_{obsd}) for reactions of *cis*-$L_2M(CO)_4$ substrates with group IV-A metal oxidants

Substrate + oxidant *T*, °C, solvent	[Oxidant] *M*	Rate constant sec^{-1}
(dipy)$W(CO)_4$ + $(C_6H_5)SnCl_3$		k_{obsd}[a]
25.0 ± 0.1°, toluene	0.0389	0.0582
	0.181	21.2
	0.226	37.5
	0.271	54.6
	0.318	70.9
	0.359	95.6
(dipy)$W(CO)_4$ + $(n\text{-}C_4H_9)SnCl_3$		10^4k_{obsd}[a]
25.0 ± 0.1°, toluene	0.0308	0.161
	0.0583	0.403
	0.0863	0.608
	0.178	2.11
	0.238	3.56
	0.275	4.88
	0.323	6.36
	0.361	8.40
(dipy)$W(CO)_4$ + $(C_6H_5)_2SnCl_2$		10^4k_{obsd}[a]
95.0 ± 0.05°, Chlorobenzene	0.0343	0.583
	0.0405	0.701
	0.0471	0.639
	0.0497	1.07
	0.0570	0.745
	0.0626	1.05
	0.0674	1.06
	0.0805	1.65
	0.0993	1.40
	0.137	2.76
	0.175	3.88
	0.234	6.06
	0.262	6.98
	0.290	8.64
	0.296	9.59
	0.426	18.0
105.0 ± 0.05°	0.0456	2.35
	0.0539	2.64
	0.0712	3.65
	0.119	4.48
	0.158	6.12
	0.174	7.12
	0.188	7.26
	0.224	9.73
	0.263	12.7
115.0 ± 0.05°	0.0704	7.07
	0.101	8.59
	0.124	9.37
	0.158	12.5
	0.186	13.5
(phen)$Mo(CO)_4$ + GeI_4		10^3k_{obsd}[b]
25.0 ± 0.1°, 1,2-dichloroethane	0.00436	0.635
	0.00629	1.00
	0.00724	0.804
	0.00809	0.874
	0.00889	1.17
	0.0113	1.42
	0.0118	1.26
	0.0153	1.69
	0.0162	1.84
	0.0218	2.44
	0.0254	2.96
	0.0269	3.30
	0.0334	3.89
	0.0370	4.17

[a] Calculated from plots of ln $(A_t\text{–}A\infty)$ *vs*. *t*.

[b] Calculated through use of Guggenheim's method.

tions of the oxidizing agents. For $(C_6H_5)SnCl_3$ and $(n\text{-}C_4H_9)SnCl_3$ in toluene, extrapolations of these plots to a zero concentration of the tin compound yield a zero rate, while for reaction of $(C_6H_5)_2SnCl_2$ at 95–115° in chlorobenzene, finite intercepts were observed (Figure 1), indicative of a competing first order process. Thus, data for these systems can be emcompassed in a rate law,

$$-d[(\text{dipy})W(CO)_4]/dt = k_1[(\text{dipy})W(CO)_4] + k_3[(\text{dipy})W(CO)_4][R_nSnCl_{4-n}]^2 \qquad (III)$$

The first and third order rate constants for these reactions are presented in Table II. The first order term, observed only at elevated temperatures, is best ascribed to rate-determining dissociation of CO, followed by attack of $(C_6H_5)_2SnCl_2$ at the resulting five-coordinated activated complex or intermediate, and other, rapid steps. This reaction was carried out in chlorobenzene solvent for comparison to the results of Graham and Angelici for the reaction of (dipy)$W(CO)_4$ with various Lewis bases (alkyl phosphites) at 100–120°.[15] The rate law for these reactions contained a ligand-independent term, of comparable magnitude to that observed in this study. However, those results were puzzling in that different values of k_1, the rate constants for presumed carbonyl dissociation, were observed for various nucleophiles, and negative entropies of activation were obtained for a process which should involve more bond breaking than bond making in the transition state. The data of Graham and Angelici, together with other data for that system, will be discussed in detail elsewhere.[16] However, the observation of rate laws containing a term dependent only upon substrate concentration with approximately equal rates at comparable temperatures for two very different reactions of the same substrate, together with the positive entropy of activation obtained in the present study, provides strong support for the mechanism proposed in both systems.

The third order term, observed for all three oxidizing agents, is consistent with the overall mechanism proposed for reactions of $HgCl_2$ with similar substrates.[2,3] This mechanism,

$$\begin{aligned}&(\text{dipy})\text{W(CO)}_4 + TX \underset{k_5}{\overset{k_4}{\rightleftharpoons}} (\text{dipy})\text{W(CO)}_4\cdot TX\\&(\text{dipy})\text{W(CO)}_4\cdot TX + TX \underset{k_6}{\rightarrow} (\text{dipy})\text{W(CO)}_4\cdot 2TX \qquad \text{(IV)}\\&(\text{dipy})\text{W(CO)}_4\cdot 2TX \xrightarrow{\text{fast}} (\text{dipy})\text{W(CO)}_3(T)(X) + \text{CO} + TX\end{aligned}$$

involves the presumed successive formation of 1:1 and 1:2 "adducts" of the oxidizing agent and substrate, followed by other rapid steps. Mechanism (IV) yields the steady-state expression,

$$-d[(\text{dipy})\text{W(CO)}_4]/dt = k_4k_6[(\text{dipy})\text{W(CO)}_4][TX]^2/(k_5 + k_6[TX]). \qquad \text{(V)}$$

In the limit, $k_5 >> k_6$, this expression simplifies to the observed rate law; for $HgCl_2$, this limiting rate law was observed only at very low concentrations of the oxidizing agent.[2,3]

For the reactions of $(C_6H_5)_2SnCl_2$, the carbonyl stretching spectrum obtained for the product, as well as that reported by Kummer and Graham,[4] indicated the presence of only one product, the capped octahedral isomer. Thus this isomer evidently is formed *via* two independent paths. The rates of these reactions were found to increase in the order $(C_6H_5)_2SnCl_2 < (n\text{-}C_4H_9)SnCl_3 < (C_6H_5)SnCl_3 < SnCl_4$, in the order of increasing electron withdrawal from Sn, as might be expected for reactions in which these species are functioning as oxidizing agents. It is of further interest to note that the third order rate constants increase by perhaps 10^8–10^{10} along the series. In contrast,

TABLE II

Rate constants and activation parameters for reactions of *cis*-$L_2M(CO)_4$ substrates with group IV-A metal oxidants

Substrate, Oxidant T, °C, Solvent	k_1 (sec^{-1})	k_2 M^{-1}sec^{-1}	k_3 M^{-2} sec^{-1}
$(dipy)W(CO)_4 + C_6H_5SnCl_3$			
25.0 ± 0.1°, toluene	—	—	[a]$(7.43 \pm 0.20) \times 10^2$
$(dipy)W(CO)_4 + n\text{-}C_4H_9SnCl_3$	—	—	$(6.21 \pm 0.10) \times 10^{-3}$
25.0 ± 0.1°, toluene			
$(dipy)W(CO)_4 + (C_6H_5)_2SnCl_2$[b]			
95.0 ± 0.05°, chlorobenzene	$(6.87 \pm 0.81) \times 10^{-5}$	—	$(9.55 \pm 0.13) \times 10^{-3}$
105.0 ± 0.05°	$(2.34 \pm 0.14) \times 10^{-4}$	—	$(1.48 \pm 0.04) \times 10^{-2}$
115.0 ± 0.05°	$(6.15 \pm 0.45) \times 10^{-4}$	—	$(2.25 \pm 0.22) \times 10^{-2}$
$(phen)Mo(CO)_4 + GeI_4$			
25.0 ± 0.1°, 1,2-dichloroethane	—	$(1.12 \pm 0.03) \times 10^{-1}$	—

[a] Limits of error—one standard deviation.
[b] $\Delta H_1^* = 30.7 \pm 2.6$ kcal/mole; $\Delta S_1^* = 5.3 \pm 7.2$ e.u.
$\Delta H_3^* = 11.3 \pm 0.2$ kcal/mole; $\Delta S_3^* = -37.6 \pm 0.5$ e.u.

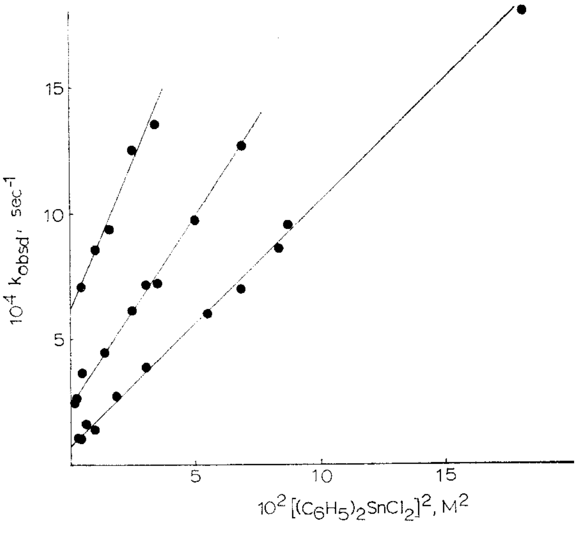

FIGURE 1 Plots of k_{obsd} *vs.* $[(C_6H_5)_2SnCl_2]^2$ for the reaction of (2,2′-dipyridyl)$W(CO)_4$ with diphenyltin dichloride in toluene solvent at various temperatures.

changes in the basicities of o-phenanthrolines as a consequence of substitution in the 5-position of the phen ring system resulted in only a three-fold change in reaction rate of the (5-X-phen)Mo(CO)$_4$ substrates with mercuric chloride.[3]

If it is assumed that the electrophilic attack at the substrates involves an interaction between filled metallic d_π orbitals and vacant orbitals of appropriate symmetry of the oxidizing agents, presumably p orbitals, these trends in reactivity suggest a relatively small change in metallic d_π electron density in the (5-X-phen)Mo(CO)$_4$ substrates despite appreciable changes in the basicities of the 5-X-phen substituents.

However, it should also be noted that there is no obvious trend in reactivity of the Sn compounds as a function of the carbonyl stretching frequencies for the reaction products; for example, rates of reaction of (dipy)W(CO)$_4$ with (C_6H_5)SnCl$_3$ and (n-C_4H_9)SnCl$_3$ differ by five orders of magnitude, the carbonyl stretching frequencies of the corresponding (dipy)W(CO)$_3$(T)(X) products differ by five cm^{-1} at most.

The reaction of (dipy)Mo(CO)$_4$ with GeI$_4$ in toluene solvent at 25.0° was also studied because the infrared spectrum of the reaction product, together with the infrared spectrum[4] and an X-ray structural determination for (dipy)W(CO)$_3$(Br)(GeBr$_3$)[8] indicate it to possess capped trigonal prismatic geometry. Thus this study constitutes an initial effort to ascertain possible influences of reaction mechanism on the observed product stereochemistry.

Rate data for this reaction are presented in Table I. A plot (not shown) of the pseudo first order rate constants (k_{obsd}) $vs.$ [GeI$_4$] is linear, and, when extrapolated to zero concentration of GeI$_4$ affords a zero rate, consistent with a rate law,

$$-d[(\text{phen})\text{Mo(CO)}_4]/dt = k_2[(\text{phen})\text{Mo(CO)}_4][\text{GeI}_4]. \qquad \text{(VI)}$$

The second order rate constant is given in Table II. The observed rate law is also consistent with mechanism (IV), for which $k_6[\text{GeI}_4] >> k_5$. However, the data provide no indication that at low [GeI$_4$] (to $4 \times 10^{-3}\,M$), k_5 becomes significant relative to $k_6[\text{GeI}_4]$. Thus it would appear more reasonable to attribute the rate law to formation of but a single adduct in the rate-determining step,

$$\begin{array}{r} (\text{phen})\text{Mo(CO)}_4 + \text{GeI}_4 \xrightarrow{k_2} (\text{phen})\text{Mo(CO)}_4\cdot\text{GeI}_4 \\ \swarrow^{\text{fast}} \qquad \\ (\text{phen})\text{Mo(CO)}_3(\text{GeI}_3)(\text{I}) + \text{CO} \quad \text{(VII)} \end{array}$$

At present it is not possible to say whether or not the observed differences in rate law are related to the contrasting stereochemistry of the reaction products, or precisely what influences (transition metal atom, substituents on M', identify of M') contribute to changes in reactivity and rate law. Such studies will necessarily involve systems which yield mixtures of both isomers, and will thus require use of more specialized kinetic techniques.

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REFERENCES

1. Part XXVII: M. N. Memering and G. R. Dobson, *J. Inorg. Nucl. Chem.*, in press.
2. J. W. McDonald and F. Basolo, *Inorg. Chem.* **10,** 492 (1971).
3. R. T. Jernigan and G. R. Dobson, *Inorg. Chem.* **11,** 81 (1972).
4. R. Kummer and W. A. G. Graham, *Inorg. Chem.* **7,** 310 (1968).
5. For a review of Group IV-A derivatives of metal carbonyls, see, E. H. Brooks and R. J. Cross, *Organometal. Chem. Rev.* **6A,** 227 (1970).
6. M. Elder and D. Hall, *Inorg. Chem.* **8,** 1268 (1968).
7. M. Elder and D. Hall, *Inorg. Chem.* **8,** 1273 (1968).
8. E. M. Cradwick and D. Hall, *J. Organometal. Chem.* **25,** 91 (1970).
9. E. K. Plyler, A. Danti, R. L. Blaine and E. D. Tidwell, *J. Res. Nat. Bur. Stand., Sect. A,* **64,** 29 (1964).
10. M. H. B. Stiddard, *J. Chem. Soc.* 4712 (1962).
11. R. J. Angelici and J. R. Graham, *Inorg. Chem.* **6,** 988 (1967).
12. L. G. Foster and A. F. Williston, *Inorg. Syn.* **2,** 113 (1946).
13. G. R. Dobson and J. R. Paxson, *J. Chem. Educ.* **49,** 67 (1972).
14. See, *e.g., Comprehensive Chemical Kinetics,* C. H. Bamford and C. F. H. Tipper. Eds., Elsevier Publishing Co., New York, Vol. 1, 1969, pp. 388–390.
15. J. R. Graham and R. J. Angelici, *J. Amer. Chem. Soc.* **87,** 5590 (1965).
16. M. N. Memering and G. R. Dobson, manuscript in preparation.