

it is clear that the following ligands do not significantly labilize the remaining CO groups when introduced into Cr(0), Mo(0), and Mn(I) octahedral complexes: CO, CN-R, RO₂S⁻, PR₃, P(OR)₃, and As(C₆H₅)₃. On the other hand, investigations of [XMo(CO)₅]⁻¹⁹ (X = Cl, Br, or I), (py)Mo(CO)₅,³ Cr(CO)₄(dipy),² Cr(CO)₄(*o*-phen), Cr(CO)₄(1,2-diamino-2-methylpropane), XMn(CO)₅ (X = Cl, Br, or I),²⁰ HMn(CO)₅,²¹ and Mn(CO)₄(hfac), where hfac = hexafluoroacetylacetonate,²² indicate that the CO groups in these complexes have been substantially labilized as a result of the introduction of the following ligands into the complexes: Cl⁻, Br⁻, I⁻, H⁻, py, dipy, *o*-phen, 1,2-diamino-2-methylpropane, and hfac. The donor atoms

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of these labilizing ligands are either first row elements or halogens. The nonlabilizing ligands, however, exhibit second- and third-row element donor atoms with the exception of CO and CN-R. In general, the labilizing ligands could be classified as class a or "hard" bases, and the nonlabilizing ligands, as class b or "soft" bases.²³ Although it is not clear why these relationships should necessarily be valid, they do provide a useful basis for the synthesis of metal carbonyl complexes containing CO groups of a desired lability.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA 50010

Kinetic Studies of Group VI Metal Carbonyl Complexes. V. Substitution Reactions of *o*-Phenanthroline Complexes of Molybdenum and Tungsten Hexacarbonyls

BY JAMES R. GRAHAM AND ROBERT J. ANGELICI

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Complexes of the type M(CO)₄(X-*o*-phen), where M = Mo and W, undergo substitution reactions with phosphine and phosphite ligands, L, to form *cis*-M(CO)₃(L)(X-*o*-phen) as the reaction product. The rates of reaction follow the two-term rate law: rate = $k_1[M(CO)_4(X-*o*-phen)] + k_2[M(CO)_4(X-*o*-phen)][L]$. The rate constant k_1 increases as the pK_a of the substituted *o*-phenanthroline is increased in a manner which is predictable from a linear free energy relationship. The second-order rate constant, k_2 , which also follows a linear free energy relationship surprisingly well, decreases as the pK_a of the X-*o*-phen is increased. The magnitude of k_2 is determined by such factors as the ligand structure and basicity, the amount of steric hindrance caused by the substituted *o*-phenanthroline, and the basicity of the *o*-phenanthroline. All of these factors are considered in discussing possible reaction mechanisms for the portion of the rate law governed by k_2 .

Introduction

Only a relatively small number of octahedral transition metal complexes have been found to undergo reactions with nucleophiles at a rate which is dependent upon the concentration of the nucleophilic reagent. Most of the reactions studied and found to exhibit a ligand-dependent reaction rate involved positively charged metal ions,¹ although a few cases have been reported where the central metal atom was in a zero oxidation state.²⁻⁴ The mechanism for these reactions can be and in some cases has been discussed in terms of a displacement (S_N2) mechanism. Since reactions of this type for octahedral complexes are so rare and since alternate mechanisms which do not involve a nucleo-

philic attack can be proposed for most of the reactions studied, the validity of assigning a displacement mechanism is in some dispute.

A number of reasons have been given¹ for not expecting octahedral complexes to react by displacement mechanisms and these reasons involve factors ranging from steric repulsions resulting from an expanded coordination shell to electrostatic repulsions between the metals with filled or partially filled d orbitals and the attacking nucleophile. Despite this, Mo(CO)₆ has been found⁵ to react with phosphines and phosphites at a rate which is dependent on the concentration of the ligand. The most plausible mechanism which explains the second-order character of these reactions is a displacement mechanism at the Mo atom, although an attack at the carbonyl C cannot be ruled out. Since the octahedral group VI metal hexacarbonyls probably react by a displacement mechanism, considerable support is thereby given to the operation of this same type

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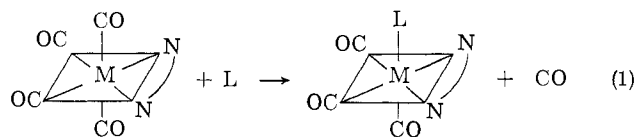
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of mechanism for other octahedral complexes of Mo and W which have been found to show ligand-dependent reaction rates.

In the present paper the kinetics of the reaction of $M(\text{CO})_4(\text{N-N})$ (where $M = \text{Mo}$ or W and $\text{N-N} = \text{X-}o\text{-phenanthroline}$ or 1,2-diamino-2-methylpropane) with various phosphines and phosphites are reported (eq 1). These complexes of Mo and W have been



found to react with L at a rate which is dependent upon the concentration of L. Since this system is kinetically fairly simple to study and yet very versatile in the number of factors which can be varied, it was hoped that these investigations would answer many of the questions concerning octahedral complexes undergoing displacement reactions.

Experimental Section

The methods used in determining the reaction rates were the same as those described earlier.⁵ The preparation, purification, and identification of the starting complexes and reaction products were described in considerable detail in the same paper.⁵ The solvents, 1,2-dichloroethane and chlorobenzene, were purified by fractional distillation. The ligands $\text{P}(\text{OC}_2\text{H}_5)_3$ (Matheson Coleman and Bell), $\text{P}(\text{C}_6\text{H}_5)_3$, and $\text{P}(\text{OC}_6\text{H}_5)_3$ (Eastman Chemicals) were used as obtained. $\text{P}(n\text{-C}_4\text{H}_9)_3$ (Aldrich Chemical Co.) was purified by fractional distillation at reduced pressure. $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ and $\text{PO}_3\text{C}_6\text{H}_9$ were prepared and purified by the method used by Verkade, *et al.*⁶

Results

$\text{Mo}(\text{CO})_4(\text{N-N})$ and $\text{W}(\text{CO})_4(\text{X-}o\text{-phen})$, where $\text{N-N} = \text{X-}o\text{-phen}$ or 1,2-diamino-2-methylpropane, have been found to react with phosphines and phosphites, L, to form *cis*- $\text{M}(\text{CO})_3(\text{N-N})(\text{L})$ as a reaction product. In the case where the bidentate ligands are substituted *o*-phenanthrolines, this is the only product formed (eq 1). When the complex is $\text{Mo}(\text{CO})_4(\text{diamine})$, where diamine = 1,2-diamino-2-methylpropane, not only is $\text{Mo}(\text{CO})_3(\text{diamine})(\text{L})$ formed ($\text{L} = \text{P}(\text{OCH}_2)_3\text{CCH}_3$) as a reaction product but $\text{Mo}(\text{CO})_4\text{L}_2$ and $\text{Mo}(\text{CO})_3\text{L}_3$ also are formed. The $\text{Mo}(\text{CO})_3\text{L}_3$ is formed from the $\text{Mo}(\text{CO})_3(\text{diamine})(\text{L})$ by the further reaction of this complex with excess L, as observed spectroscopically.

The rate of reaction of $\text{M}(\text{CO})_4(\text{N-N})$ with L is dependent upon the ligand concentration used and obeys a two-term rate law (eq 2). Since all of the reactions

$$\text{rate} = k_1[\text{M}(\text{CO})_4(\text{N-N})] + k_2[\text{L}][\text{M}(\text{CO})_4(\text{N-N})] \quad (2)$$

were carried out under pseudo-first-order conditions (*i.e.*, $[\text{L}] > 15[\text{M}(\text{CO})_4(\text{N-N})]$), the observed rate constants, k_{obsd} , obtained from plots of $\ln(A - A_\infty)$ vs. time are of the form $k_{\text{obsd}} = k_1 + k_2[\text{L}]$. Values of k_{obsd} at different $[\text{L}]$ and at different temperatures are listed in Tables I-III. Values of k_1 and k_2 which are

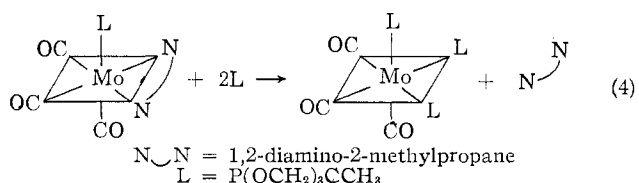
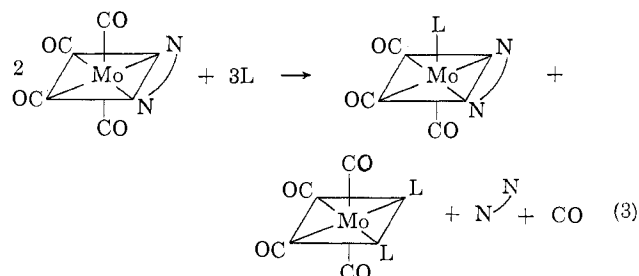
TABLE I

RATES OF REACTION OF $\text{Mo}(\text{CO})_4(\text{X-}o\text{-phen})$ WITH $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ IN $\text{CH}_2\text{ClCH}_2\text{Cl}$ AT 47.9°

X- <i>o</i> -phen no.	X	$[\text{P}(\text{OCH}_2)_3\text{CCH}_3], M$	$10^4 k_{\text{obsd}}, \text{sec}^{-1}$
1	5,6-Dichloro	0.0284	0.668
		0.0800	0.792
		0.200	1.08
		0.400	1.63
		0.800	2.52
2	5-Nitro	0.0284	0.628
		0.0800	0.832
		0.200	1.21
		0.400	1.79
		0.800	2.87
3	4,7-Diphenyl	0.0284	1.06
		0.0800	1.14
		0.200	1.21
		0.400	1.34
		0.800	1.51
4	Unsubstituted	0.0776	1.22
		0.156	1.37
		0.365	1.58
		0.656	1.83
		1.09	2.50
5	3-Methyl	1.41	2.74
		0.0776	1.33
		0.3650	1.59
		0.518	1.70
		1.411	2.64
6	3,5,7-Trimethyl	0.156	1.75
		0.365	1.95
		0.656	2.18
		1.41	2.65
		0.0776	2.04
7	3,4,7,8-Tetramethyl	0.365	2.28
		0.656	2.48
		1.09	2.74
		0.156	2.26
		0.365	2.37
8	3,4,6,7-Tetramethyl	0.656	2.49
		1.41	2.86

listed in Tables V and VI were obtained from k_{obsd} and $[\text{L}]$ data by using a least-squares computer program.

A thorough study of the reaction of $\text{Mo}(\text{CO})_4(\text{diamine})$ with $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ was made because it did differ from the $\text{M}(\text{CO})_4(\text{X-}o\text{-phen})$ reactions in that more than one product was formed. The initial products were formed according to eq 3. One of these products, $\text{Mo}(\text{CO})_3(\text{diamine})(\text{L})$, then reacts with additional L to yield $\text{Mo}(\text{CO})_3(\text{L})_3$ (eq 4). The amount



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TABLE II
RATES OF REACTION OF $\text{Mo}(\text{CO})_4(\text{X-}o\text{-phen})$ AND
 $\text{Mo}(\text{CO})_4(1,2\text{-diamino-2-methylpropane})$ WITH L AT 47.9°

L	[L], M	$10^4 k_{\text{obsd}}$, sec ⁻¹
$\text{Mo}(\text{CO})_4(o\text{-phen})$		
$\text{PO}_3\text{C}_6\text{H}_9$	0.0266	1.17
	0.193	1.70
	0.541	2.90
	0.846	3.64
$\text{P}(\text{OC}_2\text{H}_5)_3$	0.0340	1.04
	0.0912	1.13
	0.228	1.24
	0.456	1.36
$\text{P}(\text{C}_6\text{H}_5)_3$	0.911	1.63
	0.0229	1.14
	0.106	1.19
	0.334	1.20
$\text{P}(\text{OC}_6\text{H}_5)_3$	0.584	1.20
	0.0342	1.15
	0.159	1.17
	0.498	1.16
	0.873	1.19
$\text{Mo}(\text{CO})_4(4,7\text{-diphenyl-}o\text{-phen})$		
$\text{PO}_3\text{C}_6\text{H}_9$	0.0266	1.16
	0.193	1.50
	0.541	2.12
	0.846	2.68
$\text{P}(\text{OC}_2\text{H}_5)_3$	0.0340	1.04
	0.0912	1.14
	0.228	1.31
	0.456	1.59
$\text{P}(\text{C}_6\text{H}_5)_3$	0.911	2.01
	0.0285	1.07
	0.130	1.09
	0.389	1.09
	0.648	1.09
$\text{Mo}(\text{CO})_4(1,2\text{-diamine-2-methylpropane})$		
$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	0.0584	1.11
	0.156	2.00
	0.365	3.72
	0.520	5.31
	0.656	5.93

of each product formed during the reaction was experimentally found to be a function of the concentration of $\text{P}(\text{OCH}_2)_3\text{CCH}_3$. This reaction is very similar to the previously reported reaction of $\text{Mo}(\text{CO})_4(\text{dipy})$ with $\text{P}(\text{OCH}_2)_3\text{CCH}_3$.² As in the previous work, if it is assumed that only $\text{Mo}(\text{CO})_3(\text{diamine})(\text{L})$ is formed by the reaction path governed by k_1 (as observed in the analogous Cr complex)⁵ and all other products (including some $\text{Mo}(\text{CO})_3(\text{diamine})(\text{L})$) are formed by the reaction path governed by k_2 , a ratio of the products formed by the k_2 path can be determined. This can be done because the amounts of each product obtained from the two reaction paths must be proportional to the ratio of the first-order rate constants describing the rate of formation of these products. That is

$$\frac{k_1}{k_2[\text{L}]} = \frac{[\text{Mo}(\text{CO})_3(\text{diamine})(\text{L})]_1}{[\text{Mo}(\text{CO})_3(\text{diamine})(\text{L})]_2 + [\text{Mo}(\text{CO})_4\text{L}_2]_2}$$

where 1 and 2 refer to the first- and second-order paths, respectively. Using the same reasoning applied to the $\text{Mo}(\text{CO})_4(\text{dipy})$ system,² the expression for the ratio of

TABLE III
RATES OF REACTION OF $\text{W}(\text{CO})_4(\text{X-}o\text{-phen})$
WITH L IN CHLOROBENZENE

L	Temp, °C	[L], M	$10^4 k_{\text{obsd}}$, sec ⁻¹
$\text{W}(\text{CO})_4(o\text{-phen})$			
$\text{P}(n\text{-C}_4\text{H}_9)_3$	114.0	0.0299	1.76
		0.0898	2.00
		0.224	2.67
		0.449	3.81
$\text{P}(\text{OC}_2\text{H}_5)_3$	114.0	0.898	6.01
		0.0258	1.66
		0.0775	1.96
		0.194	2.28
$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	106.2	0.487	3.45
		0.775	4.44
		0.0259	0.716
		0.103	0.943
	114.0	0.194	1.10
		0.388	1.42
		0.776	2.11
		0.0259	1.71
		0.103	2.12
		0.194	2.31
		0.388	3.06
		0.776	4.27
	122.8	0.115	5.41
		0.218	6.26
		0.436	7.87
		0.861	10.7
$\text{P}(\text{C}_6\text{H}_5)_3$	114.0	0.0207	1.62
		0.0610	1.57
		0.155	1.70
		0.310	1.67
		0.620	1.68
$\text{W}(\text{CO})_4(5\text{-nitro-}o\text{-phen})$			
$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	114.0	0.0259	1.28
		0.103	1.52
		0.194	2.17
		0.388	3.52
		0.776	5.82
$\text{W}(\text{CO})_4(3,4,7,8\text{-tetramethyl-}o\text{-phen})$			
$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	114.0	0.0259	3.76
		0.103	4.00
		0.194	4.35
		0.388	4.73
		0.776	5.69

products formed only by the second-order path is

$$\frac{[\text{Mo}(\text{CO})_3(\text{diamine})(\text{L})]_2}{[\text{Mo}(\text{CO})_4\text{L}_2]_2} = \left\{ [\text{Mo}(\text{CO})_3(\text{diamine})(\text{L})]_{1,2} - \frac{k_1[\text{Mo}(\text{CO})_3(\text{diamine})]_1}{k_1 + k_2[\text{L}]} \right\} / [\text{Mo}(\text{CO})_4\text{L}_2]_2$$

Using k_1 and k_2 for the reaction of $\text{Mo}(\text{CO})_4(\text{diamine})$ with $\text{P}(\text{OCH}_2)_3\text{CCH}_3$, L, in 1,2-dichloroethane at 47.9°, $[\text{Mo}(\text{CO})_4(\text{diamine})]_1 = 2.10 \times 10^{-3} M$, and the reactant and product concentrations listed below, a value

[L], M	$[\text{Mo}(\text{CO})_4\text{L}_2]$, M	$[\text{Mo}(\text{CO})_3\text{L}_2]$, M	$[\text{Mo}(\text{CO})_3\text{L-}(\text{diamine})]$, M	$[\text{Mo}(\text{CO})_3\text{-}(\text{diamine})\text{L}_2]_2 / [\text{Mo}(\text{CO})_4\text{L}_2]_2$
0.060	0.000747	0.000552	0.000870	0.39
0.120	0.000968	0.000528	0.000595	0.36
0.210	0.00120	0.000681	0.000385	0.45
0.300	0.00126	0.000635	0.000270	0.48
0.600	0.00133	0.000612	0.000150	0.41
0.900	0.00125	0.000622	0.000090	0.38

TABLE IV
 ACTIVATION PARAMETERS FOR THE REACTION OF $M(\text{CO})_4(o\text{-phen})$ WITH $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ IN $\text{CH}_2\text{ClCH}_2\text{Cl}$

$M(\text{CO})_4(o\text{-phen})$	ΔH_1^\ddagger , kcal/mole	ΔS_1^\ddagger , eu	ΔH_2^\ddagger , kcal/mole	ΔS_2^\ddagger , eu
$\text{Cr}(\text{CO})_4(o\text{-phen})$	26.4 ± 0.8	7.0 ± 2.6		
$\text{Mo}(\text{CO})_4(o\text{-phen})$	25.1 ± 1.2	2.4 ± 2.4	19.1 ± 1.2	-17.0 ± 2.0
$\text{W}(\text{CO})_4(o\text{-phen})^a$	33.4 ± 1.0	-10.6 ± 3.0	23.6 ± 0.8	-37.6 ± 2.8

^a In chlorobenzene.

 TABLE V
 RATE CONSTANTS FOR THE REACTION OF $M(\text{CO})_4(X-o\text{-phen})$ WITH $\text{P}(\text{OCH}_2)_3\text{CCH}_3$

X	No.	$\text{p}K_a^a$	$-\text{Cr}(\text{CO})_4(X-o\text{-phen})^b-$		$-\text{Mo}(\text{CO})_4(X-o\text{-phen})^b-$		$-\text{W}(\text{CO})_4(X-o\text{-phen})^c-$	
			10^4k_1 , sec ⁻¹	10^4k_2 , l./mole sec	10^4k_1 , sec ⁻¹	10^4k_2 , l./mole sec	10^4k_1 , sec ⁻¹	10^4k_2 , l./mole sec
5,6-Dichloro	1	3.47	1.34	0.0	.610	2.41		
5-Nitro	2	3.57	1.10	0.0	.600	2.87	1.01	6.22
4,7-Diphenyl	3	4.84	2.65	0.0	1.09	.547		
Unsubstituted	4	4.86	2.71	0.0	1.14	1.16	1.63	3.48
3-Methyl	5	5.00	2.79	0.0	1.23	.993		
3,5,7-Trimethyl	6	5.90	4.83	0.0	1.68	.703		
3,4,7,8-Tetramethyl	7	6.31	6.12	0.0	2.01	.686	3.76	2.51
3,4,6,7-Tetramethyl	8	6.45	7.17	0.0	2.19	.475		
1,2-Diamino-2-methylpropane	(1)	10.00						
	(2)	6.79	46.0	0.0	6.93	82.3		

^a Values as reported by A. A. Schilt and G. F. Smith, *J. Phys. Chem.*, **60**, 1546 (1956). ^b Rate constants determined in 1,2-dichloroethane at 47.9°. ^c Rate constants determined in chlorobenzene at 114.0°.

 TABLE VI
 RATE CONSTANTS FOR THE REACTION OF $M(\text{CO})_4(o\text{-phen})$ AND $\text{Mo}(\text{CO})_4(4,7\text{-diphenyl-}o\text{-phen})$ WITH L

L	$-\text{Mo}(\text{CO})_4(o\text{-phen})^a-$		$-\text{Mo}(\text{CO})_4(4,7\text{-diphenyl-}o\text{-phen})^a-$		$-\text{W}(\text{CO})_4(o\text{-phen})^b-$	
	10^4k_1 , sec ⁻¹	10^4k_2 , l./mole sec	10^4k_1 , sec ⁻¹	10^4k_2 , l./mole sec	10^4k_1 , sec ⁻¹	10^4k_2 , l./mole sec
$\text{P}(n\text{-C}_4\text{H}_9)_3$	c		c		1.63	4.86
$\text{PO}_3\text{C}_6\text{H}_5$	1.14	3.04	1.09	1.90
$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	1.14	1.16	1.09	0.547	1.63	3.48
$\text{P}(\text{OC}_2\text{H}_5)_3$	1.14	0.940	1.09	0.592	1.63	3.65
$\text{P}(\text{C}_6\text{H}_5)_3$	1.14	0.130	1.09	0	1.63	0
$\text{P}(\text{OC}_6\text{H}_5)_3$	1.14	0.057

^a Rate constants determined in 1,2-dichloroethane at 47.9°. ^b Rate constants determined in chlorobenzene at 114.0°. ^c $\text{P}(n\text{-C}_4\text{H}_9)_3$ reacts with 1,2-dichloroethane.

of 0.42 ± 0.06 for the ratio of second-order products can be calculated from the above equation. This ratio is of considerable interest, because, first of all, since it is independent of the concentration of L, any proposed mechanism for this reaction must be one which accounts for the constant product ratio of the second-order path, and, second, it is also a useful measure of the ease with which the bidentate ligand is lost from the complex.

Using the ratios of second-order products, the reactions of $\text{Mo}(\text{CO})_4(\text{diamine})$ (0.42), $\text{Mo}(\text{CO})_4(\text{dipy})$ (1.0),² and $\text{Mo}(\text{X-}o\text{-phen})$ (very large, only one product) with $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ can be compared as to the ease with which the bidentate ligand is lost. The ease of replacement increases as $o\text{-phen} < \text{dipy} < \text{diamine}$. From this ordering, the only immediately apparent correlation is with the rigidity of the bidentate ligand structure. On this basis the observed ordering is expected since the nonrigid 1,2-diamino-2-methylpropane and semirigid dipyrindyl can dissociate one bond at a time in being replaced by L groups while this path is not available to the rigid $o\text{-phenanthroline}$. There is no correlation between the bidentate ligand basicity

and the ratio of products though one might have been expected: diamine, $\text{p}K_{a1} = 10.00$, $\text{p}K_{a2} = 6.79$; $o\text{-phen}$, $\text{p}K_a = 4.86$; 2,2'-dipyridyl, $\text{p}K_a = 4.50$.

Discussion

$\text{M}(\text{CO})_4(\text{X-}o\text{-phen})$ and $\text{Mo}(\text{CO})_4(\text{diamine})$ react with various phosphines and phosphites at a rate which is governed by a two-term rate expression (eq 2). The first term of this rate law which is independent of [L] is the term normally observed for the reaction of octahedral complexes with nucleophilic reagents. Its mechanism probably involves a simple dissociative rate-determining step. This type of mechanism for the reactions of octahedral complexes has been discussed in considerable detail elsewhere.^{5,7}

If the basicity of the substituted $o\text{-phenanthroline}$ in the $\text{M}(\text{CO})_4(\text{X-}o\text{-phen})$ complexes is increased, the first-order rate constants, k_1 , are also observed to increase in a predictable manner. There is a very good linear correlation between the $\log k_1$ and the $\text{p}K_a$ of the substituted $o\text{-phenanthroline}$ (Figure 1). This had been observed for the analogous $\text{Cr}(\text{CO})_4(\text{X-}o\text{-phen})$

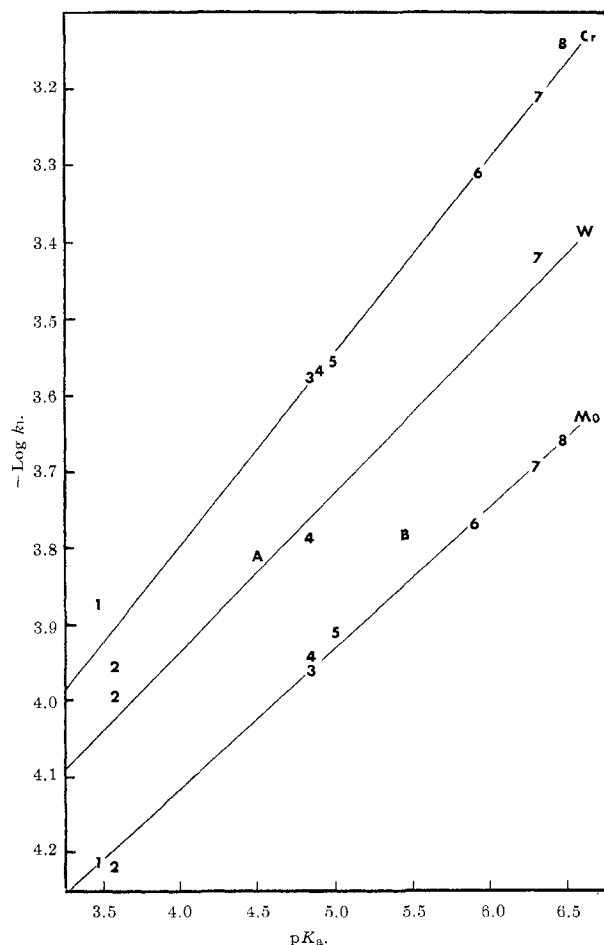


Figure 1—Free energy plots of $-\log k_1$ vs. pK_a for the reaction of $M(\text{CO})_4(\text{X-}o\text{-phen})$ (where $M = \text{Cr, Mo, W}$) with $\text{P}(\text{OCH}_2)_3\text{CCH}_3$. The numbers represent the $\text{X-}o\text{-phen}$ as listed in Table V. A and B represent the reactions of $\text{Mo}(\text{CO})_4(\text{dipy})$ and $\text{Mo}(\text{CO})_4(4,4'\text{-dimethyldipy})$ with $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ in 1,2-dichloroethane at 47.9° .

system and was discussed in detail.⁵ The slope of the line obtained from plotting $\log k_1$ vs. pK_a is negative. This is consistent with a reaction mechanism which involves a decrease of electron density at the reaction center in the transition state.⁸ Such a mechanism could be a simple $\text{S}_{\text{N}}1$ dissociative mechanism. The value of the Hammett reaction constant ($\rho = -0.26$ for the Cr system, $\rho = -0.18$ for the Mo system) obtained for these reactions is fairly small compared to most organic reactions which are known proceed to by $\text{S}_{\text{N}}1$ -type reaction mechanisms. However since no change in charge occurs in going from the reactants to the activated complex, a small value for ρ would be expected. The value of ρ obtained for these reactions is comparable with Hammett reaction constants obtained for other inorganic reactions as exemplified by the results of Margerum and Steinhaus in a similar study on $\text{Ni}(\text{H}_2\text{O})_4(\text{X-}o\text{-phen})^{2+}$.⁹

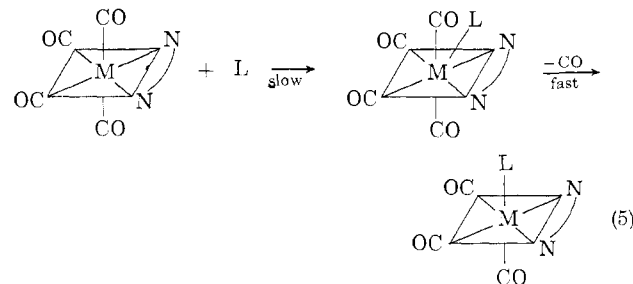
The correlation of $\log k_1$ with the pK_a of the bidentate ligand is good within the substituted o -phenanthroline

(8) K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964.

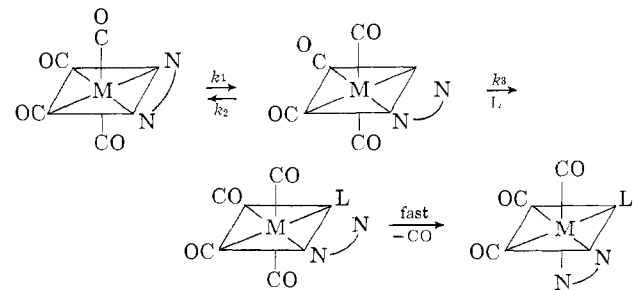
(9) D. W. Margerum and R. K. Steinhaus, *J. Am. Chem. Soc.*, **88**, 441 (1966).

series. However, if other bidentate ligands such as 1,2-diamino-2-methylpropane, 4,4'-dimethyl-2,2'-dipyridyl, and 2,2'-dipyridyl are compared with the o -phenanthroline series, the correlation is poor (Figure 1). An uncertainty arises in comparing 1,2-diamino-2-methylpropane with the other bidentate ligands since it can protonate each nitrogen separately and two pK_a values are available. It is not known what pK_a should be used in conjunction with its coordination with a metal. Using the largest pK_a value (10.0) of 1,2-diamino-2-methylpropane, the rate is slower than would be predicted from the o -phenanthroline series and using the smallest pK_a value (6.79) the rate is considerably faster than would be predicted. The two dipyridyl ligands have first-order rates which are faster than would have been predicted. Clearly, the free energy correlation is limited to the o -phenanthroline series.

The second term of the two-term rate law, $k_2[\text{L}][\text{M}(\text{CO})_4\text{N-N}]$, is most unusual for an octahedral complex because it involves the concentration of L. The most probable mechanism which best explains this part of the rate law involves a nucleophilic attack by the ligand upon the metal forming a seven-coordinated intermediate or transition state which in turn yields the reaction product, $\text{cis-M}(\text{CO})_3(\text{L})(\text{N-N})$ (eq 5).



However, a special type of dissociation mechanism has been used to explain the second-order character of some octahedral complexes containing one or more bidentate ligands. This mechanism (eq 4) using a steady-state



treatment will yield a rate expression of the form

$$\text{rate} = \frac{k_1 k_3 [\text{M}(\text{CO})_4\text{N-N}][\text{L}]}{k_2 + k_3[\text{L}]}$$

which does depend on the $[\text{L}]$. This mechanism may be of considerable merit for a bidentate ligand such as 1,2-diamino-2-methylpropane or 2,2'-dipyridyl which have nonrigid structures and may be capable of forming the proposed dissociated intermediate. o -Phenanthroline, however, has a rigid structure with the donor

nitrogen atoms held rigidly in the same plane. A molecular model of the *o*-phenanthroline complex clearly indicates that a dissociative mechanism of this type is not reasonable. That the *o*-phenanthroline complexes do not react by a mechanism involving *o*-phen dissociation is supported by the fact that $M(\text{CO})_4\text{-L}_2$ is not one of the products. For the dipyriddy and 1,2-diamino-2-methylpropane complexes some of the $M(\text{CO})_4\text{L}_2$ product is formed.

$\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ have been found to undergo displacement reactions with phosphines and phosphites.^{8,10} Since a dissociation mechanism to account for the second-order character of these reactions is not plausible here, support is given to a displacement mechanism for the *o*-phenanthroline complexes as well. This result also suggests that $\text{Mo}(\text{CO})_4(\text{dipy})$ and $\text{Mo}(\text{CO})_4(\text{diamine})$ likewise partially react according to an $\text{S}_\text{N}2$ mechanism.

Since the metal hexacarbonyls should be more susceptible to a nucleophilic attack than the sterically more demanding *o*-phenanthroline complexes, a greater percentage of their reaction should occur by a displacement mechanism than for the corresponding *o*-phenanthroline complexes. If the ratios of k_2/k_1 for $\text{Mo}(\text{CO})_6$ (>3.1)¹¹ and $\text{Mo}(\text{CO})_4(\text{o-phen})$ (0.82) are compared for the reaction with the same ligand, $\text{P}(\text{OC}_2\text{H}_5)_3$, this seems to be the case. The ratio of k_2/k_1 used here gives a good though probably only a very qualitative measure of how steric hindrance within the octahedral complex affects the ability of the complex to undergo a nucleophilic attack. Other effects such as electronic effects could appreciably alter the magnitude of k_1 and k_2 .¹²

If $\text{M}(\text{CO})_4(\text{X-}o\text{-phen})$ does undergo a true substitution reaction, the magnitude of the second-order rate constant, k_2 , should be sensitive to such factors as changes in the electron density on the metal, changes in steric properties of the substituted *o*-phenanthroline and attacking nucleophile, and changes in the base strength of the nucleophilic reagent. This has been observed to be true for all of the X-*o*-phen ligands studied.

When the $\text{p}K_\text{a}$ of the substituted *o*-phenanthroline is changed from a value of 3.5 to 6.5, k_2 is observed to decrease (Table V). This is expected since an increase in the basicity of the X-*o*-phen would increase the electron density on the metal thus making it less susceptible to a nucleophilic attack. The decrease in k_2 with increasing $\text{p}K_\text{a}$ follows a linear free energy relationship surprisingly well (Figure 2). The only large deviation from the linear relationship is for 4,7-diphenyl-*o*-phenanthroline. The two phenyl groups of this ligand are very large and bulky compared to the other X substituents used in this study and steric hindrance probably accounts for its significantly lower value of k_2 . The positive slope of the line obtained from the plot of $\log k_2$ vs. $\text{p}K_\text{a}$ is in it-

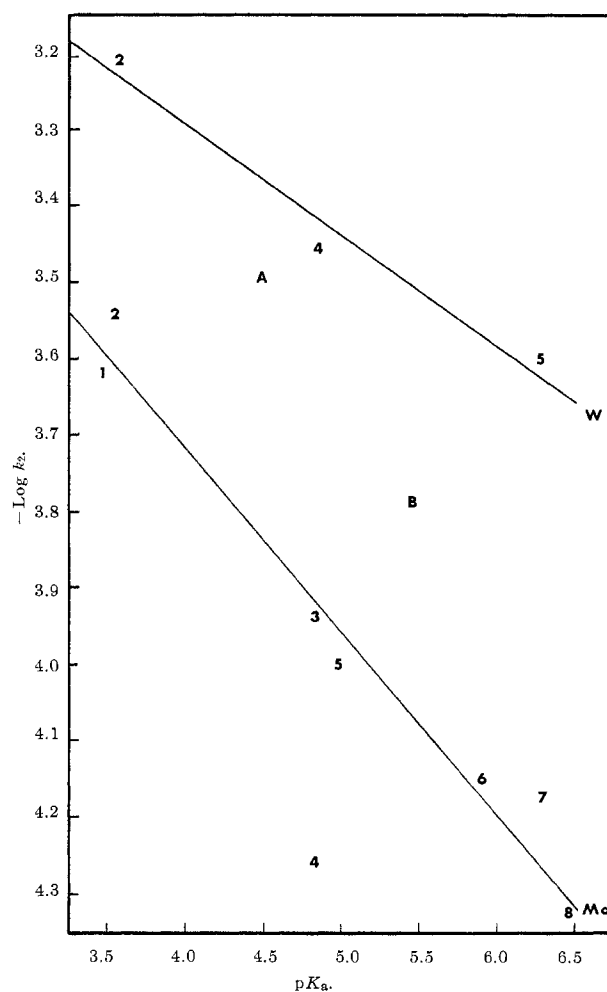


Figure 2.—Free energy plots of $-\log k_2$ vs. $\text{p}K_\text{a}$ for the reaction of $\text{Mo}(\text{CO})_4(\text{X-}o\text{-phen})$ and $\text{W}(\text{CO})_4(\text{X-}o\text{-phen})$ with $\text{P}(\text{OCH}_2)_3\text{-CCH}_3$. A and B represent the reactions of $\text{Mo}(\text{CO})_4(\text{dipy})$ and $\text{Mo}(\text{CO})_4(4,4'\text{-dimethyldipy})$ with $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ in 1,2-dichloroethane at 47.9° .

self consistent with a displacement mechanism in the reaction.⁸

The effect of steric hindrance of the bidentate ligand can be readily seen if the second-order rate constants for the reaction of *o*-phenanthroline and 4,7-diphenyl-*o*-phenanthroline complexes of Mo with various phosphines and phosphites are compared (Table VI). Both of these bidentate ligands have approximately the same $\text{p}K_\text{a}$ values and thereby approximately the same first-order rate constants. Since the electron density around the Mo atoms for both of these complexes should be essentially the same, any deviations in the k_2 values should be due only to an increase in electrostatic and steric hindrance. Table VI shows k_2 does decrease substantially in going from *o*-phen to 4,6-diphenyl-*o*-phen for all of the ligands studied. This effect of the bidentate ligand on the value of k_2 can be further seen if a number of other bidentate ligands are considered. Again using the ratio k_2/k_1 as a qualitative measure of the susceptibility of a system to a nucleophilic attack,¹⁰ the following ordering is observed for the reactions of $\text{Mo}(\text{CO})_4(\text{N-N})$ complexes with $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ in 1,2-dichloroethane at 47.9° : 1,2-di-

(10) J. R. Graham and R. J. Angelici, in preparation.

(11) This is the ratio of k_2/k_1 for the reaction of $\text{Mo}(\text{CO})_6$ with $\text{P}(\text{OC}_2\text{H}_5)_3$ at 112° . Since $\Delta H_1^\ddagger > \Delta H_2^\ddagger$ for this reaction,⁸ the value of k_2/k_1 will increase as the rate constants are extrapolated to the lower temperature of 47.9° .

(12) U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, **87**, 241 (1965).

amino-2-methylpropane (11.9) > 2,2'-dipyridyl (2.4) > *o*-phen (1.0) > 4,7-diphenyl-*o*-phen (0.5). This is also the expected order of increasing electrostatic and steric hindrance to a nucleophilic attack.

The basicity of the attacking ligand also plays an important role in the magnitude of k_2 as can be assessed from the data in Table VI. The exact effect of the ligand basicity on k_2 however is difficult to ascertain because all too often steric hindrance caused by the geometry of the ligand greatly complicates the interpretation. In general, k_2 decreases with L in the order: $P(n-C_4H_9)_3 > PO_3C_6H_9 > P(OCH_2)_3CCH_3 > P(OC_2H_5)_3 > P(C_6H_5)_3 > P(OC_6H_5)_3$. This is the same trend in second-order rate constants as was found by Basolo, *et al.*,^{13,14} in the reaction of some Rh and Co carbonyl complexes with a number of different nucleophilic reagents.

The size of the central metal atom is of considerable

(13) H. G. Schuster-Woldan and F. Basolo, *J. Am. Chem. Soc.*, **88**, 1657 (1966).

(14) E. M. Thorsteinson and F. Basolo, *ibid.*, **88**, 3929 (1966).

importance in determining the value of k_2 . For the group VI metals, the smallest atom, Cr, shows no k_2 term in its rate law for complexes of the type $Cr(CO)_4(N-N)$. Although $Cr(CO)_6$ does follow a two-term rate law, dependence on $[L]$ is very small. The relative importance of k_2 over k_1 for the group VI hexacarbonyls increases in going from Cr to Mo to W.¹⁰ This is readily apparent if the ratios of k_2/k_1 for their reaction with $P(n-C_4H_9)_3$ at 112° are compared. Values of k_2/k_1 for the $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ reactions are 0.7, 9.6, and 34.8, respectively. A similar trend in k_2/k_1 is obtained for the Cr-, Mo-, and $W(CO)_4(o\text{-phen})$ reactions with $P(OCH_2)_3CCH_3$ at 47.9°. For these reactions values of k_2/k_1 are: Cr, 0.0; Mo, 1.0; and W, 9.5.

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ANN ARBOR, MICHIGAN 48105

Dialkyldithiocarbamate Complexes of Molybdenum(V) and Molybdenum(VI)

BY FRED W. MOORE AND MELVIN L. LARSON

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Improved methods were developed for preparing dialkyldithiocarbamate complexes of Mo(VI) of the type $MoO_2[R_2NCS_2]_2$ (where R = methyl, ethyl, *n*-propyl, *n*-butyl) and of Mo(V) of the type $[(R_2NCS_2)_2Mo=O]_2O$ (where R = methyl, ethyl). A new compound whose analysis approximated $(C_4H_9)_2NCS_2MoOS$ was isolated by hydrogen sulfide treatment of a benzene solution of $MoO_2[(n-C_4H_9)_2NCS_2]_2$ or an aqueous solution of sodium molybdate and sodium di-*n*-butyldithiocarbamate. The Mo(V) complexes of dimethyl- and diethyldithiocarbamate and ethylxanthate were isolated in good yield by treating an aqueous solution of an alkali metal salt of the ligand with ammonium oxopentachloromolybdate(V). Infrared bands assignable to Mo-S absorption were found in the 460–515- cm^{-1} region, and the dimeric Mo(V) complexes showed a band at about 435 cm^{-1} due to a Mo-O-Mo stretching mode. It was concluded that the Mo(VI) complexes contain a *cis* O=Mo=O group since their infrared spectra contain two Mo=O bands at about 900 cm^{-1} . The Mo(V) dithiocarbamates contain a ligand field band at about 19,500 cm^{-1} .

Introduction

The dithiocarbamate group, $R_2NCS_2^-$ (R = H or alkyl), is a common univalent, bidentate ligand, and the preparation of some dialkyldithiocarbamate complexes of Mo(V) and Mo(VI) was briefly described by Malatesta.¹ The molybdenum(VI) dioxobis(dialkyldithiocarbamate) complexes, $MoO_2(R_2NCS_2)_2$ (where R = methyl, ethyl, and *n*-butyl), were prepared by dilute HCl acidification of solutions containing molybdate ions and the appropriate sodium dialkyldithiocarbamate. The diamagnetic Mo(V) complex, which we formulate as μ -oxo-dioxotetrakis(diethyldithiocarbamate)molybdenum(V), $\{[(C_2H_5)_2NCS_2]_2Mo=O\}_2O$, was prepared by the sulfur dioxide or sodium dithionite reduction of a solution containing molybdate and di-

ethyldithiocarbamate ions. The related diamagnetic Mo(V) alkylxanthate complexes, $[(ROCS_2)_2Mo=O]_2O$ (R = alkyl), have also been prepared,^{2,3} and recent determination of the molecular structure of the ethyl derivative⁴ confirmed the dinuclear formulation with a bridging Mo-O-Mo group. The only other dithiocarbamate complex of molybdenum that appears to have been isolated is π -cyclopentadienyldicarbonyl(dimethyldithiocarbamate)molybdenum(II), $\pi-C_5H_5Mo(CO)_2S_2CN(CH_3)_2$, prepared by the reaction of tetramethylthiuram disulfide and π -cyclopentadienylmolybdenum tricarbonyl dimer.⁵

(2) R. Montequi and M. Gallego, *Anales Real Soc. Espan. Fis. Quim.* (Madrid), **31**, 434 (1933).

(3) L. Malatesta, *Gazz. Chim. Ital.*, **69**, 408 (1939).

(4) A. B. Blake, F. A. Cotton, and J. S. Wood, *J. Am. Chem. Soc.*, **86**, 3024 (1964).

(5) F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, **3**, 1398 (1964).

(1) L. Malatesta, *Gazz. Chim. Ital.*, **69**, 752 (1939).