Contribution from the Department of Chemistry, University of Ottawa,
Ottawa, Ontario, Canada K1N 9B4

Peroxo Complexes of Molybdenum and Tungsten Stabilized by Oxides of Amines, Phosphines, and Arsines. Stability Studies

ALAN D. WESTLAND,* FERIAL HAQUE, and JEAN-MARC BOUCHARD

Several diperoxo complexes, $MO(O_2)_2 \cdot LL'$, where M = Mo or W, L = amine oxide, tertiary phosphine oxide, or tertiary arsine oxide, and L' = L or H_2O, have been prepared. The frequency of the ν_1 mode of the $M(O_2)$ grouping, which is essentially an O–O stretch, varies somewhat with choice of L, arsine oxides giving rise to generally lower frequencies. Proton and ^{13}C NMR spectra are discussed. The energies of activation for loss of dioxygen from the dry or the dissolved complexes are independent of whether the ligand is a phosphine or arsine oxide, but E_a is lower for a pyridine oxide complex. The complexes stoichiometrically oxidize olefins to epoxides and catalyze the epoxidation of olefins by *tert*-butyl hydroperoxide.

Dioxygen ligand generates interest not only because of its intrinsic nature but also because of its role in metal-catalyzed oxidation reactions: epoxidation of olefins,[1] preparation of hydroxy ketones,[2] secondary alcohols,[3] etc.

In a review, Vaska argued that dioxygen is always found in complexes either as covalently bound peroxide or superoxide, and it is largely insensitive to the molecular surroundings.[4] Thus, O–O bond distances and stretching frequencies are fairly constant over a range of examples of transition-metal compounds, the only significant factor being whether the dioxygen is peroxide or superoxide in type. Drago has recently challenged this terminology however.[5]

Notwithstanding these conclusions, there is a wide variation in the reversibility of dioxygen addition to metal complexes and in the kinetic or thermodynamic stability of peroxo complexes. This work attempts to define whether the electronic nature of auxiliary ligands influences the rate of oxygen evolution from group 6B peroxo complexes and to compare the relative stability of such complexes of molybdenum and tungsten. A considerable number of unstable peroxo complexes of chromium have been reported.[6] Complexes of molybdenum and tungsten are considerably more stable.[7]

To make a comparative study of the rate of O_2 evolution, we chose a series of compounds in which the central atom and the first coordination sphere were nearly identical in all cases. The covalent radii of Mo and W are nearly equal (1.29 and 1.30 Å, respectively). We limited the choice of ligands to ones which have oxygen as a donor atom. We thereby examined electronic effects while steric considerations were limited to

remote features of the ligands. Two modes of decomposition were studied: (a) thermally induced decomposition in the pure state and (b) base-catalyzed decomposition in aqueous methanol solution.

Experimental Section

General Procedures. Infrared spectra (Nujol mulls, KBr, and solution) were recorded with a Pye Unicam SP 1100 instrument. ^1H and ^{13}C NMR spectra of the complexes in deuteriochloroform or hexamethylphosphoramide were obtained on Varian HA-100 and FT-80 spectrometers. Tetramethylsilane was employed as internal standard.

Reagents. Trimethylamine oxide, pyridine oxide, triphenylphosphine oxide, triphenylarsine oxide, and tri-*n*-butylphosphine oxide were used as supplied. Tri-*n*-propylphosphine oxide, tri-*n*-propylarsine oxide, and tri-*n*-butylarsine oxide were prepared by a modification of a reported method.[8] An example of the procedure follows.

A stirred solution of a tri-*n*-butylarsine (7.7 g, 3.1 mmol) in ether (40.0 mL) was treated dropwise with 30% H_2O_2 (3.5 mL, 3.1 mmol) under nitrogen. The mixture was refluxed for 1 h and stirred at room temperature for 1 h. The water layer containing tri-*n*-butylarsine oxide was separated and heated under reduced pressure to remove water. The product crystallized at room temperature. Sublimation under reduced pressure yielded colorless needles (7.05 g, ~86%) melting at 109–110 °C.

Oxodiperoxo(pyridine *N*-oxide)chromium(VI), $CrO_5 \cdot ONC_5H_5$ (1). Pyridine *N*-oxide (2.0 g, 21.0 mmol) dissolved in water (2 mL) was added to a saturated solution of CrO_3 in glacial acetic acid (275 mL) with stirring. The resulting solid (2.0 g) was separated, washed with ether, and dried. To a solution of this solid, $CrO_3 \cdot ONC_5H_5$, in methylene chloride was added dropwise 50% aqueous H_2O_2. The organic phase was evaporated at room temperature to give blue crystals of 1.

A method similar to that of Mimoun et al.[9] was used for the preparation of Mo and W complexes. A typical example is the preparation of oxodiperoxobis(trimethylamine oxide)molybdenum(VI), $MoO_5 \cdot 2ON(CH_3)_3$ (2):

Peroxomolybdic acid was prepared by heating MoO_3 (0.65 g, 4.5 mmol) in 10 mL of 30% H_2O_2 at 45 °C (usually overnight). The solution was filtered and a methanol solution of trimethylamine oxide (0.5 g, 4.5 mmol) was added dropwise. Upon standing for a week, 2 was obtained which decomposed at 156 °C. This compound could not be obtained in an analytically pure state.

The butyl analogues and the propyl analogues containing molybdenum were crystallized by cooling to 0 °C or lower. $MoO_5 \cdot 2OP(n-C_4H_9)_3$ (7) formed a gum, but this crystallized upon adding cold water. Other products formed immediately or formed upon standing overnight. Products were washed with methanol–water and ether or hexane. Products 6 and 7 were recrystallized from benzene–hexane.

Differential Thermal Analysis. A Fisher Model 260 differential analyzer was used in conjunction with a Hewlett-Packard Model 2D-AM X-Y recorder. DTA curves were obtained for 100-mg samples of a mixture of finely ground compound and alumina in a 1:5 ratio

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Table I. Analytical Data

compd	% yield	mp, °C	% C calcd	% C found	% H calcd	% H found	% M[a] calcd	% M[a] found
$CrO_5 \cdot ONC_5H_5$	50		26.44	27.57	2.22	2.33		
$MoO_5 \cdot ONC_5H_5 \cdot H_2O$	82		20.78	21.12	2.44	2.57	33.19	33.49
$MoO_5 \cdot 2ONC_5H_5$	66		32.84	32.81	2.75	2.98	26.18	26.57
$MoO_5 \cdot OP(n-C_3H_7)_3$	65	108–110	30.68	30.49	5.97	6.11	27.26	27.09
$MoO_5 \cdot OP(n-C_4H_9)_3$	36	70–72	36.58	36.60	6.88	6.92	24.38	24.16
$MoO_5 \cdot 2OP(n-C_4H_9)_3$	61	96–97	47.06	47.05	8.88	8.38	15.66	14.90
$MoO_5 \cdot 2OP(C_6H_5)_3$	82	180–182	59.02	59.15	4.14	4.25	13.10	13.16
$MoO_5 \cdot OAs(n-C_3H_7)_3$	68	140–142	27.28	27.03	5.30	5.30	24.25	24.27
$MoO_5 \cdot OAs(n-C_4H_9)_3$	42	50–52	32.89	33.09	6.16	6.30	21.91	22.20
$MoO_5 \cdot 2OAs(C_6H_5)_3$	83		52.70	52.90	3.69	3.82	11.69	11.40
$WO_5 \cdot OP(n-C_3H_7)_3$	49	109–110	24.55	24.48	4.77	4.96	41.80	41.90
$WO_5 \cdot 2OP(n-C_4H_9)_3$	60	115	41.15	41.51	7.77	7.64	26.24	26.22
$WO_5 \cdot 2OP(C_6H_5)_3$	95		52.70	52.53	3.69	3.80		
$WO_5 \cdot OAs(n-C_3H_7)_3$	41	102–104	22.33	22.04	4.34	4.52	37.82	38.00
$WO_5 \cdot OAs(n-C_4H_9)_3$	36	69–73	27.39	27.02	5.13	5.16	34.96	35.00
$WO_5 \cdot 2OAs(C_6H_5)_3$	83		47.60	47.77	3.34	3.38	20.24	20.80

[a] M ≡ molybdenum or tungsten.

Table II. Infrared Spectral Data for Peroxomolybdenum and -tungsten Complexes

no.	compd	band maxima,[b] cm⁻¹ $\nu(M=O)$	$\nu(E=O)$	$\nu_1(O-O)$	$\nu_3(M-O)$	other bands, cm⁻¹
1	$CrO_5 \cdot ONC_5H_5$	985 ms	1170 ms	930 s	570 s	645 mw
2	$MoO_5 \cdot 2ON(CH_3)_3$	905 ms	1250 w	852 ms, 880 s	575 w	660 mw
3	$MoO_5 \cdot ONC_5H_5 \cdot H_2O$	970 vs	1215 s	873 s	577 s	640 m
4	$MoO_5 \cdot 2ONC_5H_5$	947 s	1192 s, 1212 s	859 s, 870 m	572 sh	645 m
5	$MoO_5 \cdot OP(n-C_3H_7)_3 \cdot H_2O$	957 s	1084 vs	857 vs, 867 vs	577 ms	653 ms
6	$MoO_5 \cdot OP(n-C_4H_9)_3 \cdot H_2O$	961 vs	~1100 s	863 vs, 877 vs	587 s	664 m
7	$MoO_5 \cdot 2OP(n-C_4H_9)_3$	947 s	n.c.	857 s, 874 m	575 s	652 s
8	$MoO_5 \cdot 2OP(C_6H_5)_3$	950 s	1160 s, 1170 s	865 s, 880 s	580 s	663 ms
9	$MoO_5 \cdot OAs(n-C_3H_7)_3 \cdot H_2O$	957 vs	860 vs	830 vs, 847 vs	583 m	644 w
10	$MoO_5 \cdot OAs(n-C_4H_9)_3 \cdot H_2O$[a]	955 s	853 s	811 s, ~820 s	577 w	643 ms
11	$MoO_5 \cdot 2OAs(C_6H_5)_3$	952 s	872 m, 892 m	837 vs, 855 m	572 sh	652 w
12	$WO_5 \cdot OP(n-C_3H_7)_3 \cdot H_2O$	960 vs	1070 vs	835 s, 846 s	584 ms	645 ms
13	$WO_5 \cdot 2OP(n-C_4H_9)_3$	949 vs	1079 s	835, 847 s	580 m	644 s
14	$WO_5 \cdot 2OP(C_6H_5)_3$	960 vs	1158 s, 1165 sh	836 s, 858 m	580 sh	652 w
15	$WO_5 \cdot OAs(n-C_3H_7)_3 \cdot H_2O$	958 vs	862 s	815 s, 830 vs	575 m	638 vw
16	$WO_5 \cdot OAs(n-C_4H_9)_3 \cdot H_2O$	944 m	854	814 vs, 828 vs	569 m	631 m
17	$WO_5 \cdot 2OAs(C_6H_5)_3$	958 m	880 s, br	823 vs, 850 w	575 w	

[a] KBr disk. [b] s ≡ strong, vs ≡ very strong, ms ≡ medium strong, m ≡ medium, mw ≡ medium weak, w ≡ weak, sh ≡ shoulder, br ≡ broad.

by weight. A calibrated Pt–Pt,Rh thermocouple was inserted in the sample block. Heating rates were determined by recording the signal from this thermocouple as a function of time indicated by an accurate electrical timer.

Solution Kinetics. Oxygen evolution from solution was determined by means of a thermostated dilatometer. This consisted of a small vessel with a horizontal capillary side arm and scale. A moveable plug of mercury in the capillary served as indicator. The vessel contained a small bucket to hold the potassium iodide reagent solution. Inverting the bucket started the reaction. Gas volumes were corrected to normal conditions. Vigorous agitation throughout a run minimized supersaturation of the solution with oxygen. The solutions were presaturated with oxyen.

Results and Discussion

Elemental analyses appear in Table I. The samples were heated in vacuo prior to analysis; this removed the coordinated water from 1:1 complexes. Oxo complexes of chromium(VI) of the type $CrO_3 \cdot L$ were prepared, and solutions of these in methylene chloride turned blue when treated with hydrogen peroxide. Such solutions in methylene chloride were stable for periods of up to several hours, but all attempts to isolate solid products failed except in the case where L = pyridine N-oxide.

Molybdenum and tungsten readily formed crystalline complexes, but we were unable to obtain an analytically pure complex containing tungsten with pyridine N-oxide, and triphenylstibine oxide failed to form complexes. Syntheses with trialkylstibine oxides were not attempted. Compounds **3**, **8**, and **14** have been reported previously.[6,7] The molybdenum

complexes were yellow and those of tungsten were colorless.

Infrared Spectra. Table II gives the absorption maxima for the more significant infrared bands. The metal–peroxo grouping gives rise to three infrared-active stretching frequencies, ν_1, ν_2, and ν_3, which correspond to a mixed mode having considerable O–O stretching character and symmetric M–O and antisymmetric M–O stretching, respectively. Griffith[10] and Wendling[11] assigned a band which appeared in peroxo complexes at 800–900 cm⁻¹ to the ν_1 mode. Bands between 500 and 600 cm⁻¹ were attributed to the other two modes.

The two dioxygens are virtually equivalent in the peroxo complexes for which X-ray structure analyses have been performed.[6d,12] Thus the appearance of two ν_1 bands appears to be a consequence of the coupling of the two groups. There was a band, possibly an overtone, in the range 635–655 cm⁻¹. Bands around 1200, 1100, and 870 cm⁻¹ are characteristic of N–O, P–O, and As–O stretching modes, respectively.

There is, on the whole, a decrease in ν_1 upon passing from a molybdenum complex to the corresponding tungsten compound. The other modes exhibit no significant trends. On the other hand, the ν_1 band is found at 876 and 856 cm⁻¹ for $K_2MoO(O_2)F_4$ and at 905 cm⁻¹ for $K_2WO(O_2)F_4$.[13]   It

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Table III. Proton NMR Chemical Shifts for Peroxomolybdenum Complexes

no.	compd	mean chemical shifts, ppm (no. of protons shown in parentheses)			
		α	β	γ	δ
	OP(C₃H₇)₃	1.64 (4) q		1.05 (3) m	
5	MoO₅·OP(C₃H₇)₃·H₂O	1.96 (4) m		1.13 (3) t	
	OP(C₄H₉)₃		1.56 (6) m		0.94 (3)
6	MoO₅·OP(C₄H₉)₃·H₂O	2.13 (2) m		1.59 (4) m	0.96 (3)
	OAs(C₃H₇)₃		1.66 (4) m	0.96 (3) m	
9	MoO₅·OAs(C₃H₇)₃·H₂O	2.5 (2) q	1.82 (2) m	1.09 (3) m	
	OAs(C₄H₉)₃	1.85 (2) m		1.5 (4) m	0.88 (3) t
10	MoO₅·OAs(C₄H₉)₃·H₂O	2.45 (2)		1.53 (4) m	0.88 (3) t

Table IV. ¹³C NMR Chemical Shifts (δ) and Coupling Constants (J_PC) of Peroxo Complexes

no.	ligand and compd	α	$J_{C_\alpha P}$, Hz	β	$J_{C_\beta P}$, Hz	γ	$J_{C_\gamma P}$, Hz	δ
	C₅H₅NO[a]	150.72		138.37		135.68		
3	MoO₅·ONC₅H₅·H₂O[a]	151.26		138.34		138.17		
	OP(n-C₃H₇)₃	30.373[b]	64.7	15.83[b]	17.4	15.57		
5	MoO₅·OP(n-C₃H₇)₃·H₂O	27.92[b]	62.8	15.56[b]	18.6	15.26		
	OP(n-C₄H₉)₃	27.8[b]	65.2	24.22[b]	18.5	23.96		13.64
6	MoO₅·OP(n-C₄H₉)₃·H₂O	25.51[b]	63.3	24.0[b]	15.5	23.24[b]	4.1	13.47
7	MoO₅·2OP(n-C₄H₉)₃	27.79[b]		24.15	15.1	23.50		13.54
	OAs(n-C₃H₇)₃	30.75[b]		16.15[b]		15.8		
9	MoO₅·OAs(n-C₃H₇)₃·H₂O	30.37[b]		16.12[b]		15.56		
	OAs(n-C₄H₉)₃	28.55[b]		24.55[b]		24.4		13.48
10	MoO₅·OAs(n-C₄H₉)₃·H₂O	28.04[b]		24.46[b]		24.16[b]		13.46

[a] Solvent was HMPA. Otherwise CDCl₃ was used. [b] Mean of two components of doublet.

therefore seems that no general conclusion can be drawn from these ν_1 values.

When the ligands bonded to a given central atom are replaced by others, the peroxide modes may possibly reflect changes in the degree of ionic character in the M–O bonds. Griffith has noted that when fluorine replaces a less electronegative element bonded to the central atom of a peroxo complex, the O–O stretching frequency is increased.[10] The analogous phosphorus- and arsenic-containing ligands are spatially very much alike while the Pauling electronegativities are practically identical. The mean ν_1 frequencies are lower in the arsenic compounds than in the phosphorus analogues. The polarity or the polarizability of the bond from the group 5 element to oxygen should influence charge displacement toward the metal atom. Reynold and Meek report the following bond moments for Ph₃EO (E = P or As): P–O, 3.27; As–O, 4.77 D.[14] The derived charge separations in the E–O bonds show that the oxygen in the arsine oxide is more negative. Proton basicities have been determined by titration of compounds R₃EO with HClO₄ in nitromethane.[15] The following pK_a values were obtained for the protonated oxides: R₃PO, 9.72; R'₃PO, 8.54; R₃AsO, 16.14 (R = cyclooctyl, R' = n-butyl). This evidence again points to a greater polarity in the case of arsine oxides.

There is no accurate way of assigning a moment to the N–O bond in pyridine oxide. However, a criterion of polarity is the basicity toward p-fluorophenol. The enthalpy of hydrogen bonding with the OH group is 7.5 ± 0.2 kcal mol⁻¹.[16] The corresponding value with trimethylphosphine oxide and p-fluorophenol is 7.7 ± 0.2 kcal mol⁻¹, i.e., an essentially identical value.

Thus the O–O stretching frequencies may be dependent upon the donor strength of the other ligands, but the ν_3 mode is essentially unaffected.

NMR Spectra. Proton chemical shifts of the complexes which were soluble in CDCl₃ are summarized in Table III. Parts of the spectra were poorly resolved so the table lists the mean shift of a number of protons in several cases. Protons on the carbon atoms α to the group 5 atom are shifted

downfield upon coordination of the ligand.

¹³C chemical shifts with respect to tetramethylsilane are recorded in Table IV. Owing to splitting by ³¹P, the resonances due to β- and γ-carbons overlapped in some instances. The assignments were made by rationalizing the ³¹P–C splittings. The changes upon coordination of a ligand are small. In the P- and As-containing ligands coordination caused slight upfield shifts, particularly in the α position of the phosphorus compounds.

There is a downfield shift of the α- and γ-carbon resonances upon coordination of pyridine N-oxide. Apparently, conjugation of the N–O bond with the ring protons permits strong electron withdrawal by the metal atom.

Compound 7 with two phosphine oxide ligands gave a broad singlet α-carbon resonance rather than a doublet. Also there was little or no resolution of the α, β, and γ resonances in the proton spectrum. When this was run at lower temperatures, splitting occurred, and this reached a maximum at –20 °C. Apparently the 2:1 complex is in equilibrium with the 1:1 complex and free ligand in solution. The exchange between free and complexed ligand destroyed the ³¹P splitting of the α-carbon resonance but not that of the β-carbon resonance.

Study of Thermal Decomposition. We have examined the rate of thermal O₂ evolution of some of the complexes. The chromium complexes are by far the least stable: the one isolated complex decomposed rapidly at 82 °C and slowly when kept below 0 °C. The pyridine oxide adducts of all three group 6 metals were explosive, the chromium compound being the most sensitive. Molybdenum and tungsten compounds were kept in the dark.

We used the method of Kissinger[17] to derive activation energies for thermal decomposition of Mo and W compounds. Differential thermal analysis scans were performed at heating rates ranging from 5 to 35 °C/min. A set of typical scans is shown in Figure 1. Kissinger obtained the expression (1)

$$d(\ln \phi/T_m^2)/d(1/T_m) = -E_a/R \qquad (1)$$

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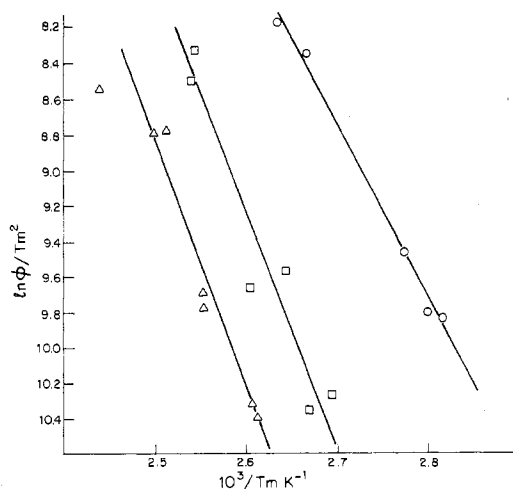(19) H. E. Kissinger, *Anal. Chem.*, **29**, 1702 (1957).

Figure 1. Plots of $\ln \phi/T_m^2$ against $10^3/T_m$ for DTA scans: (O) $WO_5 \cdot OAs(n\text{-}C_4H_9)_3$; (□) $WO_5 \cdot OAs(n\text{-}C_3H_7)_3$; (△) $WO_5 \cdot OP(n\text{-}C_3H_7)_3$.

Table V. Energies of Activation for Decomposition of Some Peroxomolybdenum and -tungsten Complexes

| | | E_a, kcal mol^{-1} | |
| | | thermal decompn | decompn in soln |
no.	compd		
3	$MoO_5 \cdot ONC_5H_5 \cdot H_2O$		11.7
4	$MoO_5 \cdot 2ONC_5H_5$	18.70	
5	$MoO_5 \cdot OP(n\text{-}C_3H_7)_3 \cdot H_2O$		23.3
6	$MoO_5 \cdot OP(n\text{-}C_4H_9)_3 \cdot H_2O$	27.10	19.3
7	$MoO_5 \cdot 2OP(n\text{-}C_4H_9)_3$	25.20	
9	$MoO_5 \cdot OAs(n\text{-}C_3H_7)_3 \cdot H_2O$		21.7
10	$MoO_5 \cdot OAs(n\text{-}C_4H_9)_3 \cdot H_2O$	25.30	18.4
12	$WO_5 \cdot OP(n\text{-}C_3H_7)_3 \cdot H_2O$	27.86	
13	$WO_5 \cdot 2OP(n\text{-}C_4H_9)_3$	19.20	
15	$WO_5 \cdot OAs(n\text{-}C_3H_7)_3 \cdot H_2O$	26.70	
16	$WO_5 \cdot OAs(n\text{-}C_4H_9)_3 \cdot H_2O$	19.40	

for the energy of activation E_a where T_m is the temperature of maximum response of the instrument and ϕ is the heating rate dT/dt.

The propyl derivatives of molybdenum underwent endothermic loss of one propyl group before the onset of O_2 loss. A sample of compound **5** was heated to 110 °C for several minutes at which temperature ligand pyrolysis occurred, but dioxygen was not lost. Elemental analysis of the product indicated the formula $MoO(O_2)_2 \cdot OP(n\text{-}C_3H_7)_2$. Anal. Calcd: C, 23.31; H, 4.53. Found: C, 23.72; H, 4.35. Infrared and NMR spectra failed to show the presence of a P–H bond so the following structure is proposed:
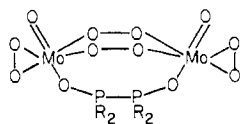
When compound **9** was heated to 135–140 °C, elemental analysis of the product showed it to be $MoO_3 \cdot As(n\text{-}C_3H_7)_2$. The ligand was apparently reduced to a diarsine. Anal. Calcd: C, 23.62; H, 4.59. Found: C, 23.82; H, 4.68. Phenyl derivatives underwent gradual loss of oxygen over a range of temperature from about 80 to 150 °C.

Figure 1 shows plots of $\ln \phi/T_m^2$ against $1/T_m$. Least-squares slopes gave the energies of activation listed in Table V. The values for the molybdenum complexes are greater than those of tungsten analogues. Thus the kinetic order of stability is Cr ≪ W < Mo.

There was no appreciable difference between phosphorus and arsenic analogues. The pyridine oxide complex **2** was less

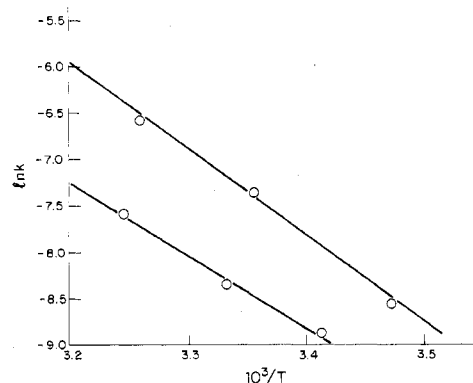**Figure 2.** Arrhenius plots: upper line, $MoO_5 \cdot OAs(n\text{-}C_4H_9)_3$; lower line, $MoO_5 \cdot OP(n\text{-}C_4H_9)_3$.

stable than the other molybdenum compounds. The activation energies for the butyl complexes were less than those for the propyl analogues. We suspect that the decomposition process is bimolecular and that the alkyl group is instrumental in determining a lattice vibrational energy which is lower for the butyl complexes and which largely determines the energy of approach of two molecules.

Decomposition in Solution. An alternative measure of stability is rate of oxygen evolution under the influence of base attack in solution. All of the peroxo complexes evolved oxygen from aqueous methanolic solution in the presence of hydroxide ions. The tungsten complexes deposited a precipitate so that quantitative rate studies were limited to molybdenum compounds.

Rates of oxygen evolution were measured between 15 and 35 °C. A 5:2 methanol–water medium was used. In order to examine a process in which only a single peroxo group reacted per metal atom, we treated the complexes with 2 equiv of potassium iodide. Only one peroxo group was reduced even in the presence of excess iodide. The reaction was initiated by adding KI (0.4 mL of 0.4 M solution) to the reaction vessel. There was an induction period of some seconds to a minute or more, the reason for which was not discovered.

The reduction by iodide, eq 2, appeared to be complete

$$LMoO(O_2)_2 + 2I^- + H_2O = LMoO_2(O_2) + I_2 + 2OH^- \tag{2}$$
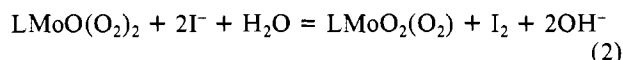
within very few seconds. The oxygen evolution continued for 0.5 h or more. The nominal concentration of hydroxide was in most cases twice that of the complex. The iodide concentration was that given by the hydrolysis reaction (3).

$$I_2 + OH^- = I^- + HOI \tag{3}$$

The energies of activation are given in Table V. Arrhenius plots are shown in Figure 2. The rate was first order in complex and second order in hydroxide concentration, but the detailed mechanism was not established. The second-order dependence suggests that hydrolysis is an elementary process. In the absence of further details of mechanism, we suggest that the data presented in Table V be taken as an empirical demonstration that the ligand L has an influence on the peroxide stability whatever the nature of the system, hydrolyzed or otherwise, may be.

The activation energies parallel those found for the thermal decomposition of the dry complexes. Thus the butyl complexes are more readily decomposed than are the corresponding propyl complexes, and the pyridine oxide complex is the most unstable.

Epoxidation Reactions. In view of the use of molybdenum and tungsten compounds as catalysts in organic oxidation reactions, we carried out the epoxidation of cyclohexane and styrene in order to verify the activity of our compounds.

Compounds **3** and **6–9** were so used.

Typically, 0.6 mmol of metal peroxo complex was suspended in boiling methanol, benzene, toluene, or mesitylene and the stoichiometric quantity of cyclohexene added. The proton NMR spectrum of the reaction solution revealed an absorption at 3.2 ppm downfield from Me$_4$Si which is characteristic of the methine hydrogens of cyclohexene epoxide.

Compound **7** was dissolved in benzene along with excess styrene. After the mixture was heated for 2 h at 70 °C, the proton NMR spectrum contained narrow multiplets centered at 2.8, 3.15, and 3.85 ppm as required for styrene oxide.

Compound **7** was also employed as a catalyst in the oxidation of excess cyclohexene by *tert*-butyl hydroperoxide. Reaction was allowed to proceed for 2 h or more at 80 °C and the solution turned first blue and then brown. The proton NMR spectrum of the solution showed a peak at 3.4 ppm which was assumed to be due to the methine protons of cyclohexene epoxide.

Sheldon has observed that catalysts such as MoO$_2$(acac)$_2$ were converted in the course of reaction to a diol (e.g., cyclohexanediol) complex which continued to catalyze the reaction.[1f] It was assumed that acac is destroyed by the peroxide.[1c,h] However, the work of Jacobson et al.[3] suggests that if a ligand on the catalyst resists oxidation by peroxide, then such a catalyst is preserved throughout the reaction. The

ligands employed in the present work are stable toward peroxide.

Photochemistry. The complexes lost oxygen over a period of weeks when they were left exposed to light. Compound **8** suspended in hexane was exposed to 3000-Å radiation in a Rayonet Srinivasan-Griffith photochemical reactor for 15 h, but no detectable decomposition occurred. However, irradiation of compounds **8** and **11** in the presence of methanol under N$_2$ atmosphere gave brown oxo complexes of molybdenum in a reduced valence state. The fate of the methanol was not established. This preliminary finding suggests that the use of irradiation should be examined further in an effort to increase the scope of application of peroxo complexes. Thermal conditions alone do not bring about oxidation of primary alcohols by peroxide.[3]

Contribution from the Department of Physical Chemistry,
Institute of Inorganic Chemistry and Technology, Technical University of Gdańsk, 80-952 Gdańsk, Poland

Effect of Chloroform on the Relative Stabilities of the CoCl$_2$(py)$_2$ and CoCl$_2$(py)$_4$ Complexes in Solution

WŁODZIMIERZ LIBUŚ,* KRYSTYNA CHACHULSKA, and MIROSŁAW MĘCIK

The effect of varying composition of pyridine–chloroform mixtures on the CoCl$_2$(py)$_4$ ⇌ CoCl$_2$(py)$_2$ + 2py equilibrium has been studied spectrophotometrically. Derived thermodynamic characteristics of the reaction show marked variations with varying composition of the mixed solvent. Separate contributions to the overall effects, viz., the thermodynamic transfer functions of the reactants, are derived from combined spectrophotometric, calorimetric, and solubility measurements. The results indicate strong specific interaction of chloroform with CoCl$_2$(py)$_4$ and weaker if any interaction with CoCl$_2$(py)$_2$. Hydrogen-bond formation of the protic solvent with the coordinated pyridine molecules cooperating with the d → π* electron delocalization is proposed as a possible explanation of the effects observed.

Introduction

The effect of noncoordinating solvents on coordination equilibria has not, so far, received any broader interest, probably being considered to be of second-order importance. However, there are indications that in certain systems strong specific interactions may occur between well-defined solution complexes and protic solvents not entering the first coordination spheres. An example is provided by the H···π type interaction of haloforms with the Co(NCS)$_2$(γ-pic)$_4$ complex, as reported by Narbutt and Siekierski.[1,2] Recently, we found that chloroform and, to a smaller extent, 1,2-dichloroethane exert a stabilizing effect on the MCl$_2$(py)$_4$ type complexes as well.[3] The effect being stronger for NiCl$_2$(py)$_4$ than for MnCl$_2$(py)$_4$ indicated that ability of the coordinated pyridine molecules to act as proton acceptors may be controlled by the

d$_\pi$ electron back-donation from the central metal atom. It also seemed necessary that the two effects, viz., the d$_\pi$ electron back-donation from the central metal atom to the amine molecules and the π···H interaction of the latter with the protic solvent, should be cooperative, enhancing each other. If real, the combined effect should critically depend on the symmetry of the complex, thus resulting in preferential stabilization of certain arrangements of the respective ligands around the central metal atom against others. In accordance with this expectation, chloroform additions to pyridine were found to displace equilibrium 1 toward the octahedral complex

$$CoCl_2(py)_4 \rightleftharpoons CoCl_2(py)_2 + 2py \qquad (1)$$
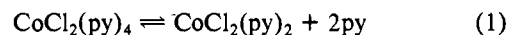
CoCl$_2$(py)$_4$, despite sharply decreasing pyridine activity.[4] Similarly, transformation of the CuCl$_2$(py)$_3$ pentacoordinate complex into CuCl$_2$(py)$_4$ was found to take place upon chloroform additions to pyridine.[5] It seems that these are but

(1) J. Narbutt and S. Siekierski, *Rocz. Chem.*, **48**, 1777 (1974).
(2) J. Narbutt and S. Siekierski, *J. Inorg. Nucl. Chem.*, **38**, 305 (1976).
(3) W. Libuś, B. Janaszewski, R. Pastewski, and H. Twardowska, submitted to *J. Solution Chem.*

(4) W. Libuś, H. Koniarska, and H. Twardowska, *Bull. Acad. Pol. Sci., Ser. Sci., Chim.*, **27**, 529 (1979).