Kinetics and Mechanism of Substitution Reactions of Trichloro-oxobis[tris(dimethylamino)phosphine oxide]molybdenum(V) in Dichloromethane Solution †

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Kinetic data for the reactions $[MoCl_3O\{P(NMe_2)_3O\}_2] + [NEt_4]X \xrightarrow{k_X} [NEt_4][MoCl_3XO\{P(NMe_2)_3O\}] + P(NMe_2)_3O$ (X = Cl, Br, or NO_3) in dichloromethane solution are reported over the temperature range 7—35 °C. These data are consistent with an S_N1 (limiting) mechanism, in which the dissociative loss of a $P(NMe_2)_3O$ molecule is the rate-determining step, with $k_X(25\ °C) = 9.1 \pm 1.5\ s^{-1}$, $\Delta H_X^‡ = 18.5 \pm 0.6$ kcal mol^{-1}, and $\Delta S_X^‡ = 8.2 \pm 2.3$ cal K^{-1} mol^{-1}. It is considered that the reaction proceeds by the initial loss of the $P(NMe_2)_3O$ ligand *trans* to the oxo-group. This is then followed by a rapid isomerisation resulting in overall *cis* substitution. In the case of X = NO_3 this then leads to a rapid redox reaction producing NO_2 and the *cis*-dioxomolybdenum(VI) complex. Comparisons of the substitution reactivity of the complexes $[MoCl_3OL_2]$ [L = PPh_3O or $P(NMe_2)_3O$] are described.

EARLIER we reported the first detailed studies of the kinetics and mechanisms of the reactions of mononuclear oxomolybdenum(V) complexes, including reactions of halide,[1] nitrate,[2] and nitrite[3] with $[MoCl_3O(PPh_3O)_2]$. As an extension of this work we have investigated related reactions of the corresponding $P(NMe_2)_3O$ complex, particularly since the molecular and electronic structures of this complex in the solid state have been characterised[4] and these details assist in the interpretation of the kinetic data.

EXPERIMENTAL

Dichloromethane was purified, and analytically pure samples of $[NEt_4]X$ (X = Cl, Br, or NO_3) were obtained as described previously.[1,2] Electronic and e.s.r. spectra recorded for solutions of $[MoCl_3O\{P(NMe_2)_3O\}_2]$[4] in CH_2Cl_2 were consistent with the molecular structure identified for the solid state remaining essentially unchanged on dissolution.

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† No reprints available.

[1] C. D. Garner, M. R. Hyde, F. E. Mabbs, and V. I. Routledge, *J.C.S. Dalton*, 1975, 1175.

[2] C. D. Garner, M. R. Hyde, F. E. Mabbs, and V. I. Routledge, *J.C.S. Dalton*, 1975, 1180.

[3] C. D. Garner and M. R. Hyde, *J.C.S. Dalton*, 1975, 1186.

[4] C. D. Garner, T. J. King, P. Lambert, and F. E. Mabbs, preceding paper.

Molecular-weight determinations using a Mechrolab 301A osmometer for 0.025, 0.050, and 0.100 mol dm^{-3} solutions of $[MoCl_3O\{P(NMe_2)_3O\}_2]$ in CH_2Cl_2 gave a value of 565 ± 30 (calc.: 577). These solutions had molar conductivities, Λ, <5 S cm^2 mol^{-1}.

Kinetic experiments were carried out in a manner analogous to that described earlier.[1,2] Pseudo-first-order conditions were maintained with $[NEt_4]X$ in a sufficiently large excess over Mo^V, the $[X^-]$ being held approximately constant by virtue of the equilibrium,[1] $[NEt_4]X \rightleftharpoons [NEt_4]^+ + X^-$. Each reaction was monitored by following transmittance changes on a Beckmann spectrophotometer at appropriate wavelengths, between 270 and 370 nm, using an Aminco-Morrow stopped-flow apparatus. Data were recorded and stored using the DASAR facility and individual plots of $\ln(D_\infty - D_t)$ * against time were treated using a least-squares analysis and were generally linear for greater than three half-lives. Activation parameters for each of the three initial reactions were determined from measurements between 7 and 35 °C, the temperature being measured using a calibrated thermistor attached to the block in which the reactant solutions were stored immediately prior to mixing.

Preliminary experiments with CH_2Cl_2 solutions of $[MoCl_3O\{P(NMe_2)_3O\}_2]$ up to 5×10^{-4} mol dm^{-3} demonstrated that Beer's law was obeyed. Spectrophotometric titrations of these solutions with $[NEt_4]Cl$ solutions indicated [5] that rapid and essentially complete formation of $[MoCl_4O\{P(NMe_2)_3O\}]^-$ occurred for $[NEt_4Cl] : [MoCl_3O\{P(NMe_2)_3O\}_2] > 2 : 1$. In contrast with a 2 : 1 ratio of $[NEt_4Br] : [MoCl_3O\{P(NMe_2)_3O\}_2]$, the rapid formation of a metastable species, $\lambda_{max.}$ 322 nm, was observed followed by the moderately slow (*ca.* 2 h) conversion into a stable species, $\lambda_{max.}$ 317 nm. Isosbestic points were retained at 294 and 331 nm during this latter conversion.

TABLE 1

Kinetic data [a] for chloride substitution of $[MoCl_3O\{P(NMe_2)_3O\}_2]$ in CH_2Cl_2 monitored at 290 nm

$\frac{\theta_c}{°C}$	$\frac{10^4[Mo^V]_0}{mol\ dm^{-3}}$	$\frac{10^3[NEt_4Cl]_0}{mol\ dm^{-3}}$	$\frac{10^4[P(NMe_2)_3O]_0}{mol\ dm^{-3}}$	$\frac{k_{obs.}}{s^{-1}}$
33.0	1.50	3.0		15.1
	1.50	30.0		14.7
25.0	2.50	4.0		6.76 [b]
	2.50	15.0		8.09
	2.50	30.0		8.01 [b]
	2.50	50.0		7.87
	2.50	2.50	1.50	6.27
	2.50	2.50	3.50	5.18
	2.50	2.50	7.50	3.84
	2.50	2.50	15.0	2.47
	2.50	2.50	35.0	1.38
17.1	1.50	3.00		2.18
	1.50	30.0		2.26
7.0	1.50	3.00		0.72
	1.50	30.0		0.66

[a] Average of two measurements. [b] Monitored at 325 nm.

The mixing of CH_2Cl_2 solutions of $[NEt_4][NCS]$ and $[MoCl_3O\{P(NMe_2)_3O\}_2]$, to produce respective molarities of 10^{-3} and 10^{-4}, resulted in a sequence of three absorbance changes with $t_{\frac{1}{2}}$ values of *ca.* 100 ms, 10s, and 200 s with isosbestic points only being retained for the slowest step. The spectrum of the final solution, which was bright red, showed absorbance maxima at 462 and 335 nm. The oxidation of $[MoCl_3O\{P(NMe_2)_3O\}_2]$ by $[NEt_4][NO_3]$ proceeded in three observable steps, the kinetic data for the latter two requiring analysis by a consecutive treatment.[6]

RESULTS AND DISCUSSION

A single-step rate process was observed for the chloride substitution of $[MoCl_3O\{P(NMe_2)_3O\}_2]$ and plots of $\ln(D_\infty - D_t)$ against time were generally linear up to at least three half-lives, thus indicating a first-order dependence on $[Mo^V]$. Rate constants evaluated from these plots at the various temperatures are listed in Table 1 which includes data obtained for variation in $[NEt_4Cl]$ and $[P(NMe_2)_3O]$. Similar kinetic behaviour was observed for the first stages of the reactions between $[NEt_4]Br$ or $[NEt_4][NO_3]$ and $[MoCl_3O\{P(NMe_2)_3O\}_2]$ and the corresponding rate constants are summarised in Tables 2 and 3, respectively.

TABLE 2

Kinetic data [a] for bromide substitution of $[MoCl_3O\{P(NMe_2)_3O\}_2]$ in CH_2Cl_2 monitored at 330 nm

$\frac{\theta_c}{°C}$	$\frac{10^4[Mo^V]_0}{mol\ dm^{-3}}$	$\frac{10^3[NEt_4Br]_0}{mol\ dm^{-3}}$	$\frac{10^3[P(NMe_2)_3O]_0}{mol\ dm^{-3}}$	$\frac{k_{obs.}}{s^{-1}}$
35.1	1.50	3.75		23.6
	1.50	37.5		20.6
25.0	2.60	5.0		10.8
	5.20	30.0		8.9
	5.20	50.0		9.9
	5.00	30.0	2.32	7.46
	5.00	30.0	3.95	6.28
	5.00	30.0	6.00	3.98
	4.00	30.0	7.90	3.46
	5.00	3.50	6.00	2.09
	5.00	5.00	6.00	2.30
	5.00	60.00	6.00	4.92
15.1	1.50	3.75		1.72 [b]
	1.50	37.5		1.66
7.5	1.50	3.75		0.71 [b]
	1.50	37.5		0.73

[a] Average of two measurements. [b] Monitored at 315 nm.

Therefore, the kinetic data obtained for the initial substitution reactions of $[MoCl_3O\{P(NMe_2)_3O\}_2]$ suggest

$$[MoCl_3O\{P(NMe_2)_3O\}_2] \overset{k_1}{\rightleftharpoons} [MoCl_3O\{P(NMe_2)_3O\}] + P(NMe_2)_3O \tag{1}$$

$$[MoCl_3O\{P(NMe_2)_3O\}] + X^- \xrightarrow{k_2} [MoCl_3XO\{P(NMe_2)_3O\}]^- \tag{2}$$

that a purely dissociative mechanism is operating according to (1) and (2) (X = Cl, Br, or NO_3). Application of the stationary-state approximation to the

$$\frac{d[MoCl_3XO\{P(NMe_2)_3O\}^-]}{dt} = \frac{k_1k_2[MoCl_3O\{P(NMe_2)_3O\}_2][X^-]}{k_{-1}[P(NMe_2)_3O] + k_2[X^-]} \tag{3}$$

concentration of the five-co-ordinate intermediate gives expression (3). In the absence of added $P(NMe_2)_3O$ the rate law simplifies such that $k_{obs.} = k_1$ and therefore rate constants measured under these conditions show no dependence on either the nature or the concentration of

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* D_∞ = Absorbance after 10 half-lives, D_t = absorbance at time t.

[5] V. I. Routledge, Ph.D. Thesis, University of Manchester, 1975.

[6] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' 2nd edn., Wiley, New York, 1961.

X^-. Furthermore, the activation parameters (Table 4) corresponding to the k_1 path are essentially identical irrespective of the nature of X^-. The choice of the poor co-ordinating solvent, CH_2Cl_2, enables the detection of a denominator term in the leaving group, $k_{-1}[P(NMe_2)_3O]$, which further defines the mechanism. Table 1 lists the values of the rate constants k_1 and the ratio $k_2 : k_{-1}$. The suppression of $k_{obs.}$ on the addition of $P(NMe_2)_3O$ was observed in each case according to expression (3). In the particular case of bromide substitution, the data relating to the variation of $k_{obs.}$ with both $[NEt_4Br]$ and $[Br^-]$ in the presence of added $P(NMe_2)_3O$ clearly indicate that Br^- rather than $[NEt_4]Br$ is the reactant. This follows from the intercept equated to $1/k_1$ and the linearity of the plot of $1/k_{obs.}$ against 1/[incoming ligand], as in the Figure.

TABLE 3

Kinetic data * for the first stage observed during the reaction between $[MoCl_3O\{P(NMe_2)_3O\}_2]$ and $[NEt_4][NO_3]$, monitored at 280 nm, in dichloromethane solution

θ_c / °C	$10^4[Mo^V]_0$ / mol dm^{-3}	$10^4[NEt_4NO_3]_0$ / mol dm^{-3}	$10^4[P(NMe_2)_3O]_0$ / mol dm^{-3}	$k_{obs.}$ / s^{-1}
25.0	1.00	6.0		10.2
	1.00	10.0		12.3
	2.50	15.0		9.3
	2.50	35.0		10.4
	2.50	50.0		9.6
	4.00	100.0		12.1
	2.50	25.0	0.50	11.5
	2.50	25.0	1.25	10.3
	2.50	25.0	2.50	7.3
	2.50	25.0	3.75	5.7
	2.50	25.0	5.0	4.6
	2.50	25.0	10.0	2.5
19.2	2.50	15.0		5.45
	2.50	75.0		5.26
14.2	2.50	15.0		3.37
	2.50	75.0		3.33
8.4	2.50	15.0		1.73
	2.50	75.0		1.62

* Average of two measurements.

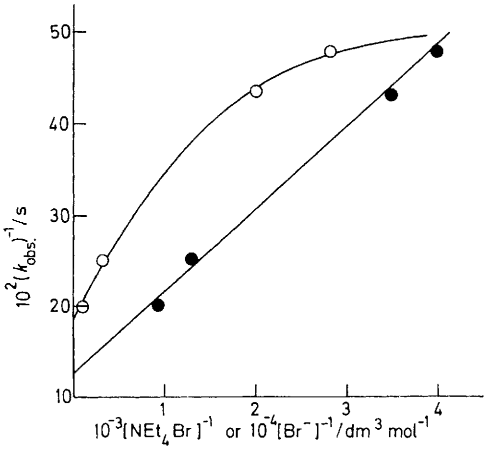
TABLE 4

Rate constants at 25 °C and activation parameters for the first stage of the reactions [a] $[MoCl_3OL_2] + X^- \longrightarrow [MoCl_3XOL]^- + L$

L	X^-	k_1 [b,c]	$k_2 : k_{-1}$ [d]	$\Delta H_1^‡$ [b]	$\Delta S^‡$ [b]
PPh_3O	Br^-	41.6	8	16.5 ± 0.3	4.2 ± 1.1
	Cl^-	42.0	27	16.2 ± 0.7	3.4 ± 2.4
	$[NO_3]^-$	40.0	31	17.1 ± 1.2	6.9 ± 4.0
	$[NO_2]^-$	51.8	47	16.6 ± 1.0	5.0 ± 3.2
$P(NMe_2)_3O$	Br^-	9.9	5.5	19.1 ± 2.1	10.3 ± 6.8
	Cl^-	7.5	3.6	18.5 ± 1.2	8.5 ± 4.0
	$[NO_3]^-$	10.6	2.1	17.8 ± 0.9	5.9 ± 3.1

[a] Dichloromethane solvent, $I \approx 0$. [b] Units of k_1, $\Delta H_1^‡$, and $\Delta S_1^‡$ are s^{-1}, kcal mol^{-1}, and cal K^{-1} mol^{-1} respectively. [c] Estimated error ± 1.0 s^{-1}. [d] Estimated error ± 2.0 s^{-1}.

The kinetic parameters for corresponding substitution reactions of $[MoCl_3O(PPh_3O)_2]$ are also included in Table 4. The values of the activation parameters for these latter reactions have been re-evaluated following a more accurate determination of the temperatures used in the kinetic studies. A comparison of the rate constants k_1 for L = PPh_3O and $P(NMe_2)_3O$ shows the expected decrease (by a factor of *ca.* 4) as the donor strength of the phosphine oxide ligand increases.[7] This difference in the tendency of the phosphine oxide ligand to dissociate from an oxomolybdenum(V) centre, which is consistent with earlier e.s.r. results,[8] appears to arise primarily from the $\Delta H^‡$ terms. The small positive value found for $\Delta S^‡$ is consistent with a dissociative path and the re-evaluation of $\Delta S^‡$ for the analogous $[MoCl_3O(PPh_3O)_2]$ reactions resolves the problem with this quantity discussed earlier.[1-3] The relative rate constants $k_2 : k_{-1}$, representing the competition between X^- and L, cover a much narrower range for L = PPh_3O than for $P(NMe_2)_3O$. Also, the relative order of reactivities appears to be inverted: $Br^- < Cl^- < [NO_3]^- < [NO_2]^-$ *versus* PPh_3O and $[NO_3]^- < Cl^- < Br^-$ *versus* $P(NMe_2)_3O$. These changes may represent either subtle differences in the characteristics of the five-co-ordinate $[MoCl_3OL]$ species or be indicative of a dissociative-interchange mechanism[9] for the initial substitution of $[MoCl_3O\{P(NMe_2)_3O\}_2]$.



Variation of $1/k_{obs.}$ against $1/[Br^-]$ (●) and $1/[NEt_4Br]$ (○) for the initial substitution reaction of $[MoCl_3O\{P(NMe_2)_3O\}_2]$ by $[NEt_4]Br$ in the presence of added $P(NMe_2)_3O$ (Data abstracted from Table 2 at 25 °C with $[Mo^0]_0 = 5.00 \times 10^{-4}$ and $[P(NMe_2)_3O] = 6.00 \times 10^{-3}$ mol dm^{-3}.)

Substitution reactions of the complexes $[MoCl_3OL_2]$ [L = $P(NMe_2)_3O$ or PPh_3O [1-3]] conform to a very similar pattern, initially involving dissociative loss of the ligand L. Available evidence suggests that the phosphine-oxide group initially lost is that molecule co-ordinated *trans* to the oxo-group. The extension of a static *trans*-bond-lengthening effect into a kinetic *trans*-labilising effect due to the presence of an oxo-group is well established, for example in the chemistry of oxovanadium(IV) complexes.[10,11] A similar static *trans*-bond-lengthening

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[7] Y. Ozari and J. Jagur-Grodzinski, *J.C.S. Chem. Comm.*, 1974, 295.

[8] P. M. Boorman, C. D. Garner, and F. E. Mabbs, *J.C.S. Dalton*, 1975, 1299.

[9] M. L. Tobe, 'Inorganic Reaction Mechanisms,' Nelson, London, 1972, p. 90.

[10] D. L. Kepert, 'The Early Transition Metals,' Academic Press, London 1972, p. 209.

[11] D. R. Rosseinsky, *Chem. Rev.*, 1972, **72**, 215 and refs. therein.

effect has been identified in a wide range of oxomolybdenum complexes,[12] including $[MoCl_3O\{P(NMe_2)_3O\}_2]$,[4] and therefore a kinetic *trans* effect seems probable for these molybdenum complexes. Secondly, although ligand-substitution processes at monomeric oxomolybdenum(V) centres [1-3,13] invariably appear to lead to the substitution of a ligand *cis* to the oxo-group, steps subsequent to the initial substitution process have been identified in the reactions of $[MoCl_3O(PPh_3O)_2]$ with Br^-, $[NO_3]^-$, $[NO_2]^-$, and $[NCS]^-$, of $[MoCl_3O\{P(NMe_2)_3O\}_2]$ with Br^-, $[NO_3]^-$, and $[NCS]^-$, and of $[MoCl_4O(PPh_3O)]^-$ with $[NCS]^-$. Such kinetic data as have been obtained for these processes, together with the spectroscopic properties [5] of the complexes obtained from these reactions, are consistent with their description as intramolecular axial to equatorial isomerisation processes. Support for such facile intramolecular rearrangements has been obtained [14] by ^1H n.m.r. studies of $[NbCl_3O\{P(NMe_2)_3O\}_2]$ and related complexes.

An alternative mechanism involving ligand substitution in positions *cis* to terminal oxo-groups has been proposed [15] for reactions of $[Mo_2O_4]^{2+}(aq)$. Similar considerations may be applied to the substitutions discussed here. However, it is considered that the only consistent interpretation of all the data obtained for these monomeric systems is that which involves the initial substitution *trans* to the oxo-group. The differences between the mechanistic behaviour of $[Mo_2O_4]^{2+}(aq)$ and $[MoO]^{3+}$ may arise from the different characteristics of these centres and/or solution effects.

The nature of the redox reaction between the nitrato-group and the oxomolybdenum(V) centre, $[MoCl_3O\{P(NMe_2)_3O\}]$, is considered to proceed in a completely analogous manner to that described [2,16] for the corresponding reaction with $[MoCl_3O(PPh_3O)]$. This interpretation is consistent with the relevant kinetic data summarised in Tables 3—5. Thus, following the initial substitution *trans* to the oxo-group, the second step observed is taken to represent *cis* substitution of the nitrato-group leading to an atomic arrangement suitable for a facile redox reaction between the two centres, producing a *cis*-dioxomolybdenum(VI) complex and NO_2. The third step observed in this reaction is believed to be substitution(s) at the $[MoO_2]^{2+}$ centre.

TABLE 5

Kinetic data at 25 °C for the second (k_3) and third stages (k_4) observed in the reaction of $[MoCl_3O\{(P(NMe_2)_3O\}_2]$ with $[NEt_4][NO_3]$ ($[Mo^V]_0 = 2.5 \times 10^{-4}$ mol dm^{-3}), monitored at 330 nm

$10^3[NEt_4NO_3]$ / mol dm^{-3}	$10^4[P(NMe_2)_3O]$ / mol dm^{-3}	10^2k_3 / s^{-1}	10^2k_4 / s^{-1}
1.50		*	1.7
2.50		*	5.6
3.50		31.4	8.1
6.50		64.6	*
7.50		66.0	*
10.0		86.0	*
15.0		101.0	*
20.0		122	*
25.0		168	*
2.50	5.0	*	2.73
2.50	10.0	7.0	1.76
2.50	15.0	6.66	1.39
2.50	20.0	8.8	1.44
2.50	25.0	6.95	1.35

* Not clearly defined or observed under these conditions.

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[12] B. Spivack and Z. Dori, *Co-ordination Chem. Rev.*, 1975, **17**, 99 and refs. therein.

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[14] L. G. Hubert-Pfalzgraf, R. C. Muller, M. Postel, and J. G. Reiss, *Inorg. Chem.*, 1976, **15**, 40.

[15] Y. Sasaki, R. S. Taylor, and A. G. Sykes, *J.C.S. Dalton*, 1975, 396.

[16] C. D. Garner, M. R. Hyde, F. E. Mabbs, and V. I. Routledge, *Nature*, 1974, **252**, 579.