# Kinetics and Mechanism of Halide-substitution Reactions of Trichloro-oxobis(triphenylphosphine oxide)molybdenum(v)

By **C. David Garner,* Michael R. Hyde, Frank E. Mabbs,** and **Vincent I. Routledge,** The Chemistry Department, Manchester University, Manchester M13 9PL

A detailed study of the substitution reactions of chloride and bromide ions with trichloro-oxobis(triphenylphosphine oxide)molybdenum(v), $[MoOCl_3(OPPh_3)_2]$, $[MoOCl_3(OPPh_3)_2] + X^- \longrightarrow [MoOCl_3X(OPPh_3)]^- + Ph_3PO$, has been accomplished in dichloromethane solution over the temperature range 1—25 °C. The rate of substitution was found to be independent of halide-ion concentration and, for constant $[X^-]$ (X = Cl or Br), to be inversely dependent on $[Ph_3PO]$. These data are consistent with an $S_N1$ (limiting) mechanism, with essentially identical values for the activation parameters for both chloride and bromide substitution: $\Delta H^\ddagger$ = 10·6 ± 0·8 and 11·4 ± 0·2 kcal mol$^{-1}$ and $\Delta S^\ddagger$ = −15·4 ± 2·9 and −12·5 ± 0·8 cal K$^{-1}$ mol$^{-1}$ at 298 K, respectively. For both reactions the rate-determining step is considered to involve loss of the $Ph_3PO$ ligand *trans* to the oxo-group in $[MoOCl_3(OPPh_3)_2]$. Subsequent to halide substitution, exchange of the substituted halide with the equatorial $Ph_3PO$ occurs. The reactions of $Cl^-$ with $[MoOCl_3Br(OPPh_3)]$ and of several nucleophiles with $[MoOCl_4]^-$ in dichloromethane solution at 25 °C have been studied and the data obtained shown to provide support for the proposed mechanism of halide substitution of $[MoOCl_3(OPPh_3)_2]$.

TRICHLORO-OXOBIS(TRIPHENYLPHOSPHINE OXIDE)MOLYBDENUM(V), $[MoOCl_3(OPPh_3)_2]$, was first reported by Horner and Tyree [1] and has subsequently been obtained by several other workers.[2,3] This green compound dissolves in dichloromethane as the covalent monomer and thus affords a convenient system for studying reactions at a discrete $Mo^V$ centre. As part of a study of the electronic structure and reactions of molybdenum complexes to obtain information relevant to the role of this metal in the various molybdenum-containing enzymes,[4] we have investigated the halide-substitution reactions of $[MoOCl_3(OPPh_3)_2]$.

## EXPERIMENTAL

Molybdenum pentachloride (Koch–Light) was purified by vacuum sublimation over a temperature gradient of *ca.* 275 to 25 °C, $Ph_3PO$ (B.D.H.) was used without further purification, and $[Et_4N]X$ (X = Cl or Br) (B.D.H.) were dried by heating at 110—120 °C *in vacuo* ($10^{-3}$ Torr) for at least 4 h.† Dichloromethane (normal solvent grade) was freshly distilled from $CaH_2$ and Karl–Fischer titrations [5] indicated that <0·004% v/v water was present. Trichloro-oxobis(triphenylphosphine oxide)molybdenum(v), $[MoOCl_3(OPPh_3)_2]$, was prepared according to the method of Horner and Tyree [1] and characterised by elemental analyses, its m.p. (275—276 °C) being identical with that reported by Lewis and Whyman.[2] Molecular-weight determinations for 0·11, 0·056, 0·028, and 0·014M-$CH_2Cl_2$ solutions, obtained using a Mechrolab 301A osmometer, afforded an average value of 756 ± 30 {calc. for $[MoOCl_3(OPPh_3)_2]$ 775}. The compound behaves essentially as a non-electrolyte in the dried $CH_2Cl_2$ solutions, $\Lambda < 5$ S cm$^2$ mol$^{-1}$. The salt $[Et_4N][MoOCl_4]$ was prepared as described elsewhere.[6]

*Determination of Dissociation Constants or* $[Et_4N]X$ (X = Cl *or* Br) *in* $CH_2Cl_2$ *Solution.*—Values of the equilibrium constants $K_X$ (25 °C) for the dissociation (1) in

$$[\mathrm{Et_4N}]\mathrm{X} \rightleftharpoons [\mathrm{Et_4N}]^+ + \mathrm{X}^- \quad (\mathrm{X} = \mathrm{Cl\ or\ Br}) \qquad (1)$$

$CH_2Cl_2$ were obtained by determining the variation of the molar conductance, measured using a Philips conductivity bridge, of these solutions with the concentration of the salt.[7] These data are summarised in Table 1 and gave $K_{Cl} = 2{\cdot}03 \times 10^{-5}$ and $K_{Br} = 1{\cdot}87 \times 10^{-5}$ mol l$^{-1}$. Corrections for ionic strength were considered to be unimportant at the concentrations employed.

TABLE 1

Variation in conductivity with concentration for $[Et_4N]X$ (X = Cl or Br) in dichloromethane at 25 °C

| $10^4[Et_4NCl]$/ mol l$^{-1}$ | $\Lambda$/S cm$^2$ mol$^{-1}$ | $10^4[Et_4NBr]$/ mol l$^{-1}$ | $\Lambda$/S cm$^2$ mol$^{-1}$ |
|---|---|---|---|
| 6·00 | 18·2 | 20·00 | 12·5 |
| 4·00 | 21·5 | 6·00 | 19·2 |
| 2·00 | 28·4 | 3·00 | 25·4 |
| 1·00 | 39·8 | 1·00 | 40·4 |
| 0·58 | 43·1 | 0·30 | 63·7 |
| 0·40 | 48·5 | 0·10 | 89·4 |
| 0·15 | 68·9 | | |
| 0·10 | 71·5 | | |

*Kinetic Measurements.*—Solutions of the reactants in $CH_2Cl_2$ were prepared under an inert atmosphere and transferred using syringe techniques to the storage chambers of an Aminco–Morrow stopped-flow apparatus coupled to a Beckmann DU spectrophotometer. A nitrogen atmosphere was maintained above the solutions, which were thermostatted for 15—20 min prior to reaction, to within ±0·1 °C at temperatures between 0 and 25 °C. The reactions were followed by monitoring transmittance changes with time, these data being stored on an oscilloscope and recorded on polaroid film.

Pseudo-first-order reaction conditions were used to study reactions (2) (X = Cl or Br). Although the concentration

$$[\mathrm{MoOCl_3(OPPh_3)_2}] + \mathrm{X}^- \rightleftharpoons [\mathrm{MoOCl_3X(OPPh_3)}]^- + \mathrm{Ph_3PO} \qquad (2)$$

of 'free' halide ion $[X^-]$ was generally not in excess of $[MoOCl_3(OPPh_3)_2]$, its concentration was maintained essentially constant throughout a reaction by virtue of

---

† 1 Torr = (101 325/760) Pa, 1M = 1 mol dm$^{-3}$, 1 cal = 4·184 J.

[1] S. M. Horner and S. Y. Tyree, *Inorg. Chem.*, 1962, **1**, 122.

[2] J. Lewis and R. Whyman, *J. Chem. Soc.*, 1965, 6027.

[3] F. J. Kohl, J. Lewis, and R. Whyman, *J. Chem. Soc.* (*A*), 1966, 630; W. M. Carmichael and P. A. Edwards, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2641; M. Gerlicke, jun., and L. Bowden, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 151.

[4] J. T. Spence, *Co-ordination Chem. Rev.*, 1969, **4**, 475; R. C. Bray and J. C. Swann, 'Structure and Bonding,' Springer-Verlag, Berlin, 1972, **11**, 107.

[5] J. Mitchell, jun., and D. N. Smith, 'Chemical Analysis,' vol. 5, 'Aquametry,' Interscience, New York, 1948, p. 132.

[6] P. M. Boorman, C. D. Garner, F. E. Mabbs, and V. I. Routledge, unpublished work.

[7] R. M. Fuoss and C. A. Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 476.

equilibrium (1). For chloride substitution, the transmittance changes were generally monitored at 318 nm; however, readings at 330 and 285 nm were also obtained, and a single-stage rate process was observed under all the conditions employed. Two stages were observed in the case of bromide substitution, the first being studied by monitoring optical-density changes at 322 nm and the second at 315 nm. First-order rate constants for all these reactions were determined from plots of log $(D_\infty - D_t)$ against time ($D_\infty$ = optical density after 10 half-lives, $D_t$ = optical density at time $t$). Activation parameters were computed using a least-squares analysis * with equal weighting for all points.

Reaction (3) was followed by monitoring the transmittance changes at various wavelengths, principally 290 and 340 nm, the rate process observed being the same at all wavelengths. Second-order reaction conditions were employed for the major part of this study. The 1 : 1 reaction (4) was followed by monitoring the transmittance change at 350 nm. In the case of the analogous reactions of $[MoOCl_4]^-$ with $Cl^-$, $Br^-$, $Ph_3PO$, or $(Me_2N)_3PO$ no transmittance changes were observed in the range 280—350 nm for 1 : 1 reactions. However, under conditions of a large excess (6—30 : 1) of these ligands a reaction was observed and transmittance changes were monitored.

$$[MoOCl_3Br(OPPh_3)]^- + Cl^- \rightleftharpoons [MoOCl_4Br]^{2-} + Ph_3PO \quad (3)$$

$$[MoOCl_4]^- + NCS^- \rightleftharpoons [MoOCl_4(NCS)]^{2-} \quad (4)$$

RESULTS

*Chloride Substitution of* $[MoOCl_3(OPPh_3)_2]$.—Plots of $\log(D_\infty - D_t)$ against time were generally linear to at least 85% completion of reaction and the values of $k_{obs.}$ obtained at 0·5, 15·0, and 25 °C at the various concentrations of $[MoOCl_3(OPPh_3)_2]$ and $[Et_4N]Cl$ are listed in Table 2. The observed rate constants were independent of $[Cl^-]$ and rate law (5) is applicable. At 25 °C $k_{obs.}$ = 42·0 $s^{-1}$, $\Delta H^\ddagger$ = 10·6 ± 0·8 kcal $mol^{-1}$, and $\Delta S^\ddagger$ = −15·4 ± 2·9 cal $K^{-1}$ $mol^{-1}$. Under conditions where the concentrations of $[MoOCl_3(OPPh_3)_2]$ and $Cl^-$ were maintained at a constant value and the concentration of added $Ph_3PO$ was varied from 0 to 0·012 mol $l^{-1}$, the values obtained for $k_{obs.}$ (25 °C) (Table 3) obey the relation (6) where $a = 2{\cdot}1 \times 10^{-2}$ s and $b$ = 5·44 l $mol^{-1}$ s (Figure 1).

TABLE 2

Kinetic data for chloride substitution of $[MoOCl_3(OPPh_3)_2]$ in dichloromethane monitored at 318 nm

| $\theta_c$/°C | $10^4[MoOCl_3(OPPh_3)_2]$/ mol $l^{-1}$ | $10^4[EtNCl]$/ mol $l^{-1}$ | $10^4[Cl^-]$ [a]/ mol $l^{-1}$ | $k_{obs.}$ [b]/ $s^{-1}$ |
|---|---|---|---|---|
| 25·0 | 2·50 | 67·5 | 3·60 | 49·5 [c] |
| | 1·52 | 35·1 | 2·57 | 45·3 |
| | 1·52 | 7·5 | 1·13 | 43·8 |
| | 1·52 | 7·5 | 1·13 | 42·3 [d] |
| | 1·50 | 5·0 | 0·91 | 47·8 |
| | 1·38 | 2·0 | 0·54 | 49·3 |
| | 0·50 | 5·0 | 0·91 | 48·7 |
| | 0·30 | 1·7 | 0·49 | 41·2 |
| 15·0 | 1·50 | 67·5 | 3·60 | 21·6 |
| | 1·50 | 20·0 | 1·91 | 21·8 |
| | 1·50 | 5·0 | 0·91 | 20·6 |
| | 0·30 | 1·7 | 0·49 | 21·8 |
| 0·5 | 1·00 | 67·5 | 3·60 | 7·51 |
| | 1·50 | 20·0 | 1·91 | 7·87 |
| | 1·50 | 5·0 | 0·91 | 8·52 |
| | 0·30 | 1·7 | 0·49 | 7·28 |

[a] Calculated assuming $K = 2{\cdot}03 \times 10^{-5}$ mol $l^{-1}$ at 25·0, 15·0, and 0·5 °C for $[Et_4N]Cl$. [b] Average of two measurements. [c] $\lambda$ = 330 nm, one measurement. [d] $\lambda$ = 285 nm.

$$-d[MoOCl_3(OPPh_3)_2]/dt = k_{obs.}[MoOCl_3(OPPh_3)_2] \quad (5)$$

$$1/k_{obs.} = a + b[Ph_3PO] \quad (6)$$

TABLE 3

Effect of added $Ph_3PO$ on the rate of halide substitution of $[MoOCl_3(OPPh_3)_2]$ [a] in dichloromethane at 25 °C

| Chloride | | | | Bromide [b] | |
|---|---|---|---|---|---|
| $10^3[Ph_3PO]$/ mol $l^{-1}$ | $10^4[Et_4NCl]$/ mol $l^{-1}$ | $10^4[Cl^-]$ [c]/ mol $l^{-1}$ | $k_{obs.}$ [d]/ $s^{-1}$ | $10^3[Ph_3PO]$/ mol $l^{-1}$ | $k_{obs.}$ [d]/ $s^{-1}$ |
| 3·00 | 40·00 | 2·75 | 31·7 | *e* | |
| 3·00 | 20·00 | 1·91 | 24·9 | *e* | |
| 3·00 | 8·00 | 1·18 | 19·5 | *e* | |
| 3·00 | 4·00 | 0·81 | 12·7 | *e* | |
| 3·00 | 2·75 | 0·65 | 8·6 | *e* | |
| 12·00 | 10·00 | 1·32 | 11·5 | 10·00 | 4·9 |
| 6·75 | 10·00 | 1·32 | 17·3 | 7·50 | 6·1 |
| 3·00 | 10·00 | 1·32 | 25·0 | 5·00 | 9·1 |
| 2·00 | 10·00 | 1·32 | 30·8 | 2·50 | 14·3 |
| 1·00 | 10·00 | 1·32 | 42·9 | 1·00 | 23·5 |
| 0·00 | 10·00 | 1·32 | 46·0 [f] | 0·00 | 42·0 [f] |

[a] Concentration of $[MoOCl_3(OPPh_3)_2]$ maintained at $1{\cdot}50 \times 10^{-4}$ mol $l^{-1}$. [b] These data refer to $[Br^-] = 1{\cdot}48 \times 10^{-4}$ mol $l^{-1}$. [c] Calculated assuming $K = 2{\cdot}03 \times 10^{-5}$ mol $l^{-1}$ for $[Et_4N]Cl$. [d] Average of two measurements. [e] The effect of varying $[Br^-]$ with added $Ph_3PO$ was not included because of complications due to the second stage of the reaction. [f] Average of corresponding values listed in Tables 2 and 4.

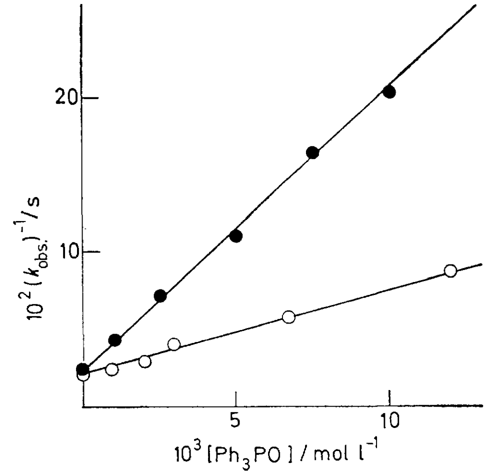


FIGURE 1 Variation of observed rate constant for chloride (○) and bromide (●) substitution of $[MoOCl_3(OPPh_3)_2]$ with added $Ph_3PO$ at 25 °C. Reactant concentrations were maintained constant at $[Mo^V] = 1{\cdot}50 \times 10^{-4}$ and $[Cl^-] = 1{\cdot}42 \times 10^{-4}$ or $[Br^-] = 1{\cdot}58 \times 10^{-4}$ mol $l^{-1}$

*Bromide Substitution of* $[MoOCl_3(OPPh_3)_2]$.—For the first stage of this reaction the plots of $\log(D_\infty - D_t)$ against time were linear to at least 85% completion and the values of $k_{obs.}$ obtained under the various reaction conditions are given in Table 4. A rate law as obtained above [equation (5)] is again applicable and at 25 °C $k_{obs.}$ = 41·6 $s^{-1}$, $\Delta H^\ddagger$ = 11·4 ± 0·2 kcal $mol^{-1}$, and $\Delta S^\ddagger$ = −12·5 ± 0·8 cal $K^{-1}$ $mol^{-1}$. At fixed bromide concentrations the value of $k_{obs.}$ once again decreased with added $Ph_3PO$ (Table 3) and the relation (6) follows where at 25 °C $a = 2{\cdot}3 \times 10^{-2}$ s and $b$ = 18·1 l $mol^{-1}$ s (Figure 1).

---

* This analysis was carried out using the computer program ARRHENIUS I of Dr. J. P. Day.

TABLE 4

Kinetic data for the first stage of bromide substitution of $[MoOCl_3(OPPh_3)_2]$ in dichloromethane monitored at 322 nm

| $\theta_c$/°C | $10^4[MoOCl_3(OPPh_3)_2]$/ mol $l^{-1}$ | $10^4[Et_4NBr]$/ mol $l^{-1}$ | $10^5[Br^-]$[a]/ mol $l^{-1}$ | $k_{obs.}$[b]/ $s^{-1}$ |
|---|---|---|---|---|
| 25·0 | 1·50 | 2·5 | 6·74 | 42·5 |
| | 1·50 | 4·0 | 8·55 | 43·5 |
| | 1·50 | 7·5 | 11·70 | 40·2 |
| | 1·50 | 20·0 | 19·20 | 43·6 |
| | 1·50 | 40·0 | 27·30 | 44·8 |
| | 5·00 | 40·0 | 27·30 | 40·5 |
| | 5·00 | 5·0 | 9·57 | 39·7 |
| | 5·00 | 2·5 | 6·74 | 39·2 |
| | 0·50 | 1·0 | 4·22 | 43·6[c] |
| 15·0 | 2·50 | 5·0 | 9·57 | 21·3 |
| | 2·50 | 20·0 | 19·20 | 20·7 |
| | 2·50 | 40·0 | 27·30 | 20·5 |
| 1·1 | 2·50 | 5·0 | 9·57 | 6·87 |
| | 2·50 | 20·0 | 19·20 | 7·21 |

[a] Estimated assuming $K = 1{\cdot}87 \times 10^{-5}$ mol $l^{-1}$ at 25·0, 15·0, and 1·1 °C for $[Et_4N]Br$. [b] Average of two measurements. [c] One measurement.

TABLE 5

Kinetic data for the second stage of $Br^-$ substitution of $[MoOCl_3(OPPh_3)_2]$ in dichloromethane at 25 °C, monitored at 315 nm

| $10^4[MoOCl_3(OPPh_3)_2]$/ mol $l^{-1}$ | $10^4[Et_4NBr]$[a]/ mol $l^{-1}$ | $k_{obs.}$[b]/$s^{-1}$ |
|---|---|---|
| 5·00 | 0[c] | 1·51 |
| 0·50 | 0·21 | 1·69 |
| 1·50 | 1·80 | 2·85 |
| 1·50 | 4·94 | 5·44 |
| 2·50 | 7·24 | 7·40 |
| 2·50 | 10·12 | 9·89 |
| 2·50 | 11·91 | 11·50 |

[a] Concentration of $[Et_4N]Br$ estimated after due allowance for $[Et_4N]^+$ and $Br^-$ with the assumption that one equivalent of $Br^-$ per $Mo^V$ was consumed during the first stage of the reaction. [b] Average of two measurements. [c] Reaction with $[Et_4NBr] : [MoOCl_3(OPPh_3)_2]$ initially in the ratio 1 : 2 and thus $k_{obs.} = k_3$ [equation (7)].

The second stage of the reaction of $[MoOCl_3(OPPh_3)_2]$ with $Br^-$ also gave linear plots of $\log(D_\infty - D_t)$ against time to at least 80% completion and the values of $k_{obs.}$ obtained at 25 °C for the various concentrations of reactants are presented in Table 5. These values of $k_{obs.}$ conform (Figure 2) to the rate law (7) where $k_3 = 1{\cdot}51 \pm 0{\cdot}07$ $s^{-1}$

$$d(\text{Products})/dt = (k_3 + k_4[Et_4NBr])[Mo^V] \qquad (7)$$

and $k_4 = (8{\cdot}2 \pm 0{\cdot}05) \times 10^3$ l $mol^{-1}$ $s^{-1}$ at 25 °C. The nature of the molybdenum species involved in this reaction will be considered below and its concentration was assessed assuming that the initial reaction proceeded to completion with a 1 : 1 $[Mo^V] : [Br^-]$ ratio. To gain more information concerning the nature of the molybdenum(v) compound participating in the second stage, reactions with $[Mo^V]$ and $[Et_4NBr]$ equal to $2{\cdot}5 \times 10^{-4}$ and $4{\cdot}2 \times 10^{-4}$ mol $l^{-1}$, respectively, were monitored *ca.* 120 ms after mixing at 25 °C. At these concentrations the first and second stages are sufficiently separated to allow the absorbance values of the intermediate to be estimated; these were determined at 5 nm intervals from 275 to 380 nm and the derived spectrum is compared to that of the final product of substitution in Figure 3.

*Chloride Substitution of* $[Et_4N][MoOCl_3Br(OPPh_3)]$.—Three types of experiment were carried out at 25 °C in an attempt to gain information about the nature of the leaving group of the anion of this compound, prepared by reacting $[Et_4N]Br$ with $[MoOCl_3(OPPh_3)_2]$. First, $[Et_4NCl]$ was varied by a factor of 14 with $[Mo^V] \ngtr [Et_4NCl]$, the conditions changing from pseudo-first to second order. No dependence on $[Cl^-]$ was observed and the rate law (8)

$$-d[MoOCl_3Br(OPPh_3)^-]/dt = k_{obs.}[MoOCl_3Br(OPPh_3)^-] \qquad (8)$$

describes the behaviour; plots of $\log(D_t - D_\infty)$ against time were linear up to 85—90% of completion of reaction. Secondly, with a 1 : 1 $[Mo^V] : [Et_4NCl]$ ratio, the dependence of the reaction rate on a ten-fold variation in $[Et_4NBr]$ was investigated. Rate law (8) was again found to be applicable. Thirdly, again with a 1 : 1 $[Mo^V] : [Et_4NCl]$ ratio, the concentration of $Ph_3PO$ was varied between $5 \times 10^{-4}$ and $50 \times 10^{-4}$M. The dependence (9) was observed, where at 25 °C $c = 5{\cdot}70$ $s^{-1}$ and $d = 1{\cdot}52 \times 10^{-2}$ mol $l^{-1}$ $s^{-1}$

$$k_{obs.} = c + d[Ph_3PO]^{-1} \qquad (9)$$

(Figure 4). Data for these three variations are listed in Table 6. In all these experiments a second stage of reaction was observed which was considerably slower than the first ($t_{\frac{1}{2}}$ *ca.* 5—10 s); however, this was not studied further.

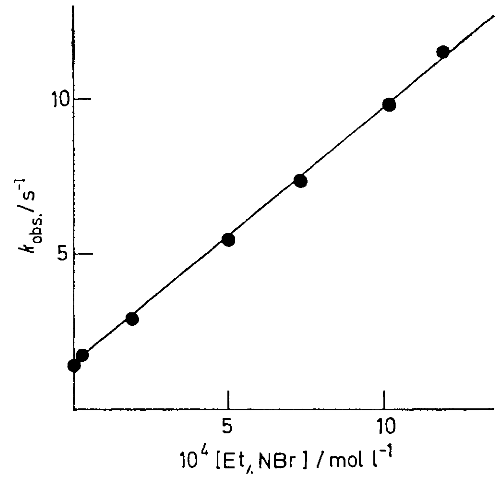


FIGURE 2 Variation of observed rate constant (25 °C) with $[Et_4NBr]$ for the second stage of bromide substitution of $[MoOCl_3(OPPh_3)_2]$

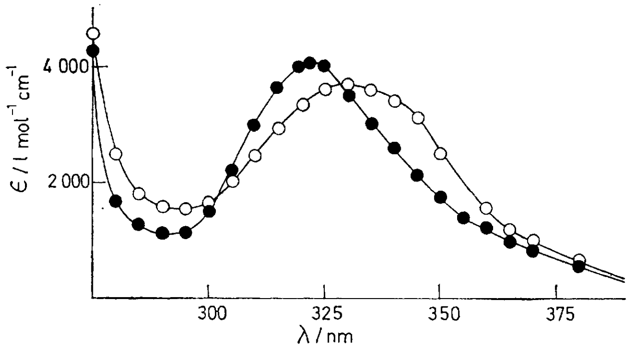


FIGURE 3 Electronic spectra of the intermediate (○) and final (●) product of the reaction of bromide with $[MoOCl_3(OPPh_3)_2]$

*Reaction of* $[Et_4N][MoOCl_4]$ *with Various Ligands*.—Reactions of $[MoOCl_4]^-$ with several ligands known to form 1 : 1 compounds with this five-co-ordinate ion[6] were studied. No spectral changes were observed for reactions with $Cl^-$, $Br^-$, $Ph_3PO$, or $(Me_2N)_3PO$ unless these ligands were in appreciable excess. However, with $NCS^-$ for $[Mo^V] : [NCS^-] = 1 : 1$ a slow reaction having $k_{obs.} = 2\ s^{-1}$ was observed at 25 °C.

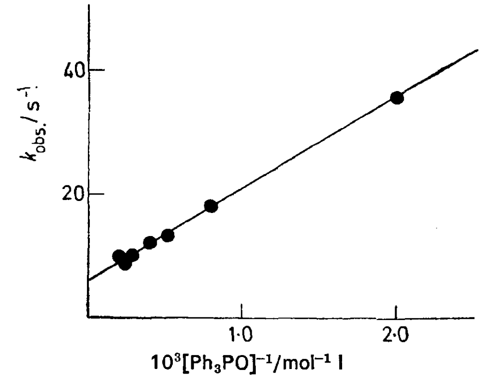


FIGURE 4 Variation of observed rate constants for chloride substitution of $[MoOCl_3Br(OPPh_3)]^-$ with added $Ph_3PO$ at 25 °C. $[MoOCl_3Br(OPPh_3)^-]$ And $[Cl^-]$ were maintained constant at $5 \times 10^{-3}$ mol $l^{-1}$

TABLE 6

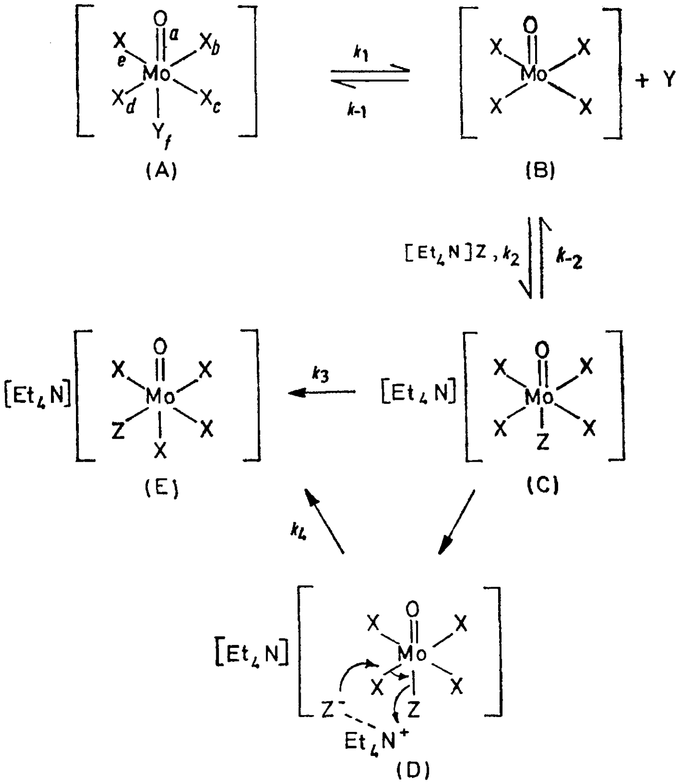
Kinetic data for chloride substitution of $[MoOCl_3Br(OPPh_3)]^-$ in $CH_2Cl_2$ at 25 °C, monitored at 340 or 290 nm. The number of runs is indicated in parentheses

| $10^4[Mo^V]$/ mol $l^{-1}$ | $10^4[Et_4NCl]$/ mol $l^{-1}$ | $10^4[Et_4NBr]$/ mol $l^{-1}$ | $10^4[Ph_3PO]$/ mol $l^{-1}$ | $k_{obs.}/s^{-1}$ |
|---|---|---|---|---|
| 1·00 | 3·50 | | | 42·4 (2) |
| 5·00 | 5·00 | | | 42·4 (2) |
| 5·00 | 15·0 | | | 49·3 (1) |
| 5·00 | 50·0 | | | 41·4 (2) |
| 5·00 | 5·00 | 5·00 | | 45·8 (2) |
| 5·00 | 5·00 | 12·5 | | 44·6 (2) |
| 5·00 | 5·00 | 25·0 | | 44·9 (2) |
| 5·00 | 5·00 | 50·0 | | 38·5 (2) |
| 5·00 | 5·00 | | 5·00 | 36·3 (1) |
| 5·00 | 5·00 | | 12·5 | 17·0 (2) |
| 5·00 | 5·00 | | 19·0 | 13·3 (2) |
| 5·00 | 5·00 | | 25·0 | 12·5 (2) |
| 5·00 | 5·00 | | 35·0 | 10·3 (2) |
| 5·00 | 5·00 | | 42·5 | 8·36 (2) |
| 5·00 | 5·00 | | 50·0 | 10·3 (2) |

## DISCUSSION

The proposed mechanism for the substitution reactions reported in this study is presented below. Labilisation of the ligand (Y) *trans* to the oxo-group in (A) leads to formation of the discrete five-co-ordinate intermediate (B), which is susceptible to nucleophilic attack (by Z) affording the substituted six-co-ordinate compound (C). This latter may rearrange either without ($k_3$), or with ($k_4$), the aid of $[Et_4N]Z$ to afford the isomer (E). Whether or not this isomerisation proceeds depends on the nature of the axial (Z) and equatorial (X) ligands (see below). In terms of the proposed mechanism, it is the nature of the ligand *trans* to the oxo-group which is important. The nature of this ligand in all the compounds isolable in this study has been assigned on the basis of spectroscopic studies to be described elsewhere.[6] For $[MoOCl_3(OPPh_3)_2]$ and the final product of halide substitution, $[MoOCl_3X(OPPh_3)]^-$ (X = Cl or Br), this *trans* ligand appears to be a $Ph_3PO$ group.

The labilisation of the ligand *trans* to an oxo-group is well established as both a thermodynamic and kinetic phenomenon for vanadium(IV) complexes.[8] Several structure determinations[9] have shown that a ligand co-ordinated *trans* to an oxomolybdenum group is usually further from the metal than such a ligand in another situation. However, the extension of this



apparent labilisation into a kinetic effect is less well characterised than for vanadium(IV). We feel that the information presented above for the halide-substitution reactions of $[MoOCl_3(OPPh_3)_2]$ indicates the presence of such a *trans* effect. Thus the kinetic data obtained for chloride substitution of this compound and for the corresponding first stage of bromide substitution are consistent[10] with an $S_N1$ (limiting) mechanism involving loss of a $Ph_3PO$ molecule and subsequent substitution by a halide ion; the five-co-ordinate intermediate (B; $X_{b,c,e}$ = Cl, $X_d$ = $Ph_3PO$) discriminates between the halide ion and a $Ph_3PO$ molecule in favour of the former. Using the stationary-state approximation $d[MoOCl_3(OPPh_3)]/dt = 0$, equation (10) is obtained such that

$$-\frac{d}{dt}[MoOCl_3(OPPh_3)_2] = \frac{k_1k_2[MoOCl_3(OPPh_3)_2][Et_4NX]}{k_{-1}[Ph_3PO] + k_2[Et_4NX]} \qquad (10)$$

---

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

[9] See, for example, A. B. Blake, F. A. Cotton, and J. S. Wood, *J. Amer. Chem. Soc.*, 1964, **86**, 3024; J. R. Knox and C. K. Prout, *Acta Cryst.*, 1969, **B25**, 1857; B. Spivack and Z. Dori, *J.C.S. Dalton*, 1973, 1173.

[10] C. H. Langford and H. B. Gray, 'Ligand Substitution Processes,' W. A. Benjamin, New York, 1965, p. 87.

(11) holds. The detection of terms involving $k_{-1}$ is

$$\frac{1}{k_{\text{obs.}}} = \frac{1}{k_1} + \frac{k_{-1}[\text{Ph}_3\text{PO}]}{k_1 k_2[\text{Et}_4\text{NX}]} \qquad (11)$$

particularly favourable in this system since there is no competition from the solvent. However, although a term in $k_{-2}$ is included in the mechanism, there was no evidence for it in these studies (Figure 1) and the data are well defined by equations (6) and (11). When $k_2[\text{Et}_4\text{NX}] \gg k_{-1}[\text{Ph}_3\text{PO}]$, equation (10) reduces to $1/k_{\text{obs.}} = 1/k_1$ and, consistent with the proposed mechanism, both chloride and bromide substitution give $k_{\text{obs.}} = k_1 = a^{-1} = 43{\cdot}7 \pm 2{\cdot}6\ \text{s}^{-1}$ [see equation (6)]. The activation parameters obtained for loss of a $\text{Ph}_3\text{PO}$ molecule from $[\text{MoOCl}_3(\text{OPPh}_3)_2]$ are $\Delta H^\ddagger = 11{\cdot}0 \pm 0{\cdot}4$ kcal mol$^{-1}$ and $\Delta S^\ddagger = -14{\cdot}0 \pm 1{\cdot}5$ cal K$^{-1}$ mol$^{-1}$. The negative entropy of activation is unexpected for an $S_{\text{N}}1$ (limiting) process. This may arise from ordering of the solvent molecules about the vacant co-ordination site of $[\text{MoOCl}_3(\text{OPPh}_3)]$ and/or association between the released $\text{Ph}_3\text{PO}$ molecules and the solvent. The latter might be expected to make the major contribution, but we were unable to demonstrate the occurrence of any substantial intermolecular interaction between $\text{Ph}_3\text{PO}$ and $\text{CH}_2\text{Cl}_2$ molecules.

The formation of the discrete five-co-ordinate species $[\text{MoOCl}_3(\text{OPPh}_3)]$ is clearly facilitated in this system by the poor co-ordinating ability of the solvent. A square-pyramidal geometry is favoured for this compound by analogy with that determined for $[\text{MoOCl}_3(\text{SPPh}_3)]$.[11] The composite rate term of equation (9) allows the relative rates ($k_2$) of $\text{Cl}^-$, $\text{Br}^-$, and $\text{Ph}_3\text{PO}$ attack on $[\text{MoOCl}_3(\text{OPPh}_3)]$ to be evaluated as 27 : 8 : 1, respectively. The order of nucleophilicity is consistent with the metal centre being ' hard ' in character.[12]

The appearance of the second stage in the bromide-substitution reaction of $[\text{MoOCl}_3(\text{OPPh}_3)_2]$ provides very good evidence for the subsequent isomerisation of the initial product (C). The spectrum of the intermediate produced at the end of the first stage of the bromide reaction (Figure 3) closely resembles that of the final product. The peak ($\lambda_{\text{max.}} = 329$ nm) is assigned to a Br→Mo charge-transfer transition [13] which requires that substitution has occurred at this juncture [as does the proposed $S_{\text{N}}1$ (limiting) mechanism].* The kinetic data obtained for the second stage of bromide substitution indicate two parallel paths for reaction. The first term suggests an isomerisation process (rate $k_3$) independent of $[\text{Et}_4\text{NBr}]$, whereas the second (rate $k_4$) is consistent with the assistance of $[\text{Et}_4\text{N}]\text{Br}$ in converting (C; $\text{X}_{b,c,e} = \text{Cl}$, $\text{X}_d = \text{OPPh}_3$, $\text{Z} = \text{Br}$) *via* (D) to (E). The driving force for the isomerisation (C) to (E) is presumed to be the increase in thermodynamic stability acquired when bromide moves to a site *cis* to the oxo-group where it may thus achieve stronger binding to the metal. Although a second stage was not observed for chloride substitution of $[\text{MoOCl}_3(\text{OPPh}_3)_2]$, it is presumed to occur since spectroscopic studies [6] indicate that the product $[\text{MoOCl}_4(\text{OPPh}_3)]^-$ contains the $\text{Ph}_3\text{PO}$ molecule *trans* to the oxo-group. Therefore we suggest that the rate of isomerisation for chloride substitution probably occurs at a rate in excess of that found for the first stage of reaction.

In support of the above arguments we carried out further kinetic studies to provide additional evidence for the observation that isomerisation reactions can occur in these systems. The first of these checks consisted of a study of (3), chloride substitution of $[\text{MoOCl}_3\text{Br}(\text{OPPh}_3)]^-$ the product of bromo-substitution of $[\text{MoOCl}_3(\text{OPPh}_3)_2]$. The relevant data for this study are summarised in Table 6, and since the observed rate constant is retarded by added $\text{Ph}_3\text{PO}$ and not $\text{Br}^-$ it is concluded that chloride substitution proceeds *via* loss of $\text{Ph}_3\text{PO}$. In the absence of $\text{Br}^-$ or $\text{Ph}_3\text{PO}$ the rate constant at 25 °C, $k_{\text{obs.}} = 43{\cdot}7 \pm 2{\cdot}3\ \text{s}^{-1}$, for loss of $\text{Ph}_3\text{PO}$ is close to the values found for $k_1$ (X = Cl or Br at 25 °C). Although the general kinetic pattern is similar to that in equations (10) and (11) it is not quite identical. The addition of a term in $k_{-2}$ for loss of halide ion from (C) gives the predicted term in the rate law for equation (8), assuming the stationary-state approximation $\text{d}[\text{MoOCl}_3\text{Br}]/\text{d}t = 0$. For the conditions listed in Table 6 with no added $\text{Ph}_3\text{PO}$, $k_{\text{obs.}} = k_1$; with added $\text{Ph}_3\text{PO}$ the term $k_{-1}[\text{Ph}_3\text{PO}]$ most probably dominates $k_2[\text{Et}_4\text{NCl}]$ and (12) reduces to (13), which is

$$k_{\text{obs.}} = \frac{k_1 k_2[\text{Et}_4\text{NCl}] + k_{-1}k_{-2}[\text{Ph}_3\text{PO}]}{k_{-1}[\text{Ph}_3\text{PO}] + k_2[\text{Et}_4\text{NCl}]} \qquad (12)$$

$$k_{\text{obs.}} = (k_1 k_2/k_{-1})[\text{Et}_4\text{NCl}][\text{Ph}_3\text{PO}]^{-1} + k_{-2} \qquad (13)$$

compatible with equation (9). At 25 °C, $k_{-2} = 5{\cdot}7\ \text{s}^{-1}$. No evidence for a term in $k_{-2}$ was detected for the halide-substitution reactions of $[\text{MoOCl}_3(\text{OPPh}_3)_2]$ and strict adherence to equation (6) was observed in both cases (Z = Cl or Br) under the conditions listed. However, for the purpose of uniformity, a term in $k_{-2}$ is included in the general scheme.

These results provide strong support for the inferred isomerisation. If isomerisation had not occurred, either bromide would have been expected to be replaced by chloride or $\text{Ph}_3\text{PO}$ would have been substituted but at a different rate to that observed. Neither of these possibilities are consistent with the observations. As a second check we sought to study the attack of various nucleophiles on $[\text{MoOCl}_4]^-$, which appears to have a square-pyramidal structure with a vacant co-ordination site *trans* to the oxo-group.[6] For thiocyanate, valuable information was obtained in this respect. The $k_{\text{obs.}}$ of *ca.* 2 s$^{-1}$ obtained in the kinetic study of this reaction is far too slow for a simple addition process and is remarkably similar to the value of $k_3 = 1{\cdot}5\ \text{s}^{-1}$ for the second stage of the bromide-substitution reaction of

---

* We were unable to prepare or even detect the existence of a disubstituted bromo-product in $\text{CH}_2\text{Cl}_2$ solution, although in EtOH $[\text{Et}_4\text{N}]_2[\text{MoOCl}_3\text{Br}_2]$ has been prepared.[6]

[11] P. M. Boorman, C. D. Garner, T. J. King, and F. E. Mabbs, *J.C.S. Chem. Comm.*, 1974, 663.

[12] R. G. Pearson, *Chem. in Britain*, 1967, **3**, 103.

[13] C. K. Jørgensen, *Progr. Inorg. Chem.*, 1970, **12**, 101 and refs. therein.

[$MoOCl_3(OPPh_3)_2$]. Accordingly we propose that both these latter are isomerisation processes.

It is possible to interpret some of the above data in terms of a primary substitution process involving a ligand *cis* to the oxomolybdenum group, as has been suggested from certain e.s.r. studies on aqueous solutions of oxomolybdenum(v) complexes.[14] However, we feel that this interpretation disregards the well characterised *trans* labilisation of an oxo-group and requires the nature of the majority of compounds studied to be at variance with that indicated by spectroscopic studies.[6] Furthermore, the isomerisation reactions reported here indicate how the *net* substitution of a ligand *cis* to the oxo-group may proceed and it is the overall substitution reaction rather than the detailed mechanism for which e.s.r. spectroscopic studies are more suited. The results reported above {including the apparent lack of isomerisation of the [$MoOCl_4X$]$^{n-}$ ions [$X = Cl$ or Br, $n = 2$; $X = Ph_3PO$ or $(Me_2N)_3PO$, $n = 1$] prepared from [$MoOCl_4$]$^-$} suggest that the stability sequence is $NCS^- > Cl^- > Br^- > (Me_2N)_3PO,Ph_3PO$; a ligand higher in this order *trans* to the oxo-group will tend to change places with one lower in the order and *cis* to the oxo-group.

We thank Dr. G. Tomalin of the Department of Biological Chemistry for the use of the stopped-flow apparatus, Dr. P. M. Boorman for valuable discussions and the preparation of [$Et_4N$][$MoOCl_4$], and the S.R.C. for financial support for M. R. H. as a post-doctoral fellow and V. I. R. as a research student.

[4/1644 *Received, 5th August*, 1974]

---

[14] I. N. Marov, *Proc. Conf. Chemistry and Uses of Molybdenum*, University of Reading, 1973, ed. P. C. H. Mitchell, p. 63; I. N. Marov, V. K. Belyaeva, A. N. Ermakov, and Yu. Dubrov, *Russ. J. Inorg. Chem.*, 1969, **14**, 1391.