# Kinetics and Mechanism of Oxidation of Trichloro-oxobis(triphenylphosphine oxide)molybdenum(V) by Nitrate in Dichloromethane

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The kinetics of the redox reaction between $[Et_4N][NO_3]$ and $[MoOCl_3(OPPh_3)_2]$ have been studied in $CH_2Cl_2$ solution at temperatures from 3·2 to 25 °C. This reaction proceeds in three observable steps when $[NO_3^-] > [Mo^V]$. The first step involves co-ordination of the nitrate ion *via* an $S_N1$ (limiting) mechanism involving loss of a triphenylphosphine oxide molecule; at 25 °C, $k_{obs.} = 40 \pm 1\ s^{-1}$ and the corresponding activation parameters are $\Delta H^\ddagger = 9{\cdot}7 \pm 0{\cdot}5$ kcal mol$^{-1}$ and $\Delta S^\ddagger = -18{\cdot}4 \pm 1{\cdot}7$ cal K$^{-1}$ mol$^{-1}$. The data obtained for the second and third steps strongly suggest that they involve intramolecular substitution at molybdenum(V) and intermolecular substitution at molybdenum(VI) centres, respectively. Rapid non-rate-determining electron transfer from molybdenum(V) to nitrate is proposed to occur between these two latter steps, $k_{e.t.} \geqslant 1\ s^{-1}$ at 25 °C, giving a dioxomolybdenum(VI) complex and nitrogen dioxide. The kinetic results imply that a specific orientation of the nitrato-group with respect to the oxomolybdenum(V) centre is necessary prior to rapid electron transfer.

INTERACTION between a molybdenum(V) centre and a nitrate ion has been proposed to occur immediately prior to the final step in the electron-transfer sequence of the reduction path of the *nitrate reductase* enzymes.[1,2] These enzymes, which require molybdenum both for their formation and activity,[3] are responsible for the first step in nitrate assimilation and for nitrate respiration, converting nitrate to nitrite with the molybdenum apparently changing between the oxidation states $Mo^V$ and $Mo^{VI}$.[4] As part of a study of the chemistry of molybdenum related to that of the molybdenum-containing enzymes, we report details of a kinetic investigation of the reaction between nitrate ions and the molybdenum(V) complex $[MoOCl_3(OPPh_3)_2]$.[†]

## EXPERIMENTAL

The complexes $[MoOCl_3(OPPh_3)_2]$ and $[Et_4N][MoOCl_4(OPPh_3)]$ were prepared, and $CH_2Cl_2$ was purified, as described previously.[5] The salt $[Et_4N][NO_3]$ was prepared from $[Et_4N]Cl$ (B.D.H.) in $CH_2Cl_2$ and $AgNO_3$ in MeCN by evaporation of the solvent following removal of the AgCl by filtration. Recrystallisation from $CH_2Cl_2$ gave analytically pure $[Et_4N][NO_3]$ which was dried *in vacuo* ($10^{-3}$ Torr) at *ca.* 80 °C for at least 4 h prior to use.[‡]

The value of the equilibrium constant, *K*, for the dissociation (1) in $CH_2Cl_2$ was obtained by determining the

$$[Et_4N][NO_3] \rightleftharpoons [Et_4N]^+ + [NO_3]^- \qquad (1)$$

variation of molar conductance of these solutions with the concentration of the salt, using a Philips PR9500 conductivity bridge.[6] These data (Table 1) gave $K = 1{\cdot}04 \times 10^{-5}$ mol l$^{-1}$ at 25 °C. Corrections for ionic strength were not applied.

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[†] A preliminary account of this work has appeared; *Nature*, 1974, **252**, 579.

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

[1] D. J. D. Nicholas and A. Nason, *J. Biol. Chem.*, 1954, **211**, 183.

[2] P. Forget and D. V. Dervartanian, *Biochim. Biophys. Acta*, 1972, **256**, 600.

[3] R. C. Bray and J. C. Swann, *Structure and Bonding*, 1969, **4**, 475 and refs. therein.

[4] D. J. D. Nicholas and H. M. Stevens, *Nature*, 1955, **176**, 1066.

[5] C. D. Garner, M. R. Hyde, F. E. Mabbs, and V. I. Routledge, preceding paper.

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

*Kinetic Measurements.*—Freshly prepared $CH_2Cl_2$ solutions of $[MoOCl_3(OPPh_3)_2]$ and $[Et_4N][NO_3]$ under an inert atmosphere were transferred using syringe techniques to the storage chambers of an Aminco–Morrow stopped-flow system coupled to a Beckmann DU spectrophotometer. A nitrogen atmosphere was maintained above the solutions, which were thermostatted for *ca.* 15 min prior to reaction to within ±0·1 °C at temperatures between 3 and 25 °C. Reactions were followed by monitoring transmittance changes with time at either 280 or 320 nm. Data were recorded on a Telequipment DM64 storage oscilloscope and stored on polaroid film. Reaction conditions were varied from pseudo-first to second order, with $[Et_4NNO_3]$ in 66- to 4-fold excess over $[Mo^V]$. Under these conditions three stages of reaction were generally observed, the first being distinct since it was always considerably faster than the other two. However, the second and third stages were not readily separable and the appropriate rate constants were evaluated by treating these stages as consecutive first-order processes.[7] Observed first-order rate constants for the first and third stages were obtained from plots of log ($\Delta D$) against time ($\Delta D$ = change in absorbance at the particular wavelength monitored). In all cases these plots were linear up to at least 80% completion of reaction. First-order rate constants for the second stage were evaluated by a consecutive treatment of the data as illustrated in Figure 1. For each stage, the dependence of the observed rate constant on $[Et_4NNO_3]$, $[MoOCl_3(OPPh_3)_2]$, $[Ph_3PO]$, and $[Et_4NCl]$ was investigated and these data are summarised in Tables 2 (first stage) and 3 (second and third stages). Computation of the kinetic data was accomplished using the unweighted least-squares procedure contained within the progam ARRHENIUS I of Dr. J. P. Day.

TABLE 1

Variation in conductivity with electrolyte concentration for $[Et_4N][NO_3]$ solutions in $CHCl_2$ at 25 °C

| $10^4[Et_4NNO_3]$/ mol $l^{-1}$ | $10^{-5}R/\Omega$ | $\Lambda$/S cm$^2$ mol$^{-1}$ |
|---|---|---|
| 11·2 | 0·705 | 17·5 |
| 6·25 | 1·15 | 19·2 |
| 2·20 | 1·90 | 32·4 |
| 0·625 | 4·45 | 49·6 |
| 0·450 | 5·15 | 59·8 |
| 0·125 | 12·2 | 90·4 |
| 0·067 | 15·5 | 132·8 |
| 0·025 | 39·0 | 142·4 |

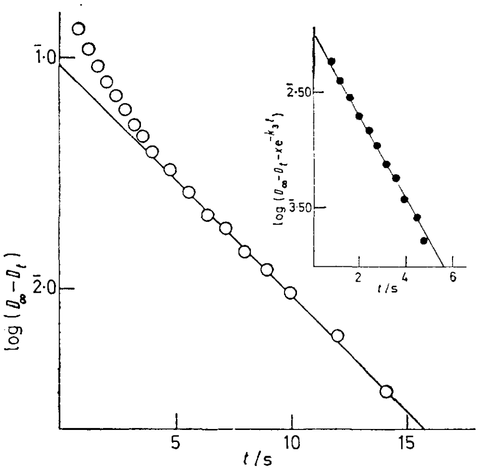

FIGURE 1 An example of the consecutive-reaction treatment for the evaluation of first-order rate constants, $k_2$ and $k_3$, for the second and third stages observed during $[NO_3]^-$ oxidation of $[MoOCl_3(OPPh_3)_2]$. The main graph gives $k_3$ for the third stage, and the inset $k_2$ for the second stage, for this run with $[Mo^V]_0 = 1{\cdot}5 \times 10^{-4}$ mol $l^{-1}$, $[Et_4NNO_3] = 1{\cdot}5 \times 10^{-3}$ mol $l^{-1}$, at 25 °C, and $\lambda$ = 280 nm

TABLE 2

Kinetic data for the first stage observed during the reaction between $[Et_4N][NO_3]$ and $[MoOCl_3(OPPh_3)_2]$, absorbance changes being monitored at $\lambda$ = 280 or 320 nm

| $\theta_c$/°C | $10^4[Mo^V]_0$/ mol $l^{-1}$ | $10^3[Et_4NNO_3]$/ mol $l^{-1}$ | $10^3[Ph_3PO]$ [a]/ mol $l^{-1}$ | $k_{obs.}$ [b]/$s^{-1}$ |
|---|---|---|---|---|
| 25·0 | 1·50 | 2·46 | 10·0 | 13·4 (2) |
| | 1·50 | 2·46 | 5·5 | 18·0 (2) |
| | 1·50 | 2·46 | 3·5 | 21·4 (1) |
| | 1·50 | 2·46 | 1·5 | 29·9 (2) |
| | 1·50 | 2·46 | 0·5 | 37·2 (2) |
| | 1·50 | 5·00 | | 37·1 (2) |
| | 1·50 | 3·00 | | 43·2 (2) |
| | 1·50 | 1·50 | | 38·9 (2) |
| | 1·50 | 0·90 | | 37·2 (2) |
| | 0·75 | 0·60 | | 35·7 (2) |
| | 0·75 | 0·30 | | 37·1 (1) |
| | 0·30 | 0·15 | | 41·5 (1) |
| | 1·50 | 8·00 | | 44·4 (5) [c] |
| 15·0 | 1·50 | 0·50 | | 23·9 (2) |
| | 1·50 | 10·0 | | 24·0 (2) |
| 3·2 | 1·50 | 0·50 | | 10·0 (2) |
| | 1·50 | 10·0 | | 9·30 (2) |

[a] Added triphenylphosphine oxide. [b] The number of runs is indicated in parentheses. [c] The average of five runs with added $Cl^-$ in the range $[Et_4NCl] = 1 \times 10^{-3}$—$5 \times 10^{-3}$M.

*Product Identification.*—The nature of the molybdenum-containing product of the reaction between $[MoOCl_3(OPPh_3)_2]$ and $[Et_4N][NO_3]$ for ratios of these reactants > 1 : 1 was dependent on the particular ratio employed, probably due to the variation in the extent of nitrate substitution of the primary molybdenum(VI) product. Thus for a $[Mo^V] : [NO_3^-]$ ratio of 1 : 3, $[MoO_2(NO_3)_2(OPPh_3)_2]$ appeared to be the predominant molybdenum-containing product, and for a 1 : 1 $[Mo^V] : [NO_3^-]$ ratio $[MoO_2Cl_2(OPPh_3)_2]$ was formed almost exclusively (⩾95%). For a $[Mo^V] : [NO_3^-]$ ratio of 2 : 1, subsequent to the stages described above, half the molybdenum was present as $[MoO_2Cl_2(OPPh_3)_2]$ and half as $[Et_4N][MoOCl_4(OPPh_3)]$.[8]

For initial concentrations of reactants $[MoOCl_3(OPPh_3)_2]$ and $[Et_4N][NO_3]$ of $1{\cdot}5 \times 10^{-4}$ and $7{\cdot}5 \times 10^{-4}$ mol $l^{-1}$, the rate constants for the first and second stages of the reaction differed by a factor of *ca.* 40. Therefore, it was possible to evaluate the u.v.–visible spectrum of the molybdenum-containing product of the first stage of the reaction, (A), by measuring absorbance data, between 275 and 400 nm at 5 nm intervals, from stopped-flow traces at the end of this stage. The u.v.–visible spectrum of the second-stage product, (B), was evaluated by a less direct approach. Each of these plots was extrapolated to a time corresponding to the end of the second stage, *ca.* 10 s, and the value of $\Delta D$ corresponding to the absorbance change between (B) and the final product was recorded. Each value was then added to the absorbance values of the final product at that particular wavelength to give the absorbance due to (B).

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

[8] P. M. Boorman, C. D. Garner, M. R. Hyde, P. Lambert, F. E. Mabbs, and V. I. Routledge, unpublished work.

The electronic spectra of the molybdenum-containing species involved in the reaction between $[MoOCl_3(OPPh_3)_2]$ and $[Et_4N][NO_3]$ at concentrations of $1{\cdot}5 \times 10^{-4}$ and $7{\cdot}5 \times 10^{-4}$ mol $l^{-1}$ are presented in Figure 2.

TABLE 3

Kinetic data (25 °C) for the second and third stages observed during the reaction of $[Et_4N][NO_3]$ with $[MoOCl_3(OPPh_3)_2]$, absorbance changes being monitored at $\lambda$ = 280 or 320 nm

| $10^4[Mo^V]_0$ [a]/ mol $l^{-1}$ | $10^3[Et_4NNO_3]$/ mol $l^{-1}$ | $10^3[Ph_3PO]$ [b]/ mol $l^{-1}$ | $10^3[Et_4NCl]$/ mol $l^{-1}$ | $k_2$ [c]/$s^{-1}$ | $k_3$ [d]/$s^{-1}$ |
|---|---|---|---|---|---|
| 1·50 | 0·40 | | | | 0·036 (2) |
| 1·50 | 0·55 | | | | 0·054 (2) |
| 1·50 | 0·70 | | | | 0·087 (2) |
| 1·50 | 0·90 | | | 1·05 (2) | 0·174 (2) |
| 1·50 | 1·50 | | | 0·86 (2) | 0·255 (2) |
| 1·50 | 3·00 | | | 1·17 (2) | 0·525 (2) |
| 1·50 | 5·00 | | | 0·98 (2) | *ca.* 0·98 [e] |
| 1·50 | 7·00 | | | 1·19 (2) | *e* |
| 1·50 | 9·00 | | | 1·19 (2) | *e* |
| 0·60 | 2·00 | | | 1·18 (2) | *ca.* 0·9 (2) |
| 0·80 | 2·00 | | | 1·27 (1) | 0·686 (2) |
| 1·00 | 2·00 | | | 1·08 (2) | 0·568 (2) |
| 1·20 | 2·00 | | | 1·36 (1) | 0·535 (2) |
| 2·00 | 2·00 | | | 0·78 (1) | 0·284 (2) |
| 2·50 | 2·00 | | | 0·87 (1) | 0·180 (2) |
| 1·50 | 2·46 | 1·50 | | 1·23 (1) | 0·51 (2) |
| 1·50 | 2·46 | 5·50 | | 1·21 (2) | 0·19 (2) |
| 1·50 | 2·46 | 7·50 | | 0·85 (1) | 0·16 (2) |
| 1·50 | 2·46 | 10·0 | | 1·00 (2) | 0·13 (2) |
| 1·50 | 8·00 | | 0·50 | 0·92 (2) | *e* |
| 1·50 | 8·00 | | 1·00 | 0·287 (2) | *e* |
| 1·50 | 8·00 | | 2·00 | 0·093 (2) | *e* |
| 1·50 | 8·00 | | 5·00 | 0·022 (2) | *e* |

[a] Initial concentration of $Mo^V$ reactant. [b] Added triphenylphosphine oxide. [c] $k_2$ Is the observed first-order rate constant for the second stage of reaction as obtained by analysis of consecutive reactions. The number of runs is indicated in parentheses. [d] $k_3$ Is the observed first-order rate constant for the third stage of reaction. The number of runs is indicated in parentheses. [e] The third stage could not be observed under these conditions.

The nature of the primary nitrogen-containing product was investigated for reaction mixtures involving initial $[NO_3^-] : [Mo^V]$ ratios of 3 : 1 to preclude any competition between nitrate and the nitrogen-containing product as oxidants for molybdenum(V). The complex $[MoOCl_3(OPPh_3)_2]$ (0·42 g, 0·54 mmol) was dissolved in $CH_2Cl_2$ (7 $cm^3$) and $[Et_4N][NO_3]$ (0·32 g, 1·66 mmol) added. The flask was then stoppered and shaken, resulting immediately in the formation of a brown solution, and then left to stand at room temperature for *ca.* 5 min. The flask was then attached to a vacuum line and the solvent distilled under gentle heat into a trap cooled to −196 °C. The resulting light brown solution was diluted to 10 $cm^3$ with $CH_2Cl_2$ and its u.v.–visible spectrum recorded on a Pye–Unicam SP 800 spectrophotometer. This spectrum was found to be identical with that recorded for an authentic sample of dinitrogen tetraoxide (B.D.H.) dissolved in $CH_2Cl_2$. Estimation of the absorption coefficients for the stock solution indicated a yield of $NO_2 \geqslant 80\%$ based on the amount of molybdenum(V) and assuming the stoicheiometry (2). Subsequent to reaction, solutions involving

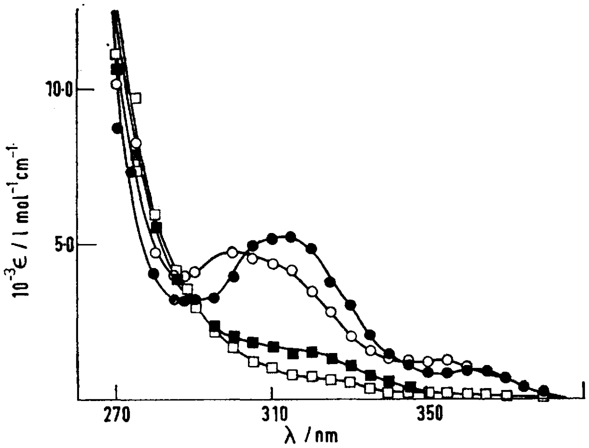

FIGURE 2 Spectra of molybdenum-(V) and -(VI) species observed during the $[NO_3]^-$ oxidation of $[MoOCl_3(OPPh_3)_2]$ at 25 °C, $[Mo^V]_0 = 1{\cdot}5 \times 10^{-4}$ mol $l^{-1}$, and $[Et_4NNO_3] = 7{\cdot}5 \times 10^{-4}$ mol $l^{-1}$. (○), Starting material; (●), 1 : 1 product after first stage, (A); (■), 1 : 1 product after second stage, (B); (□), final product in the presence of excess of $[Et_4N][NO_3]$ (five-fold)

$$Mo^V + [NO_3]^- \longrightarrow Mo^{VI} + NO_2 \qquad (2)$$

initial $[Mo^V]$ and $[NO_3^-]$ ratios of 1 : 1—6 were hydrolysed and the quantity of nitrite produced was estimated colorimetrically [9] and found to be that (±5%) anticipated for (2) followed by the disproportionation (3).[10]

$$2NO_2 + H_2O \longrightarrow HNO_3 + HNO_2 \qquad (3)$$

## RESULTS AND DISCUSSION

The proposed mechanism for the reaction between $[MoOCl_3(OPPh_3)_2]$ and $[Et_4N][NO_3]$ is given in the scheme. The geometry of $[MoOCl_3(OPPh_3)_2]$ has been assigned on the basis of e.s.r., i.r., and electronic spectral results.[8]

The kinetic data (Table 2) obtained for the first stage of the reaction are described by the expressions (4) and

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[9] Adapted from A. I. Vogel, 'A Text Book of Macro and Semimicro Qualitative Inorganic Analysis,' Longmans, 4th edn., 1953 p. 338.

[10] J. T. Spence and J. A. Frank, *J. Amer. Chem. Soc.*, 1963, **85**, 116; J. T. Spence, *Arch. Biochem. Biophys.*, 1970, **137**, 287.

(5). The steady-state approximation d[$MoOCl_3(OPPh_3)$]/d$t = 0$ in respect of the scheme gives the rate equations (6) and (7), thus $k_{obs.}$ is suppressed when $Ph_3PO$ is added to the reactant solutions (Table 2, Figure 3). This behaviour parallels that described[5] for chloride- and bromide-substitution reactions of

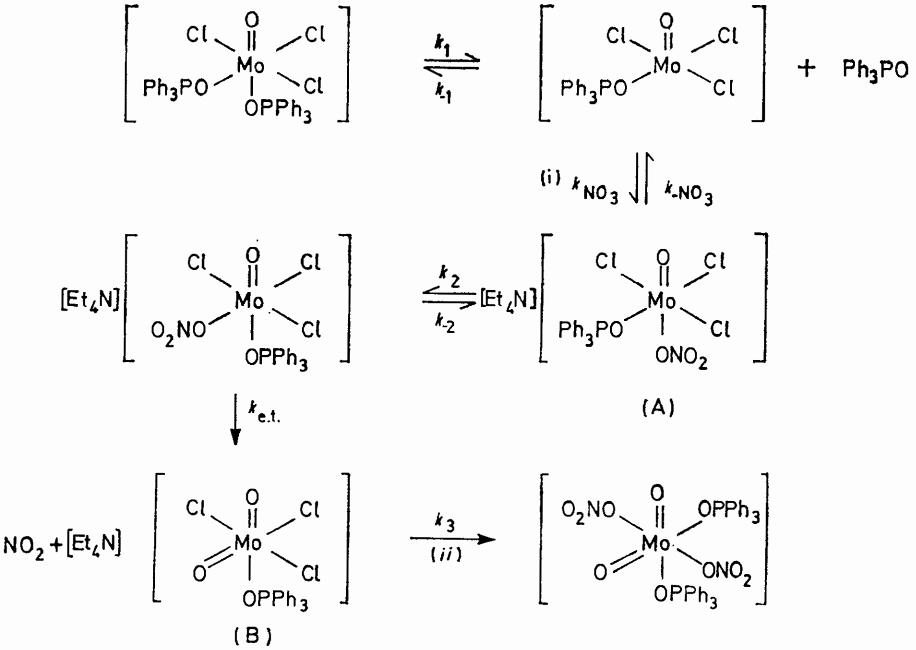
$$-d[MoOCl_3(OPPh_3)_2]/dt = k_{obs.}[MoOCl_3(OPPh_3)_2] \quad (4)$$

$$k_{obs.} = \frac{a[Et_4NNO_3]}{b[Ph_3PO] + [Et_4NNO_3]} \quad (5)$$

$$\frac{-d}{dt}[MoOCl_3(OPPh_3)_2] = \frac{k_1 k_{NO_3}[MoOCl_3(OPPh_3)_2][Et_4NNO_3]}{k_{-1}[Ph_3PO] + k_{NO_3}[Et_4NNO_3]} \quad (6)$$

$$\frac{1}{k_{obs.}} = \frac{1}{k_1} + \frac{k_{-1}[Ph_3PO]}{k_1 k_{NO_3}[Et_4NNO_3]} \quad (7)$$

[$MoOCl_3(OPPh_3)_2$], where it was concluded that the rate-determining step involves loss of a $Ph_3PO$ group *trans* to the oxo-group. As required for such an interpretation, the activation parameters for these halide substitutions ($\Delta H^‡ = 10{\cdot}6 \pm 0{\cdot}8$ or $11{\cdot}4 \pm 0{\cdot}2$ kcal mol$^{-1}$, $\Delta S^‡ = -15{\cdot}4 \pm 2{\cdot}9$ or $-12{\cdot}5 \pm 0{\cdot}8$ cal K$^{-1}$ mol$^{-1}$ for $Cl^-$ or $Br^-$, respectively) closely resemble those for nitrate substitution, $\Delta H^‡ = 9{\cdot}7 \pm 0{\cdot}5$ kcal mol$^{-1}$ and $\Delta S^‡ = -18{\cdot}4 \pm 1{\cdot}7$ cal K$^{-1}$ mol$^{-1}$. Also consistent with the $S_N1$ (limiting) mechanism proposed for these reactions, the values determined for $k_1$, 40·3 (nitrate), 42·0 (chloride), and 41·6 s$^{-1}$ (bromide), are identical within experimental error. A comparison of the data calculated for competition between $[NO_3]^-$, $Cl^-$, or $Br^-$,[5] and $Ph_3PO$ for the five-co-ordinate intermediate [$MoOCl_3(OPPh_3)$] (= $k_{NO_3}$ here) suggests that the order of nucleophilicity towards this centre varies as $[NO_3]^- > Cl^- > Br^- > Ph_3PO$ in the ratios 31 : 27 : 8 : 1. Although no evidence for a term in $k_{-NO_3}$ was observed, it is included in the scheme since its presence may be obscured by the $k_2$ path. The spectrum of (A) contains a band centred at 312 nm (ε *ca.* 5 700 l mol$^{-1}$ cm$^{-1}$) (Figure 2) and comparison with spectra of other oxomolybdenum-(V) and -(VI) complexes suggests[8] that it corresponds to a molybdenum(V)→nitrate charge-transfer transition.



(*i*), $[Et_4N][NO_3]$; (*ii*), $Ph_3PO$ and excess $[NO_3^-]$.

The observed first-order rate constant, $k_2$, corresponding to the second stage of the reaction between [$MoOCl_3(OPPh_3)_2$] and $[Et_4N][NO_3]$ showed a considerable fluctuation (±20%) for most of the conditions listed in Table 3. This is attributed to the similarity in values of the rate constants for the second and third stages which could only be estimated using a consecutive

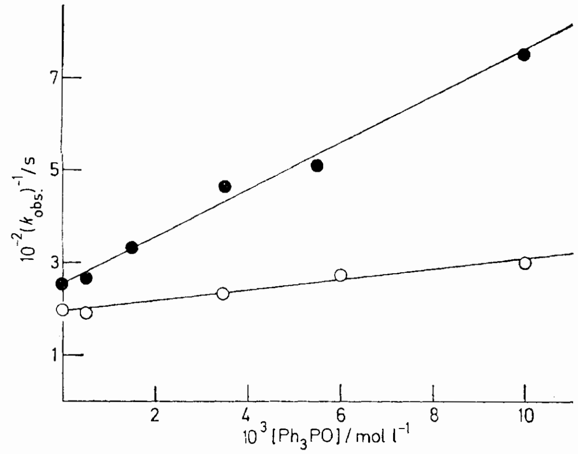


FIGURE 3 Dependence of observed rate constant on [$Ph_3PO$] for the first stage in the reaction of $[NO_3]^-$ with [$MoOCl_3(OPPh_3)_2$] (●) and [$MoOCl_4(OPPh_3)$]$^-$ (○) at 25 °C

treatment.[7] No significant dependence of $k_2$ on $[Et_4N][NO_3]$ or $Ph_3PO$ concentrations was observed, whereas the addition of $[Et_4N]Cl$ considerably suppressed the value of $k_2$. It is considered that this effect arises at least partially because of the effective competition between $Cl^-$ and $[NO_3]^-$ for the five-co-ordinate intermediate $[MoOCl_3(OPPh_3)]$. Therefore, ignoring the last four entries of Table 3, the second stage of the reaction may be represented by equation (8); the concentration

$$-d[A]/dt = k_2[A] \qquad (8)$$

of (A) has been assumed equal to that of the $[MoOCl_3(OPPh_3)_2]$ initially present ($[Mo^V]_0$). At 25 °C, $k_2 = 1{\cdot}0 \pm 0{\cdot}2\ s^{-1}$.

Data obtained for the second stage of the reaction suggest a mechanism involving an intramolecular rearrangement of $[MoOCl_3(NO_3)(OPPh_3)]^-$. There appear to be two possibilities for this process. That presented in the scheme involves site exchange of $[NO_3]^-$ and $Ph_3PO$ groups in a manner analogous to the isomerisation of $[MoOCl_3Br(OPPh_3)]^-$.[5] The driving force for this isomerism is the greater thermodynamic stability achieved when the better donor towards this metal centre is bonded *cis* to the oxo-group where the stronger metal–ligand bond may be formed. Consequently the complex containing the *O*-donor $[NO_3]^-$ *cis* and the bromo-group *trans* to the oxo-groups is expected to be more stable than the opposite arrangement.

The value of $k_2$ determined for this process is very similar to that ($k = 1{\cdot}5 \pm 0{\cdot}1\ s^{-1}$) observed for such a concerted rearrangement of $[MoOCl_3Br(OPPh_3)]^-$.[5] However, unlike the bromo-complex,[5] the isomerisation of the nitrato-complex does not appear to be catalysed by the corresponding tetramethylammonium salt. An alternative mechanism for the second stage of the reaction, which would also be consistent with the kinetic data, is chelation of the nitrato-group such that one of its oxygen atoms is co-ordinated *cis* and another *trans* to the oxo-group. Chelation displaces $Cl^-$ rather than $Ph_3PO$, not only because $k_2$ is independent of $[Ph_3PO]$ and suppressed by an increase in $[Et_4NCl]$ but also [5] as $[Et_4N][MoOCl_4(OPPh_3)]$ has been isolated following the oxidation of $[MoOCl_3(OPPh_3)_2]$ by $[Et_4N][NO_3]$, 2 : 1. The data presently available do not allow for a distinction between these two mechanisms. It is, however, emphasised that *both* these mechanisms lead to the feature essential for the next stage of the proposed mechanism, a fast electron-transfer process, which requires that one (and only one) of the nitrato-group's oxygen atoms be co-ordinated *cis* to the oxomolybdenum(v) centre.

The absorbance spectrum of (B) (Figure 2) closely resembles that of the final molybdenum(VI) product and is quite different from the spectra of the molybdenum(v) complexes studied here $\{[MoOCl_3(OPPh_3)_2]$ and (A)$\}$ and elsewhere.[8] On this basis the species (B) is considered to be a molybdenum(VI) complex and therefore it is required that a rapid internal electron-transfer process, $k_{e.t.}$ (25 °C) $\geqslant 1\ s^{-1}$, occurs subsequent to $k_2$ and prior to $k_3$. Such a process requires [11] the orbital containing the electron on the molybdenum(v) centre to overlap to some extent with a low-lying empty orbital on the nitrato-group. The typical electronic ground state for oxomolybdenum(v) complexes appears to be [7,12] $(4d_{xy})^1$ (where the Mo=O direction defines the *z* axis). *Ab initio* molecular-orbital calculations [13] suggest that the lowest virtual orbital of the nitrate group is the $\pi^*$ orbital. Therefore, facile electron transfer requires overlap between the partially filled $4d_{xy}$ orbital of the metal and the empty $\pi^*$ orbital of the nitrato-group. Such overlap is *only* possible when the nitrato-group has one (and only one) oxygen atom co-ordinated *cis* to the oxomolybdenum group (see Figure 4). Subsequent to the electron transfer $Mo^V \rightarrow [NO_3]^-$, the electron rearrangement $\pi^* \rightarrow \sigma^*$ within the nitrato-group, coupled with the slight adjustment in atomic positions to produce $NO_2$ and a *cis*-$Mo^{VI}O_2$ moiety, would be expected to proceed rapidly. The *cis* requirement described above is therefore *also* demanded * by the configuration of the $MoO_2$ unit.[14]

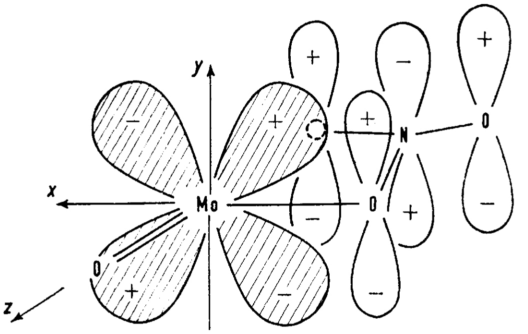


FIGURE 4 Overlap between the $\pi^*$ orbital of the nitrato-group and the $4d_{xy}$ orbital of the molybdenum atom

The kinetic data obtained for the third stage of the reaction between $[MoOCl_3(OPPh_3)_2]$ and $[Et_4N][NO_3]$ (Table 3) are described by the rate expression (9). The

$$-d[B]/dt = (d + e[Ph_3PO]_s^{-1})[Et_4NNO_3]_s[B] \quad (9)$$

concentration of (B) has been assumed equal to the initial molybdenum concentration, $[Mo^V]_0$; $[Et_4NNO_3]_s$ and $[Ph_3PO]_s$ are the concentrations of these reagents available after the second stage assuming that, during the first two stages of the reaction, 1 mol of $[Et_4N][NO_3]$ is removed and 1 mol of $Ph_3PO$ is liberated per mol of $Mo^V$. At constant $[Ph_3PO]_s$ and $[Mo^V]_0$ a first-order dependence of the observed rate constant on $[Et_4NNO_3]_s$ was observed (Figure 5); at constant $[Et_4NNO_3]_s$ $k_3$ showed an inverse dependence on $[Ph_3PO]_s$ and $[Mo^V]_0$

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* If the assignment of the band at 312 nm to a $Mo^V \rightarrow [NO_3]^-$ charge-transfer transition is correct, this suggests that the activation energy for the redox reaction in (A) is *ca.* 15 kcal $mol^{-1}$; furthermore, substantial adjustment in the position of one oxygen atom is required to complete the reaction.

[11] H. Taube, *J. Chem. Educ.*, 1968, **45**, 452; R. G. Pearson, *Accounts Chem. Res.*, 1971, **4**, 152.

[12] H. B. Gray and C. R. Hare, *Inorg. Chem.*, 1962, **1**, 363.

[13] I. H. Hillier, personal communication.

[14] P. C. H. Mitchell, *Quart. Rev.*, 1966, **20**, 103 and refs. therein.

(Figures 6 and 7, respectively). Least-squares fitting of the kinetic data gave $d = 22{\cdot}4 \pm 1{\cdot}9$ l mol$^{-1}$ s$^{-1}$ and $e = 0{\cdot}31 \pm 0{\cdot}02$ s$^{-1}$. The dioxomolybdenum(VI) complex, (B), has two potentially labile sites for substitution,

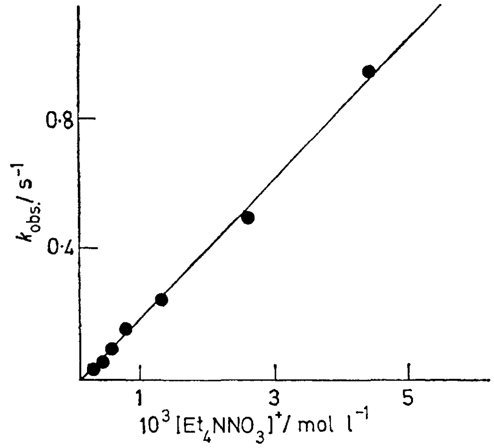

FIGURE 5 Effect of $[Et_4NNO_3]$ on the observed rate constant $k_3$ for the third stage at 25 °C; $[Et_4NNO_3]_s$ is the concentration of $[Et_4N][NO_3]$ after consumption of one equivalent by molybdenum(V) during the course of the first two stages

one *trans* to each oxo-group. Attack by $[NO_3]^-$ at either of these sites would probably lead to co-ordination of this ligand followed by an isomerisation similar to that described above for (A), the thermodynamically more stable product containing the nitrato-group(s) *cis* to *both* oxo-groups. Although the kinetic data for stage three are somewhat complicated, they do conform to a general pattern of nitrate substitution by a dissociative mechanism involving loss of $Ph_3PO$ as the rate-determining step.

Production of $[MoO_2(NO_3)_2(OPPh_3)_2]$ or $[MoO_2Cl_2(OPPh_3)_2]$ as the molybdenum-containing product of the reaction between $[Et_4N][NO_3]$ and $[MoOCl_3(OPPh_3)_2]$ in the ratios 3 : 1 or 1 : 1, respectively, calls for some comment. E.s.r. studies [8] of molybdenum(V) complexes in $CH_2Cl_2$ solution have shown that negatively charged ligands complexed *trans* to the oxo-groups are readily replaced by neutral molecules such as $Ph_3PO$. Thus the *trans*-chloro-ligand of $[MoOCl_5]^{2-}$ is readily replaced by the ' poorer ' nucleophile $Ph_3PO$ to produce $[MoOCl_4(OPPh_3)]^-$. Ion-pairing interactions, together with the relatively weak binding that may be achieved *trans* to an oxo-group in such systems, are believed to lead to this behaviour. Similar considerations are expected to apply for dioxomolybdenum(VI) complexes in $CH_2Cl_2$. Therefore, we attribute the formation of $[MoO_2(NO_3)_2(OPPh_3)_2]$ {or $[MoO_2Cl_2(OPPh_3)_2]$ for $[Mo^V] : [NO_3^-] = 1 : 1$} as the ultimate product of ligand substitution at the $[MoO_2]^{2+}$ centre, to the replacement of the negatively charged ligand(s) *trans* to the oxo-group(s) by $Ph_3PO$, subsequent to the substitution of any nitrate in excess of that required for reaction (2) at the $[MoO_2]^{2+}$ centre.

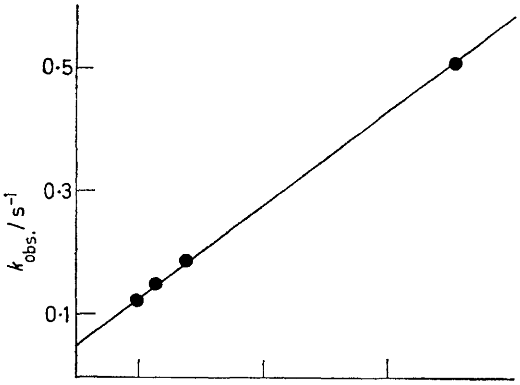

FIGURE 6 Inverse dependence of the observed rate constant $k_3$ on added $Ph_3PO$ for the third stage of reaction

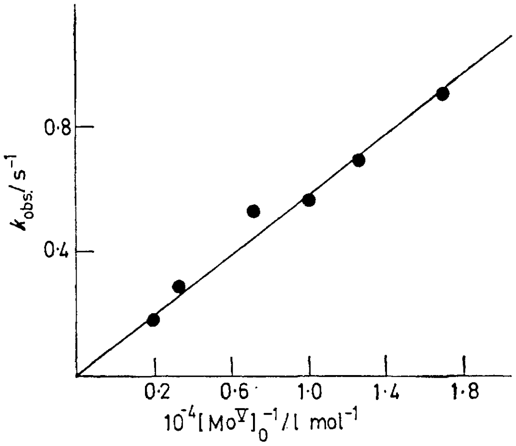

FIGURE 7 Apparent inverse dependence of observed rate constant $k_3$ (25 °C) on $[Mo^V]_0$

The nitrogen(IV) oxide produced in the reaction between $[MoOCl_3(OPPh_3)_2]$ and $[Et_4N][NO_3]$ has been identified and estimated spectrophotometrically. For initial $[Mo^V] : [NO_3^-]$ ratios of $\geqslant 2 : 1$, subsequent to the initial fast reaction described and discussed above, a much slower reaction proceeded in which the nitrogen(IV) oxide oxidised $Mo^V$ to $Mo^{VI}$, itself being reduced to nitrogen(III). Furthermore, we have shown * that $[NO_2]^-$ will oxidise $[MoOCl_3(OPPh_3)_2]$ under non-aqueous conditions to give $Mo^{VI}$ and NO. These results provide some explanation of the failure of other workers [4,15–17] to reduce nitrate to nitrite using other systems containing molybdenum(V). There seem to be two essential aspects of our work which differ from studies previously reported: the mononuclear molybdenum(V) centre and the non-aqueous conditions used here.

These two aspects are related since aqueous conditions tend to promote the formation of dimeric diamagnetic molybdenum(V) complexes in which the metal centres

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* See following paper.

[15] E. P. Guyman and J. T. Spence, *J. Phys. Chem.*, 1966, **70**, 1964.

[16] R. J. P. Williams and P. C. H. Mitchell, *J. Chem. Soc.*, 1962, 4570.

[17] A. G. Sykes, personal communication.

are linked by one or two oxo-bridges. At present there is no evidence which suggests that binuclear molybdenum(v) complexes such as $Na_2[Mo_2O_4(edta)]\cdot 2OH_2$[16] (edta = ethylenediaminetetra-acetate) or $Na[Mo_2O_4(cysteinato)_2]$[17] will reduce nitrate; Guyman and Spence's study[15] required that the reduction of nitrate by molybdenum(v) involved dissociation of molybdenum(v) dimers into monomers. Assuming that nitrate can co-ordinate to the metal atoms in these dimers (see below), we suggest that one possible reason for the lack of reaction is due to the $[NO_3]^-$ groups being unable to take up a position on the dimeric centre where overlap is achieved between the $\pi^*$ orbital of the nitrato-group and the orbital containing the two *d* electrons of the $Mo^V{}_2$ unit. It is possible that this latter orbital is concentrated in the region between the two metal atoms[18] which is effectively blocked to an incoming ligand by the oxo-group(s).

Non-aqueous conditions are important in allowing the nitrate group to behave as a good ligand.[19] This co-ordination of the nitrate group leads to a marked increase in its reactivity as an oxidising agent[19] and *ab initio* calculations[13] suggest that this arises because of the considerable lowering in energy of the $\pi^*$ orbital of the nitrato-group which occurs on co-ordination. Co-ordination of nitrate to molybdenum(v) therefore aids the redox process first by lowering the activation energy for electron transfer to the nitrate group and secondly by facilitating immediate formation of the dioxomolybdenum(VI) centre typical of this latter oxidation state.[14] The $NO_2$ produced by reaction (2) will be stable in a non-aqueous medium and, unless present in relatively high concentrations, will not effectively compete with $[NO_3]^-$ for any unreacted molybdenum(v). However, in the presence of water disproportionation (3) will proceed and the nitrite produced will react preferentially with any molybdenum(v) since, under aqueous conditions, $[NO_2]^-$ is a better nucleophile than $[NO_3]^-$.[20] This latter reduction produces NO. Hence, in aqueous media, the selective reduction of $[NO_3]^-$ to $[NO_2]^-$ by molybdenum(v) in general cannot be achieved; the principal nitrogen product will be NO.

In order to achieve selective reduction of nitrate to nitrite at the molybdenum(v) centre of *nitrate reductases* the above discussion suggests that the metal centre should be mononuclear and maintained in a non-aqueous environment. Equation (2) represents an attractive redox process in that the $NO_2$ formed is readily lost from the vicinity of the metal and subsequently reacts with water producing $[NO_2]^-$ to give the impression that the enzyme converts $[NO_3]^-$ to $[NO_2]^-$ directly.

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[4/2033 *Received, 7th October,* 1974]

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[18] D. H. Brown, P. G. Perkins, and J. J. Stewart, *J.C.S. Dalton*, 1972, 1105.

[19] C. C. Addison, N. Logan, S. C. Wallwork, and C. D. Garner, *Quart. Rev.*, 1971, **25**, 289 and refs. therein.

[20] See, for example, C. H. Bamford and C. F. N. Tipper, 'Chemical Kinetics,' Elsevier, Amsterdam, 1972, vol. 7, p. 23.