Kinetics and Mechanism of Nitrite Reduction by Trichloro-oxobis(triphenylphosphine oxide)molybdenum(V)

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In the presence of excess of nitrite ion the complex $[MoOCl_3(OPPh_3)_2]$ is completely oxidised to Mo^{VI} in CH_2Cl_2. The reaction proceeds by three observable stages. Data for the first stage correspond to co-ordination of nitrite at molybdenum(V), *via* a limiting S_N1 mechanism, involving loss of a triphenylphosphine oxide molecule. At 25 °C, $k_1 = 51{\cdot}8 \pm 2{\cdot}1\ s^{-1}$, $\Delta H_1^{\ddagger} = 12{\cdot}6 \pm 0{\cdot}3$ kcal mol^{-1}, and $\Delta S_1^{\ddagger} = -8{\cdot}2 \pm 1{\cdot}0$ cal K^{-1} mol^{-1}. The data for the second stage of reaction are taken to indicate chelation and/or isomerisation of co-ordinated nitrito-ligand into a position *cis* to the oxo-group, followed by rapid non-rate-determining electron transfer. The third and final stage of reaction appears to involve co-ordination of the available nitrite to the primary molybdenum(VI) product, and subsequent rearrangement of these molybdenum(VI) products.

KINETIC and isotopic studies of the reduction of nitrate [1,2] and nitrite [3] ions by simple transition-metal complexes have shown that both one- and two-electron paths are possible. Subsequent formation of a series of lower oxides of nitrogen may result, some of which are also redox active. Oxidation of aqueous acidic solutions of, for example Mo^{V},[1] V^{II},[4] and Eu^{II},[5] by $[NO_3]^-$ results in eventual formation of NO and/or N_2O. This is attributed in part to the favourable redox couple for $[NO_2]^-$–NO (+1·0 V) as compared to $[NO_3]^-$–$[NO_2]^-$

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

[2] L. L. Brown and J. S. Drury, *J. Chem. Phys.*, 1967, **46**, 2833.

[3] J. A. Frank and J. T. Spence, *J. Phys. Chem.*, 1964, **68**, 2131.

[4] K. Tanaka, *Bull. Chem. Soc. Japan*, 1970, **43**, 2030; K. Tanaka, K. Morinago, and K. Nakano, *ibid.*, p. 2778.

[5] R. T. M. Fraser, R. N. Lee, and K. Hayden, *J. Chem. Soc.* (*A*), 1967, 741.

(+0·94 V).[6] Contrasting these observations, the available data for *nitrate reductase* enzymes indicate that reduction of nitrate to nitrite is specific and probably occurs at a molybdenum(V) centre.[7] This study is concerned with the reduction of nitrite ion by $[MoOCl_3(OPPh_3)_2]$ in CH_2Cl_2, ionic strength $I < 10^{-3}$ mol l^{-1}, as a direct comparison with the corresponding reduction of nitrate.[8]

RESULTS

Determination of the Dissociation Constant for $[Et_4N][NO_2]$ *in* CH_2Cl_2 *Solution*.—Samples of $[Et_4N][NO_2]$ were prepared as described in the Experimental section. The dissociation constant, *K* [equation (1)], was evaluated as described

$$[Et_4N][NO_2] \rightleftharpoons [Et_4N]^+ + [NO_2]^- \qquad (1)$$

previously.[8] Conductance data are listed in Table 1, and evaluation of these [9] gave $K = 2{\cdot}14 \times 10^{-5}$ mol l^{-1} at 25 °C.

TABLE 1

Variation in conductivity with concentration for $[Et_4N][NO_2]$ in dichloromethane at 25 °C

$10^4[Et_4NNO_2]$/ mol l^{-1}	Λ/S cm^2 mol^{-1}
15·71	14·3
3·93	23·9
0·79	45·9
0·16	71·3
0·03	108·2

Product Identification and Reaction Stoicheiometry.—A series of experiments with initial concentrations of $[MoOCl_3(OPPh_3)_2]$ ($[Mo^V]_0$) in the range $1{\cdot}64 \times 10^{-4}$—$2{\cdot}47 \times 10^{-4}$ mol l^{-1} and $[Et_4NNO_2]_0$ in 1·0—30-fold excess of $[Mo^V]_0$, monitored by u.v. spectroscopy, indicated that formation of the final Mo^{VI} species in solution did not occur until a six-fold excess of $[Et_4N][NO_2]$ was used. Reactions with $[Et_4NNO_2]_0 : [Mo^V]_0 \geqslant 6 : 1$ gave spectra identical to that of the final product in Figure 2. With a reactant ratio $<6 : 1$, initial spectra gave $\lambda_{max.} = 317$ nm, identical to the first-stage product spectrum obtained from the stopped-flow apparatus (Figure 2).

The final spectrum of a 1 : 1 mixture of reactants had a peak at $\lambda = 303$ nm (ε 2 750 l mol^{-1} cm^{-1}), identical with that recorded for $[MoO_2Cl_4]^{2-}$; i.r. spectra of such solutions indicated complete consumption of molybdenum(V), and were consistent with the production of essentially equal amounts of $[MoO_2Cl_4]^{2-}$ and $[MoO_2Cl_2(OPPh_3)_2]$ (the latter does not absorb significantly at *ca.* 300 nm). Increasing the ratio $[Et_4NNO_2]_0 : [Mo^V]_0$ above 1 : 1 resulted in successive removal of $[MoO_2Cl_4]^{2-}$ {and possibly $[MoO_2Cl_2(OPPh_3)_2]$ also} until at 6 : 1 ratios this species could no longer be detected. In the presence of at least a six-fold excess of nitrite the only *solid* Mo^{VI} species obtained was identified as $[Et_4N]_4[Mo_8O_{26}]$ from elemental analyses and i.r. spectra [10] {Found: C, 22·0; H, 4·6; N, 3·7. Calc. for $[Et_4N]_4[Mo_8O_{26}]$: C, 22·5; H, 4·7; N, 3·3%}. This species was produced in essentially quantitative yield.

The complex $[MoOCl_3(OPPh_3)_2]$ (*ca.* 0·25 g, 0·323 mmol) and $[Et_4N][NO_2]$ (*ca.* 0·46 g, 2·61 mmol) were mixed and introduced to a closed glass system which was evacuated and dry CH_2Cl_2 introduced *in vacuo*. The reaction vessel was shaken to aid dissolution of the reactants whereupon a colourless gas was immediately evolved. This gas was condensed in a liquid-nitrogen trap together with a small amount of CH_2Cl_2. The sample was then allowed to warm to room temperature and the gas collected in a 10 cm path-length gas cell (NaCl windows) and the i.r. spectrum recorded between 4 000 and 625 cm^{-1} on a Perkin-Elmer 257 i.r. spectrometer. Apart from bands due to CH_2Cl_2, the only remaining absorption band was centred at 1 876 cm^{-1} and exhibited *P*, *Q*, and *R* branches. After expansion (×10) of the spectrum in the range 1 818—1 938 cm^{-1}, all the peak positions of the rotational fine structure agreed within experimental error to that observed for NO.[11] Further confirmation was derived from the formation of NO_2–N_2O_4 mixtures when oxygen was admitted to the gas

$$2NO + O_2 \longrightarrow 2NO_2 \qquad (2)$$

cell [1] [reaction (2)]. There was no evidence for the production of any other nitrogen-containing species from these experiments.

The quantitative estimation of NO was effected in two ways: first, by the above reaction with oxygen [equation (2)], followed by spectrophotometric determination [8] of NO_2–N_2O_4; secondly, by condensing the gas onto aqueous acidic $KMnO_4$, followed by back titration with Fe^{II}.[12] Yields of NO, based on Mo^V, were in the range 77—105%. The stoicheiometry of the reaction is therefore essentially as in equation (3).

$$Mo^V + [NO_2]^- \longrightarrow Mo^{VI} + NO \qquad (3)$$

Kinetic Studies.—Solutions of both reactants were handled under anaerobic and moisture-free conditions. The course of reaction was followed by monitoring absorbance changes at 280 and 330 nm using an Aminco–Morrow stopped-flow spectrophotometer. Conditions were chosen such that pseudo-first-order or first-order rate plots could be obtained, with $[Et_4NNO_2]$ in 7—130-fold excess over $[Mo^V]$. Three stages of reaction were observed under these conditions.

The first stage was easily separable from the second and third, observed first-order rate constants, $k_{obs.}$, being generally at least 500-fold faster for the first stage. Rate constants were evaluated from stopped-flow traces by conversion of the transmittance output to absorbance, and plots of $\log_{10}(\Delta D)$ against time gave a gradient $= k_{obs.}/2{\cdot}303$ (ΔD is the absorbance change at the particular wavelength used). For the first and third stages, $\log_{10}(\Delta D)$ against time plots were linear for at least three half-lives and often better. Rate constants for the second stage were obtained from a consecutive-reaction treatment [13] (Figure 1). In certain cases the observed rate constants for the second and third stages differed by only a factor of three, and the quality of data for the second stage was necessarily poorer although still linear for *ca.* 75% completion of reaction. For each stage the dependence of $k_{obs.}$ on $[Et_4NNO_2]_0$, $[MoOCl_3(OPPh_3)_2]_0$, and $[Ph_3PO]$ was investigated, and data

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[6] W. M. Latimer, 'Oxidation Potentials,' 2nd edn., Prentice-Hall, 1953; the values cited are for acidic solutions.

[7] See, for example, C. A. Adams, G. M. Warnes, and D. J. D. Nicholas, *Biochim. Biophys. Acta*, 1971, **235**, 398.

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

[9] R. M. Fuoss and H. Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 476.

[10] J. Aveston, E. W. Anacker, and J. S. Johnson, *Inorg. Chem.*, 1964, **3**, 735.

[11] R. H. Gillette and E. H. Eyster, *Phys. Rev.*, 1939, **56**, 1113.

[12] A. I. Vogel, 'Quantitative Inorganic Analysis,' 2nd edn., Longmans, Green, and Co., 1953, p. 285.

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

for the first (Table 2) and second and third stages (Table **3**) are as listed.

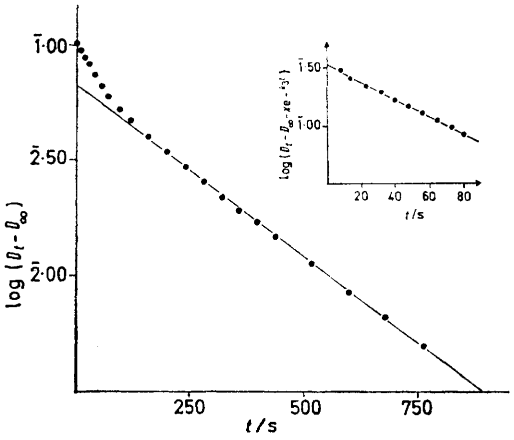

FIGURE 1 An example of the evaluation of rate constants for the second and third stages from a consecutive-reaction treatment. Conditions for this run are: $[\mathrm{Mo^V}]_0 = 5 \times 10^{-4}$ mol $\mathrm{l^{-1}}$, $[\mathrm{Et_4NNO_2}]_0 = 5 \times 10^{-3}$ mol $\mathrm{l^{-1}}$, and 25 °C. The main diagram gives k_3 for the third stage, and the inset k_2 for the second stage

TABLE 2

Kinetic data for the first stage observed during oxidation of $[\mathrm{MoOCl_3(OPPh_3)_2}]$ by $[\mathrm{NO_2}]^-$ at λ = 280 and 330 nm. The number of runs is indicated in parentheses

θ_c/°C	$10^4[\mathrm{Mo^V}]$/ mol $\mathrm{l^{-1}}$	$10^3[\mathrm{Et_4NNO_2}]$/ mol $\mathrm{l^{-1}}$	$10^3[\mathrm{Ph_3PO}]$/ mol $\mathrm{l^{-1}}$	$k_{\mathrm{obs.}}/\mathrm{s^{-1}}$
25·0	5·00	5·00		51·6 (2)
	3·50	5·00		53·4 (4)
	1·50	5·00		53·3 (2)
	0·50	5·00		53·2 (2)
	1·50	1·00		50·8 (2)
	1·50	1·50		55·9 (2)
	1·50	2·50		54·4 (2)
	1·50	4·00		55·2 (2)
	1·50	6·50		53·5 (2)
	1·50	8·00		50·5 (2)
	1·50	10·0		52·9 (2)
	1·50	20·0		45·7 (2)
	1·50	1·50	0·50	50·2 (2)
	1·50	1·50	1·00	48·5 (2)
	1·50	1·50	2·00	46·1 (2)
	1·50	1·50	3·00	35·4 (2)
	1·50	1·50	4·50	36·3 (2)
	1·50	1·50	6·00	32·6 (1)
	1·50	1·50	13·2	21·1 (2)
	1·50	1·50	18·2	16·0 (2)
15·0	1·70	1·00		22·8 (2)
	1·70	5·00		21·5 (2)
8·0	1·70	1·00		12·4 (2)
	1·70	5·00		13·1 (2)
1·4	1·70	1·00		8·32 (2)
	1·70	5·00		8·33 (2)

Spectra of Reaction Intermediates.—Samples of $[\mathrm{MoOCl_3(OPPh_3)_2}]$ in $\mathrm{CH_2Cl_2}$ were always freshly prepared, and test spectra [14] of these solutions showed that they were stable for at least 12 h. The kinetic data indicate that the reaction involves three observable stages and therefore two reaction intermediates, (A) and (B). The spectra of these species were obtained from stopped-flow traces and are presented in Figure 2. With $[\mathrm{Mo^V}]_0 = 2{\cdot}5 \times 10^{-4}$ mol $\mathrm{l^{-1}}$ and $[\mathrm{Et_4NNO_2}]_0 = 5 \times 10^{-3}$ mol $\mathrm{l^{-1}}$, reaction was monitored at wavelengths in the range 270—370 nm at 5 nm intervals. Since the first stage was generally some 1 000-fold faster than the second stage, the spectrum of (A) was easily obtained from transmittance readings at the end of the first stage (150 ms). A spectrum with $\lambda_{\mathrm{max.}} = 317$ nm (ε *ca.* 4·0 × 10^3 l $\mathrm{mol^{-1}}$ $\mathrm{cm^{-1}}$) was observed, consistent with a molybdenum(V) species being present.[15]

TABLE 3

Kinetic data for the second and third stages observed during the oxidation of $[\mathrm{MoOCl_3(OPPh_3)_2}]$ by $[\mathrm{NO_2}]^-$ at λ = 280 and 330 nm, 25 °C. Each rate constant is the average of two determinations, except where indicated in parentheses

$10^4[\mathrm{Mo^V}]_0$/ mol $\mathrm{l^{-1}}$	$10^3[\mathrm{Et_4NNO_2}]_0$/ mol $\mathrm{l^{-1}}$	$10^3[\mathrm{Ph_3PO}]_0$/ mol $\mathrm{l^{-1}}$	10^2k_2 */ $\mathrm{s^{-1}}$	10^3k_3*/ $\mathrm{s^{-1}}$
3·50	5·00		2·49	5·59
1·50	5·00		2·50 (4)	7·65 (4)
0·50	5·00		3·31 (1)	14·6
1·50	1·00		2·62	4·72
1·50	1·50		2·55	5·45
1·50	2·50		2·52	7·35
1·50	4·00		2·83	7·52
1·50	6·50		3·10	10·7
1·50	8·0		2·61	9·25
1·50	10·0		2·42 (1)	10·1
1·50	20·0		2·76 (1)	8·71
1·50	1·50	0·50	2·55	6·35
1·50	1·50	1·00	2·23	4·22
1·50	1·50	2·00	2·88 (1)	3·21
1·50	1·50	3·00	2·24	2·51
1·50	1·50	4·50	1·82 (1)	2·56
1·50	1·50	6·00	2·43 (1)	2·37

* Observed first-order rate constants for the respective stages.

The spectrum of (B) was obtained from estimates of transmittance readings 100 s after mixing. Under these conditions the known rate constants k_2 and k_3 enable the relative amounts of (B) and final product to be predicted. The spectrum of (B) was then derived after correction for the contribution of final product to the observed spectrum (Figure 2).

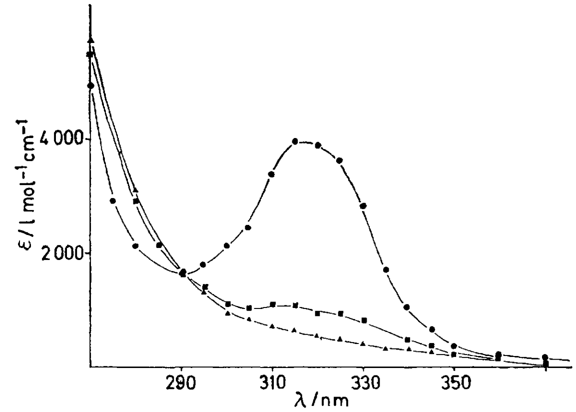

FIGURE 2 Spectra of reaction intermediates and final products for the oxidation of $[\mathrm{MoOCl_3(OPPh_3)_2}]$ by $[\mathrm{NO_2}]^-$ at 25 °C, $[\mathrm{Mo^V}]_0 = 2{\cdot}5 \times 10^{-4}$ mol $\mathrm{l^{-1}}$, and $[\mathrm{Et_4NNO_2}]_0 = 5 \times 10^{-3}$ mol $\mathrm{l^{-1}}$: (●), intermediate (A); (■), intermediate (B); (▲), final product

DISCUSSION

The kinetic and spectrophotometric data obtained in this study show a remarkable resemblance to those obtained for the corresponding oxidation using $[\mathrm{Et_4N}][\mathrm{NO_3}]$.[8] Accordingly we interpret the mechanism of

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

[15] C. D. Garner, P. M. Boorman, V. I. Routledge, M. R. Hyde, P. Lambert, and F. E. Mabbs, in preparation.

these reactions in an essentially similar manner and suggest that equations (4), (5), and (7) represent the

$$[\mathrm{MoOCl_3(OPPh_3)_2}] \xrightarrow{k_1} [\mathrm{MoOCl_3(OPPh_3)(NO_2)}]^- + \mathrm{Ph_3PO} \qquad (4)$$

$$[\mathrm{MoOCl_3(OPPh_3)(NO_2)}]^- \xrightarrow{k_2} [\mathrm{MoOCl_3(NO_2)(OPPh_3)}]^- \qquad (5)$$

$$[\mathrm{MoOCl_3(NO_2)(OPPh_3)}]^- \xrightarrow[\text{rapid}]{\text{electron transfer}} [\mathrm{MoO_2Cl_3(OPPh_3)}]^- + \mathrm{NO} \qquad (6)$$

$$[\mathrm{MoO_2Cl_3(OPPh_3)}]^- \xrightarrow[k_3]{[\mathrm{NO_2}]^-} \text{Products} \qquad (7)$$

three stages observed during the kinetic studies. Data for the first stage conform to the rate expression (8).

$$-\mathrm{d}[\mathrm{MoOCl_3(OPPh_3)_2}]/\mathrm{d}t = k_{\mathrm{obs.}}[\mathrm{MoOCl_3(OPPh_3)_2}] \qquad (8)$$

$$\text{where} \quad k_{\mathrm{obs.}} = \frac{a[\mathrm{Et_4NNO_2}]}{b[\mathrm{Ph_3PO}] + c[\mathrm{Et_4NNO_2}]} \qquad (9)$$

Consistent with equation (9) a plot of $1/k_{\mathrm{obs.}}$ against $[\mathrm{Ph_3PO}]$, at constant $[\mathrm{Et_4NNO_2}]$, was linear (Figure 3).

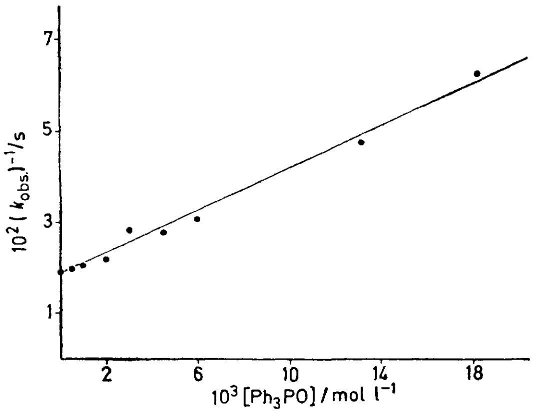


FIGURE 3 Variation of $k_{\mathrm{obs.}}$ with $[\mathrm{Ph_3PO}]$ at 25 °C for the first stage observed during $[\mathrm{NO_2}]^-$ oxidation of $[\mathrm{MoOCl_3(OPPh_3)_2}]$

TABLE 4

Rate constants and activation parameters * at 25 °C for ligand (X) substitution of $[\mathrm{MoOCl_3(OPPh_3)_2}]$

X	k_1/s^{-1}	$\Delta H_1^‡$/ kcal mol^{-1}	$\Delta S_1^‡$/ cal K^{-1} mol^{-1}	Ref.
Cl$^-$	42·0	10·6 ± 0·8	−15·4 ± 2·9	14
Br$^-$	41·6	11·4 ± 0·2	−12·5 ± 0·8	14
$[\mathrm{NO_3}]^-$	40·0	9·7 ± 0·5	−18·4 ± 1·7	8
$[\mathrm{NO_2}]^-$	51·8	12·6 ± 0·3	−8·2 ± 1·0	This work

* All data were obtained using an unweighted least-squares analysis, ARRHENIUS I, supplied by J. P. Day; errors indicate one standard deviation.

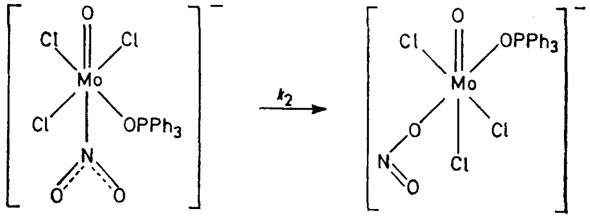
The temperature dependence of the observed rate constant, which corresponds to a/c in equation (9), allows parameters for this path to be evaluated (Table 4). Data are also presented here for substitution reactions of $[\mathrm{MoOCl_3(OPPh_3)_2}]$ with various other ligands.[8,14] All four reactions have activation enthalpies, $\Delta H^‡$, in the range 11·1 ± 1·5 kcal mol^{-1} and entropies, $\Delta S^‡$, in the range −13 ± 5 cal K^{-1} mol^{-1},† consistent with the same mechanism being operative throughout.[14,16] Therefore, for the nitrite reaction the first stage is considered to involve substitution of a triphenylphosphine oxide ligand in $[\mathrm{MoOCl_3(OPPh_3)_2}]$ by $[\mathrm{NO_2}]^-$ *via* a limiting $S_{\mathrm{N}}1$ mechanism.

The spectrum of the first intermediate, (A), has an absorbance maximum at 317 nm (ε *ca.* 4·0 × 10^3 l mol^{-1} cm^{-1}) which is considered representative of a molybdenum(V) species.[15] However, on the basis of its u.v. spectrum it is not possible to say whether (A) contains a nitro- or nitrito-ligand. It is noted that the corresponding nitrato-complex,[8] $[\mathrm{MoOCl_3(OPPh_3)(NO_3)}]$, has a similar u.v. spectrum, $\lambda_{\mathrm{max.}} = 312$ nm (ε *ca.* 5·7 × 10^3 l mol^{-1} cm^{-1}). The general preference for nitrite to be *N* rather than *O* bonded,[17] and the observation that $k_{\mathrm{NO_2}}$ for attack of nitrite upon the five-co-ordinate species $[\mathrm{MoOCl_3(OPPh_3)}]$ and $k_{\mathrm{NO_3}}$ (for the corresponding $[\mathrm{NO_3}]^-$ substitution) are in the ratio 47 : 31, supports a tentative assignment for (B) as shown in (11).

The observed first-order rate constant, k_2, at 25 °C, for the second stage of the reaction was evaluated as described above, and no apparent trend in k_2 with variation of $[\mathrm{Et_4NNO_2}]$ and $[\mathrm{Ph_3PO}]$ (Table 3) was observed. At 25 °C the data are consistent with equation (10). The concentration of (A) was assumed

$$-\mathrm{d}[\mathrm{A}]/\mathrm{d}t = k_2[\mathrm{A}] \qquad (10)$$

equal to that of the Mo$^{\mathrm{V}}$ initially present. At 25 °C, $k_2 = (2·58 \pm 0·45) \times 10^{-2}$ s^{-1} and is assigned to reaction (11). One plausible mechanism involves initial



(11)

chelation of co-ordinated nitro-ligand followed by Mo–N bond cleavage, somewhat similar to the processes described for the isomerisation of penta-amminenitritocobalt(III).[18] However, if (A) is a nitrito-complex then chelation might be expected to resemble the second stage observed during nitrate oxidation of $[\mathrm{MoOCl_3(OPPh_3)_2}]$,[8] with a specific rate $k_2 = 1·0 \pm 0·2$ s^{-1} at 25 °C. The possibility of nitro-/nitrito-isomerisation prior to chelation cannot be ruled out,[17] and this may be the rate-determining step in the k_2 path. Perhaps the only valid comment here is that $k_2([\mathrm{NO_2}]^-)$ is considerably smaller than $k_2([\mathrm{NO_3}]^-)$, and both probably involve

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† 1 cal = 4·184 J.

[16] See, for example, M. R. Hyde, R. S. Taylor, and A. G. Sykes, *J.C.S. Dalton*, 1973, 2730.

[17] D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 1965, **4**, 721.

[18] R. K. Murmann and H. Taube, *J. Amer. Chem. Soc.*, 1956, **78**, 4886.

co-ordination at a site *cis* to the oxo-group. There is no evidence for any catalysis of this second stage by $[Et_4N][NO_2]$, as observed in a related isomerisation of $[MoOCl_3Br(OPPh_3)]^-$.[14]

Comparison of u.v. spectra for molybdenum-(V) and -(VI) complexes suggests that the second intermediate is a molybdenum(VI) species.[15] Consequently (B) is not the primary product of reaction (11) and a non-rate-determining electron transfer between the second and third stages is called for. Molecular-orbital calculations for the nitrite ion indicate that the π^* orbital of $[NO_2]^-$ is the lowest virtual orbital,[19] and therefore electron transfer most probably occurs into this orbital. Favourable overlap between donor and acceptor orbitals on the Mo^VO and $[NO_2]^-$ moieties is therefore [8] possible only when a nitrite oxygen atom is co-ordinated *cis* to the oxo-group.

Absorbance spectra indicate that the final stage of reaction involves conversion of one molybdenum(VI) species into another. The kinetic data for this stage are somewhat complicated and are consistent with the rate expression (12) at 25 °C. The concentration of (B) was

$$-\mathrm{d}[B]/\mathrm{d}t = \mathrm{d}[\mathrm{Product}]/\mathrm{d}t = k_3[B] \qquad (12)$$

assumed equal to that of the Mo^V initially present. Under the conditions listed in Table 3, k_3 is given by (13).

$$k_3 = (d + e[Ph_3PO]^{-1})\left(\frac{f[Et_4NNO_2]}{1 + g[Et_4NNO_2]}\right) \qquad (13)$$

At constant $[Mo^V]_0$ and $[Ph_3PO]$, a plot of $1/k_3$ against $([Et_4NNO_2]^*)^{-1}$ was linear (Figure 4) (where $[Et_4NNO_2]^*$ is the concentration of $[Et_4N][NO_2]$ available assuming one equivalent is consumed during the first two stages). With $[Mo^V]_0 = 1{\cdot}5 \times 10^{-4}$ mol l^{-1}, the gradient of Figure **4** is 1·04 mol l^{-1} s and the intercept $1{\cdot}0 \times 10^3$ s.

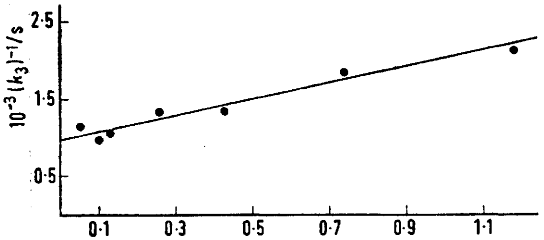

FIGURE 4 Dependence of k_3 on $[Et_4NNO_2]$ at 25 °C

Similarly, at constant $[Mo^V]_0$ and $[Et_4NNO_2]_0$, the linear dependence of k_3 on $[Ph_3PO]^{-1}$ is demonstrated (Figure 5). At $[Mo^V]_0 = 1{\cdot}5 \times 10^{-4}$ mol l^{-1} and $[Et_4NNO_2]_0 = 1{\cdot}5 \times 10^{-3}$ mol l^{-1}, the gradient is $2{\cdot}88 \times 10^{-6}$ mol l^{-1} s^{-1} and the intercept $1{\cdot}78 \times 10^{-3}$ s^{-1} at 25 °C. The release of Ph_3PO from $[MoOCl_3(OPPh_3)_2]$ prior to the third stage is illustrated by the apparent $[Mo^V]_0$ dependence shown in the first three runs of Table 3. Solid products isolated from concentrated reaction mixtures analysed well for $[Et_4N]_4[Mo_8O_{26}]$. At low concentrations (the conditions of the kinetic study) nitro- and/or nitrito-molybdenum(VI) complexes such as $[MoO_2(NO_2)_2(OPPh_3)_2]$ and $[MoO_2(NO_2)_4]^{2-}$ may be formed. The formation of the molybdenum(VI) oxo-anion presumably results from condensation reactions between nitrite complexes such as the latter with the elimination of nitrogen oxides and precipitation of the $[Mo_8O_{26}]^{4-}$ salt.

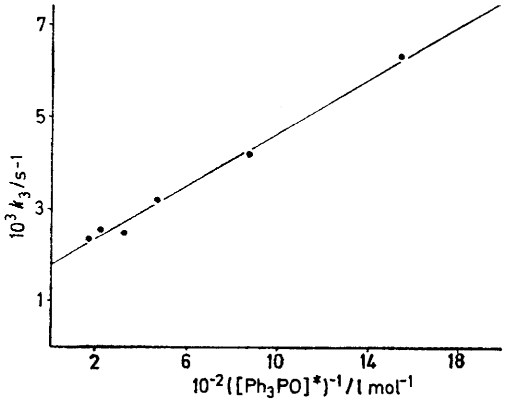

FIGURE 5 Variation of k_3 with $[Ph_3PO]$ for the third stage at 25 °C

Redox processes between an oxomolybdenum(V) centre and the oxidants nitrate [8] and nitrite have thus been shown to require the oxidant to be co-ordinated to the metal atom by one (and only one) oxygen atom *cis* to the oxo-group. Kinetic data for the second stage observed in $[NO_3]^-$ and $[NO_2]^-$ oxidations of $[MoOCl_3(OPPh_3)_2]$ are $k_{NO_3} = 1{\cdot}0 \pm 0{\cdot}2$ and $k_{NO_2} = (2{\cdot}6 \pm 0{\cdot}5) \times 10^2$ s^{-1} at 25 °C. Thus a 40-fold difference in the rate of oxidation of Mo^V to Mo^{VI} results. This difference most probably results from the marked preference of $[NO_2]^-$ to co-ordinate initially *via* a nitrogen atom, thus severely constraining a subsequent chelation step. On the other hand, if a nitrito-complex forms initially, subsequent chelation *via* either the N or O bond of the co-ordinated nitrito-ligand could produce an equilibrium between *N*- and *O*-bonded forms, only the latter resulting in electron transfer. Such an equilibrium would again be effective in reducing the rate constant for the second stage. It seems plausible to suggest [20] that the discrimination between nitrate and nitrite as exercised by the *nitrate reductases* may result from simple considerations such as these, magnified by features of the protein structure, in particular hydrogen bonding.

EXPERIMENTAL

Samples of $[MoOCl_3(OPPh_3)_2]$ were prepared and characterised as described elsewhere.[14] The salt $[Et_4N][NO_2]$ was prepared by mixing solutions of $AgNO_2$ (3·08 g, 20 mmol in MeCN) and $[Et_4N]Cl$ (3·31 g, 20 mmol) in CH_2Cl_2. The resulting white precipitate was filtered off and the filtrate transferred to a vacuum line where the solvent was removed to leave $[Et_4N][NO_2]$, a white-yellow crystalline material. The sample was recrystallised from CH_2Cl_2 and dried *in vacuo* at 110 °C for 3 h. Solid samples of $[Et_4N][NO_2]$ were stored in light-proof flasks in a dry-box (Found: C, 53·9;

[19] G. V. Pfeiffer and L. C. Allen, *J. Chem. Phys.*, 1969, **51**, 190.

[20] C. D. Garner, M. R. Hyde, and F. E. Mabbs, *Nature*, 1975, **253**, 623.

H, 11·2; N, 15·6. Calc. for $[Et_4N][NO_2]$: C, 54·5; H, 11·5; N, 15·9%).

Solutions of reactants for spectrophotometric and stopped-flow studies were always prepared within 2—3 h of use; CH_2Cl_2 was always freshly distilled from CaH_2 and stored in sealed flasks in a dry-box prior to use. Kinetic studies were made with an Aminco–Morrow stopped-flow unit coupled to a Beckmann DU spectrophotometer; u.v.–visible spectra were run on a Unicam SP 800 (recording) spectrophotometer and i.r. spectra on a Perkin-Elmer 257 grating i.r. spectrometer. Ionic strengths of run solutions were not adjusted since they were always maintained below 10^{-3} mol l^{-1}.

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