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Kinetics of oxygen-atom transfer reactions involving molybdenum dithiolene complexes†

Christian Lorber, Maria Rosaria Plutino, Lars I. Elding and Ebbe Nordlander *

Inorganic Chemistry 1, Chemical Center, Lund University, PO Box 124, S-221 00 Lund, Sweden

Oxo transfer reactions from $[MoO_2(mnt)_2]^{2-}$ [mnt^{2-} = 2,3-disulfanylmaleonitrile dianion (1,2-dicyanoethylenedithiolate)] to the abiological oxygen acceptors $PPh_{3-x}Et_x$ (x = 0–3) have been studied spectrophotometrically in acetonitrile. The pseudo-first-order rate constants depend linearly on the concentration of the oxo acceptors. The sequence of reactivity is $PEt_3 > PEt_2Ph > PEtPh_2 > PPh_3$, reflecting the basicities of the phosphines, while the steric influence of the substituents on the phosphorus atom appears to be of minor importance. The activation entropies for the reaction with PEt_3 and PPh_3 are negative. These observations are in agreement with the proposal that in the intermediate the entering phosphine binds to the molybdenum complex through the oxygen ligand. Oxidation of HSO_3^- by $[MoO_2(mnt)_2]^{2-}$ has also been studied in acetonitrile and in acetonitrile–water mixtures. The reaction exhibits Michaelis–Menten behaviour. In $CH_3CN–H_2O$, the rate of the reaction increases as the water concentration decreases; the reacting species appears to be a product from the reaction of the molybdenum starting complex with water.

Molybdenum-containing oxotransferase enzymes, such as dmso reductase (dmso = dimethyl sulfoxide),[1] nitrate reductase,[2] xanthine oxidase[3] and sulfite oxidase,[4] catalyse oxygen atom transfer to/from biological substrates.[5] The active sites of these enzymes contain a dissociable cofactor known as Moco.[6] Evidence shows that in the oxidized form this cofactor consists of a *cis*-molybdenum(VI) dioxo (or, in the case of xanthine oxidase, molybdenum oxo/sulfido) moiety that is bound to one[7] or two[8] pterins [pterin = 2-amino-4(1*H*)-pteridinone]. The pterin(s) is (are) ligated to the metal through a dithiolene moiety. Model studies[9] and ^{18}O labeling experiments[10] indicate that the oxygen-atom transfer is mediated by the transition-metal-containing cofactor in accordance with equation (1)

$$Mo^{VI}O_2L_n + X \rightleftharpoons Mo^{IV}OL_n + XO \qquad (1)$$

where X = arbitrary substrate and L = ligand(s). Hyperthermophilic bacteria contain related tungsten enzymes with similar metal–oxo/pterin cofactors.[11] Recent crystallographic work has established the structures of three oxotransferase enzymes, the molybdenum-containing aldehyde oxidoreductase from *Desulfovibrio gigas*[7] and dmso reductase[1] from *Rhodobacter sphaeroides* as well as the tungsten-containing aldehyde ferredoxin oxidoreductase (AOR) from *Pyrococcus furiosus*.[12] These protein structures show that the pterin ligands are in the closed rather than the postulated open form in all three enzymes, *i.e.* the pterin dithiolene moiety is a part of a dihydropyran ring[6] (Fig. 1). Furthermore, in two of the enzymes, dmso reductase and the *P. furiosus* AOR, the metal is ligated by two pterins; it was previously thought that the metals were ligated by only one pterin in Mo/W oxotransferase enzymes. The crystal structure of another molybdenum–pterin cofactor-containing enzyme, formate dehydrogenase H, also shows co-ordination of two pterins to one molybdenum atom.[13]

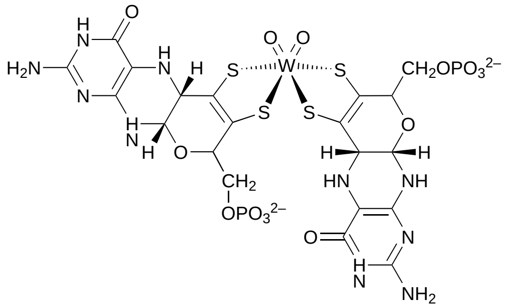

Fig. 1 Possible structural formula of the tungsten cofactor of aldehyde ferrodoxin oxidoreductase (AOR) from *Pyrococcus furiosus* (*cf.* refs. 6 and 12)

The complexes $[MO_2(bdt)_2]^{2-}$ [14,15] and $[MO_2(mnt)_2]^{2-}$ [16,17] [M = Mo or W; bdt^{2-} = benzenedithiolate, mnt^{2-} = 2,3-disulfanylmaleonitrile dianion (1,2-dicyanoethylenedithiolate)] constitute reasonable structural models for the active site of dmso reductase and *P. furiosus* AOR, and also serve as functional models for oxotransferase enzymes. It has been found that $[MoO_2(mnt)_2]^{2-}$ **1** is capable of oxidizing hydrogensulfite to HSO_4^-, a reaction directly relevant to the function of sulfite oxidase;[4,16] this reaction has been shown to exhibit a kinetic behaviour similar to the Michaelis–Menten scheme.[17] We were interested in exploring whether such kinetic behaviour can be observed when **1** is treated with other oxygen acceptors. Here, we wish to report an investigation of the kinetics of the reactions between **1** and the abiological oxygen acceptors $PPh_{3-x}Et_x$ (x = 0–3) at variable temperature, and a correlation of observed reaction rates with the basicities of the phosphines. Furthermore, a thorough investigation of the above-mentioned oxidation of hydrogen sulfite by $[MoO_2(mnt)_2]^{2-}$ **1** in acetonitrile and in acetonitrile–water mixtures is presented.

Experimental

Compounds and solvents

The disodium salt of the 1,2-dicyanoethylenedithiolate ligand, Na_2mnt, and the tetrabutylammonium salts of the molybdenum(VI) and tungsten(VI) complexes $[NBu^n{}_4]_2[MoO_2(mnt)_2]$ **1** and $[NBu^n{}_4]_2[WO_2(mnt)_2]$ **2**, were prepared by published methods.[16,17] The complexes were identified by UV/VIS spectrophotometry and IR spectroscopy and their purity was

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Supplementary data available (No. SUP 57276, 4 pp.): primary data for the kinetics studies including lists of observed rate constants for the reaction between phosphines and $[MoO_2(mnt)_2]^{2-}$ **1** in acetonitrile at 298.2 K, the temperature dependence of the observed rate constants for the reaction of phosphines with **1** in acetonitrile and related Eyring plots. See Instructions for Authors, *J. Chem. Soc.*, *Dalton Trans.*, 1997.

established by ^{13}C NMR and fast atom bombardment (FAB) mass spectrometry; the spectroscopic data were in agreement with published values.[16,17] In the course of the recrystallization of **1**, we observed the formation of an orange decomposition product of formula $[NBu^n_4]_2[(NC)C(S)C(CN)–S–S–C(CN)C(S)(CN)]$ which was identified by FAB mass spectrometry and X-ray crystallography. Triphenylphosphine (Acros), triethylphosphine (Aldrich), diethylphenylphosphine (Strem), and ethyldiphenylphosphine (Strem) were used as received; HPLC-grade acetonitrile (Lab-Scan) was distilled over CaH_2 under nitrogen, and stored under dinitrogen over molecular sieves (4 Å) in an MBraun 150 G-I dry atmosphere box. Water was doubly distilled from quartz. All experiments were performed with freshly degassed solvents.

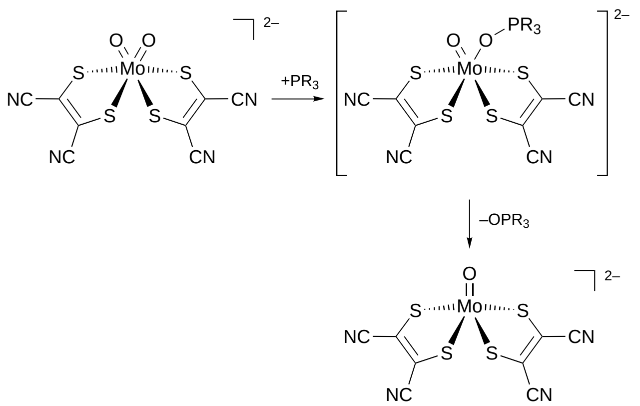
Synthesis of $[NBu^n_4][HSO_3]$

The salt $[NBu^n_4][HSO_3]$ was prepared using a column (30 × 10 cm) filled with ion-exchange resin (Dowex 50 Wx 8, 20–50 mesh, H^+ form). The column was saturated with $NBu^n_4{}^+$ using an aqueous solution of the bromide salt. It was carefully washed with distilled water, whereafter a solution of $NaHSO_3$ (2 g) in water was added. The resulting aqueous solution was collected and evaporated to dryness and extracted with hot methanol. The methanol solution was evaporated to dryness giving a colourless oil, which was dried under vacuum at 110 °C for 24 h; the oil solidifies at lower temperature. The total yield of $[NBu^n_4][HSO_3]$ was 5.5 g (90%). The purity of the product was checked by titration with I_2 and elemental analysis. In the titration, $[NBu^n_4][HSO_3]$ was treated with an excess of I_2, and the unreacted I_2 was titrated with $Na_2S_2O_3$. The purity was found to be better than 95%. IR (KBr, liquid film, cm^{-1}): 1469, 1381, 1262, 1229, 1056, 1010, 955, 885, 801, 734, 620, 563, 529 and 426. FAB$^+$ and positive-ion electron impact mass spectra (EI$^+$): *m/z* 242 ($Bu^n_4N^+$); FAB$^-$ and EI$^-$ mass spectra: *m/z* 80 and 81 ($SO_3{}^{2-}$ and $HSO_3{}^-$) (Found: C, 59.50; H, 11.42; N, 4.28; S, 9.82. Calc. for $C_{16}H_{37}NO_3S$: C, 59.40; H, 11.53; N, 4.33; S, 9.91%).

Kinetics measurements

Oxidation of phosphines and hydrogensulfite by complex 1 in acetonitrile. Reactions were initiated by mixing equal volumes (1 cm^3) of the pre-thermostatted Mo complex and ligand solutions in a tandem cuvette. All solutions were prepared and the cuvette was filled under strictly anaerobic conditions in an MBraun dry atmosphere box and all measurements were made under dinitrogen. The cuvette was located in the thermostatted compartment of the spectrophotometer for 10 min before mixing to reach temperature equilibrium. The UV/VIS spectra and kinetics were recorded by use of a Milton Roy 3000 diode array spectrophotometer. Spectra are given in Figs. 2 and 7. Reactions were monitored at 365, 425 and 520 nm. The oxo transfer reaction from **1** to the phosphines $PPh_{3-x}Et_x$ ($x = 0–3$) or to hydrogensulfite in acetonitrile were investigated at 25.0 °C under pseudo-first-order conditions with excess phosphine/sulfite. For the phosphines PPh_3 and PEt_3, the temperature-dependence of the oxo transfer reaction rates was also examined. The initial concentrations after mixing were: $[\mathbf{1}]_0 = 10^{-1}$ and $[PR_3]_0 = 100$ to 2.5 mmol dm^{-3} for the kinetics studies involving phosphines, and $[\mathbf{1}]_0 = 5 \times 10^{-2}$ and $[HSO_3{}^-]_0 = 50$ to 0.5 mmol dm^{-3} for the studies in which hydrogensulfite was used as an oxo acceptor.

Oxidation of hydrogensulfite by complex 1 in acetonitrile–water mixtures. The kinetics of oxidation of $HSO_3{}^-$ to $HSO_4{}^-$ in acetonitrile–water mixtures and the time-resolved spectral changes were followed by an Applied Photophysics Bio-Sequential SX-17 MX stopped-flow ASVD spectrofluorimeter. The reactions with sodium hydrogensulfite were initiated by mixing equal volumes of the molybdenum complex and $NaHSO_3$ solutions directly in the stopped-flow instrument. The molybdenum complex was dissolved in freshly distilled acetonitrile, while the sulfite was dissolved in water only or in a mixture of acetonitrile–water in different ratios (1 : 1, 3 : 1 or 16 : 9, v : v) with resultant measured pH values varying from 4.26 to 5.80. The spectral variation shows well defined isosbestic points at 355 and 375 nm. The kinetics were followed at 365, 425 and 540 nm.



Scheme 1 Proposed mechanism for the oxidation of phosphines by complex **1** (*cf.* ref. 22)

Reaction between water and complex 1 in acetonitrile. The measurements of the kinetics for these reactions were performed in acetonitrile solutions using $[\mathbf{1}]_0 = 10^{-1}$ and $[H_2O]_0 = 8.33$ to 27.8 mol dm^{-3}. All the experiments were performed as the kinetic runs for the oxo transfer reactions with phosphines and sulfite in pure acetonitrile.

Calculations

For an excess of the oxo acceptor, the kinetics could be described by a single exponential according to equation (2),

$$(A - A_0)/(A_0 - A_\infty) = e^{-k_{obs}t} \qquad (2)$$

where A denotes absorbance. Pseudo-first-order constants were evaluated by a least-squares fit of equation (2) to the experimental data using the PRO FIT 5.0, KALEIDAGRAPH or Applied Photophysics software packages.[18] Rate constants are reported as an average of observed rate constants at three different wavelengths. Activation parameters were derived from experiments between 291.2 and 329.3 K by use of the Eyring equation.

Results and Discussion

Previous studies[19–21] of oxo transfer from molybdenum dioxo complexes to substrates are consistent with mechanisms involving attack of the relevant substrate on the molybdenum complex followed by electron/oxygen-atom transfer, *i.e.* a reductive elimination reaction. It has been proposed[21,22] that the initial step of such oxo transfers to phosphines involves a direct attack of the phosphine at one of the oxo ligands with concerted two-electron transfer to the molybdenum centre to form a transient intermediate, as depicted in Scheme 1. Both the rate of formation of the transient intermediate as well as the final products should be dependent on the oxophilicity of the substrate (and the oxygen donor); the oxophilicity is related to the polarizability and relative basicity of the oxo acceptor. In order to investigate a possible dependence on the relative basicity of the substrate, we have studied the kinetics of oxidation of a range of phosphines with varying basicities.

Oxidation of phosphines by $[MoO_2(mnt)_2]^{2-}$ 1

A representative plot of the variation of the UV/VIS spectrum during the reaction of **1** with PPh_3 is shown in Fig. 2. The averaged values of the observed rate constants are linearly

Table 1 Rate constants and activation parameters for the k_2 pathway, and phosphine electronic and steric parameters for reactions of $[NBu^n_4]_2[MoO_2(mnt)_2]$ **1** with phosphines in acetonitrile at 298.2 K

	$10^4k_1/s^{-1}$	$k_2/dm^3\ mol^{-1}\ s^{-1}$	$\Delta H^{\ddagger}/kJ\ mol^{-1}$	$\Delta S^{\ddagger}/J\ K^{-1}\ mol^{-1}$	χ*/cm^{-1}	θ*/°
PEt_3	4.84 ± 2	0.109 ± 0.005	62 ± 6	−56 ± 20	6.30	132
$PPhEt_2$	1.23 ± 0.3	0.0784 ± 0.0005			9.30	136
PPh_2Et	7.42 ± 1	0.0614 ± 0.003			11.30	140
PPh_3	4.20 ± 0.6	0.0559 ± 0.001	45 ± 4	−119 ± 10	13.25	145

* Ref. 23.

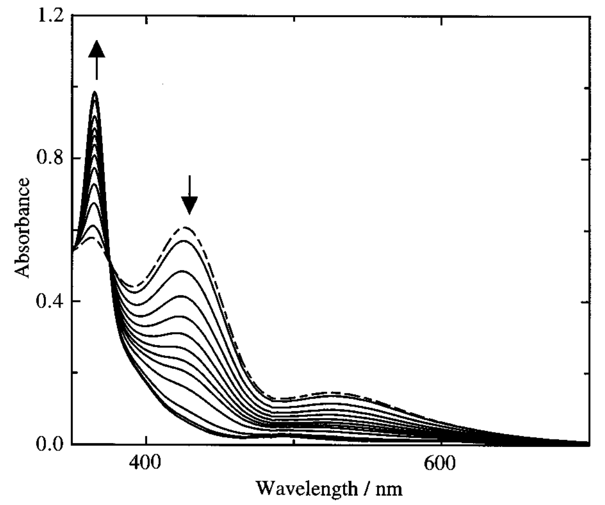


Fig. 2 The UV/VIS absorption spectra of **1** (– – –) and spectral variation for the oxo transfer reaction from complex **1** to PPh_3 (——) in acetonitrile. Conditions: $[\mathbf{1}] = 10^{-4}$, $[PPh_3] = 10^{-1}$ mol dm^{-3}, 25 °C. Time between scans 60 s, first scan obtained *ca.* 10 s after mixing

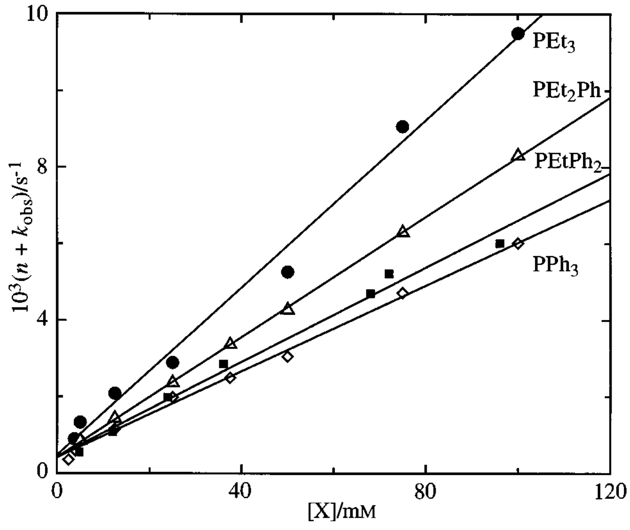


Fig. 3 Pseudo-first-order rate constants, k_{obs}, as a function of phosphine concentration [X] for the reaction of complex **1** with $PPh_{3-x}Et_x$ (x = 0–3) in acetonitrile

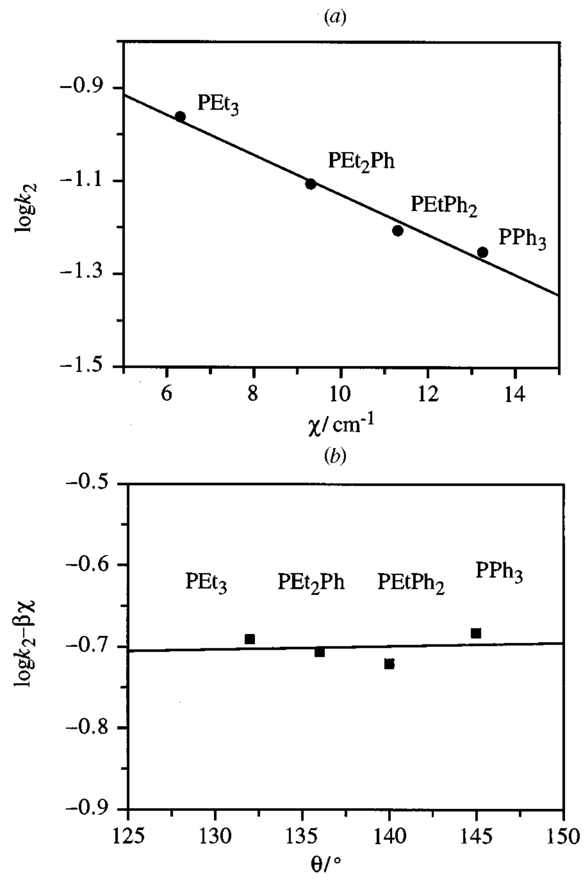


Fig. 4 (*a*) Correlation between log k_2 for the reaction of phosphines with complex **1** and the electronic parameter χ (*cf.* ref. 23); (*b*) steric profile for the same reaction, θ denoting the phosphine cone angle

dependent on the relevant phosphine concentrations according to equation (3) with an intercept k_1 of *ca.* 4.4×10^{-4} s^{-1} (Fig. 3).

$$k_{obs} = k_1 + k_2[PR_3] \qquad (3)$$

Saturation kinetics could not be observed at high phosphine concentrations. The observed pseudo-first-order rate constants are independent of the concentration of complex **1**. Table 1 contains the derived rate constants, k_1 and k_2, as well as activation parameters for the reactions of **1** with $PPh_{3-x}Et_x$ (x = 0–3). The variation of k_2 is relatively small but does nevertheless show a trend towards higher rates of oxo transfer with increasing basicity of phosphines. Rate constants for the reaction with various phosphorus-donor nucleophiles may be resolved in stereoelectronic factors by use of equation (4) where χ is a

$$\log k_2 = \alpha + \beta\chi + \gamma\theta \qquad (4)$$

measure of the relative σ donor capability, θ is the relevant phosphine cone angle, α is the intrinsic reactivity of the complex, and the terms $\beta\chi$ and $\gamma\theta$ are the electronic and steric contributions to the reactivity, respectively.[23,24] A plot of log k_2 *vs.* χ is shown in Fig. 4 together with a plot of log $k_2 - \beta\chi$ *vs.* θ. These data give $\alpha = -0.699 \pm 0.04$, $\beta = -0.043 \pm 0.004$ while γ is 0 (within experimental errors).‡ Solubility problems have prevented us from using more sterically hindered phosphines as oxo acceptors. Although the range of cone angles used in these experiments is admittedly relatively narrow (132–145°), the low values for γ indicate that steric factors (the phosphine cone angles) play a small role in these reactions. This is an expected result if the reactions proceed *via* phosphine attack on an oxo ligand; while there may be steric interactions between

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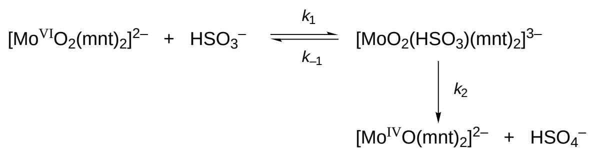
‡ Comparable results are obtained ($\beta = -0.050 \pm 0.007$ and $\gamma = -0.0002 \pm 0.003$) if the p$K_a$, which is directly related to the Brønsted basicity, is used as a measure of the ligand basicity.

Table 2 Observed and derived rate constants for the reaction between hydrogensulfite and $[NBu^n{}_4]_2[MoO_2(mnt)_2]$ **1** in acetonitrile–water mixtures at 298.2 K

	$[HSO_3^-]$/mM	10^2k_{obs}*/s^{-1}	k_2/s^{-1}	10^2K_M/M
$CH_3CN–H_2O$ (1:1, v/v)	2.50	6.91 ± 0.1	1.02 ± 0.07	3.89 ± 0.5
	3.75	9.19 ± 0.5		
	5.00	11.1 ± 0.9		
	7.50	20.6 ± 0.5		
	10.0	22.4 ± 0.8		
	15.0	29.9 ± 0.9		
	20.0	32.5 ± 1		
	25.0	36.1 ± 0.4		
	40.0	53.5 ± 2		
	50.0	54.5 ± 0.5		
	75.0	69.4 ± 1		
$CH_3CN–H_2O$ (16:9, v/v)	2.5	29.9 ± 2	1.05 ± 0.05	0.649 ± 0.9
	3.75	39.8 ± 0.9		
	5.00	50.9 ± 1		
	12.5	65.1 ± 2		
	15.0	69.9 ± 2		
	18.8	73.5 ± 2		
	37.5	90.3 ± 1		
	40.0	95.9 ± 3		
$CH_3CN–H_2O$ (3:1, v/v)	2.5	39.3 ± 3	1.19 ± 0.03	0.476 ± 0.9
	3.75	54.2 ± 5		
	5.00	62.3 ± 5		
	7.5	70.4 ± 3		
	10.0	79.8 ± 0.7		
	20.0	96.5 ± 0.8		
	25.0	99.6 ± 5		

* Standard deviations (σ) are given.



Scheme 2 Proposed mechanism for the oxidation of hydrogensulfite by complex **1** (*cf.* ref. 16)

the phosphine and the ligands co-ordinated to the molybdenum atom, these should be relatively minor when compared to those which would arise from co-ordination of the phosphine to the metal. The trend in reactivity is entirely in keeping with, and lends further support to, the postulated mechanism of oxo transfer[22] that is depicted in Scheme 1. Similarly, the negative $\Delta S^\ddagger$ is compatible with this mechanism.

Oxidation of sulfite by $[MoO_2(mnt)_2]^{2-}$ 1 in the presence of water

As mentioned above, **1** is capable of oxidizing hydrogensulfite.[16] Das and co-workers[16] have studied this oxidation reaction in acetonitrile–water mixtures and have rationalized the observed kinetics in terms of a mechanistic scheme involving a pre-equilibrium reaction in which an intermediate seven-co-ordinate complex, '$[MoO_2(HSO_3)(mnt)_2]^{3-}$', is formed. This pre-equilibrium step is assumed to be followed by the actual oxo transfer to form the products, $[MoO(mnt)_2]^{2-}$ and HSO_4^- (Scheme 2). Using stopped-flow spectrophotometry, we have investigated the above-mentioned reaction system in different acetonitrile–water mixtures (from 1:1 to 3:1, v/v) in which the water concentration varies from 27.8 to 13.9 M (Table 2). Our measurements are in qualitative agreement with those of Das and co-workers,[16] both in terms of kinetic behaviour and observed rate constants. The dependence of the observed rate constants on $[HSO_3^-]$ is curvilinear at low concentrations and becomes linear as $[HSO_3^-]$ increases, *i.e.* saturation kinetics is observed. The rate constants decrease as the water concentration increases, following the difference in solvation properties of the solvents towards the charged reactants. A double reciprocal plot of k_{obs} *vs.* $[HSO_3^-]$ for various water concentrations is shown in Fig. 5. A rate equation in accordance with Scheme 2 has been fitted to the experimental data. The values for k_2 (1.02 ± 0.07) s^{-1} and K_M (0.039 ± 0.005) M for a 1:1 acetonitrile–water solution at 25 °C are in good agreement with those obtained by Das and co-workers[16] ($k_2 = 0.87\ s^{-1}$, $K_M = 0.036$ M at 20 °C).

In order to further probe the initial reactions of **1** with water, these reactions were studied by conventional spectrophotometry in the absence of hydrogensulfite. Kinetic runs were followed in acetonitrile containing different concentrations of water. Fig. 6 shows the spectral variation for this reaction in a 1:1 (v/v) acetonitrile–water mixture. We have been unable to accurately determine rate constants for the different steps because of decomposition of **1**; however, experiments in the presence of Na_2mnt indicate that the reaction rates are independent of the free ligand concentration. At present, we cannot explain the three observed reactions but a reaction that is consistent with the observed independence of rates on free ligand concentration is one in which a water molecule forms a hydrogen bond to **1**. Two possible 'co-ordination' sites for such a hydrogen-bonded water molecule are shown in Scheme 3. Hydrogen-bonding of one or several water molecules to the dithiolene sulfurs of **1** is analogous to the designed N–H···S hydrogen bonding to the corresponding sulfur atoms in the complexes $[MoO\{S_2C_2(CONH_2)_2\}_2]^{2-}$ and $[MoO\{S_2C_2(CO_2Me)_2\}_2]^{2-}$ **3**.[25] Oku *et al.*[25] have found that such N–H···S hydrogen bonding stabilizes the $Mo^{VI}O_2^{2+}$ core; the hydrogen bond is proposed to strengthen the metal–oxo bond *trans* to the hydrogen-bonded dithiolene sulfur. Thus, the rate of oxygen transfer to the molybdenum(IV) monooxo complex **3** (reduction of Me_3NO) is enhanced when N–H···S hydrogen bonding to the dithiolene ligands of this complex is present.[25] This rate enhancement is attributed to an acceleration of the co-ordination of Me_3NO to form the proposed intermediate $[MoO(Me_3NO)\{S_2C_2(CO_2Me)_2\}_2]^{2-}$, in which the trimethylamine *N*-oxide molecule is co-ordinated *trans* to the oxo ligand.[25] An analogous rate enhancement could not be observed for the reaction of $[MoO\{S_2C_2(CN)_2\}_2]^{2-}$ with Me_3NO.[25] The hydrogen bonding of a water molecule to a dithiolene sulfur in **1** may thus stabilize one Mo–O bond and render the complex

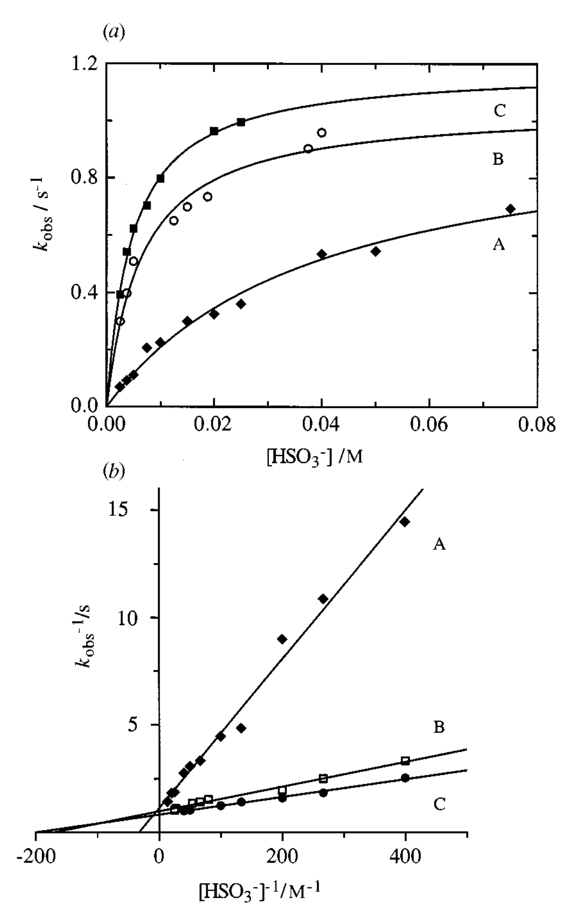


Fig. 5 (*a*) Dependence of observed rate constants for the reaction between complex **1** and hydrogensulfite in acetonitrile–water mixtures at 25 °C on the concentration of HSO_3^-; (*b*) the corresponding double reciprocal plot. A, $[H_2O] = 27.8$; B, $[H_2O] = 20.0$; C, $[H_2O] = 13.9$ M

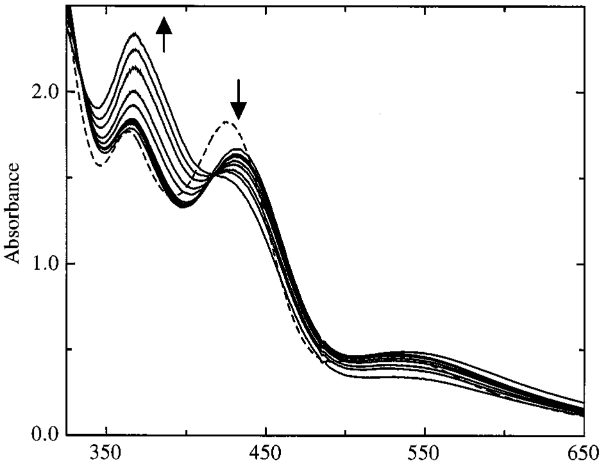
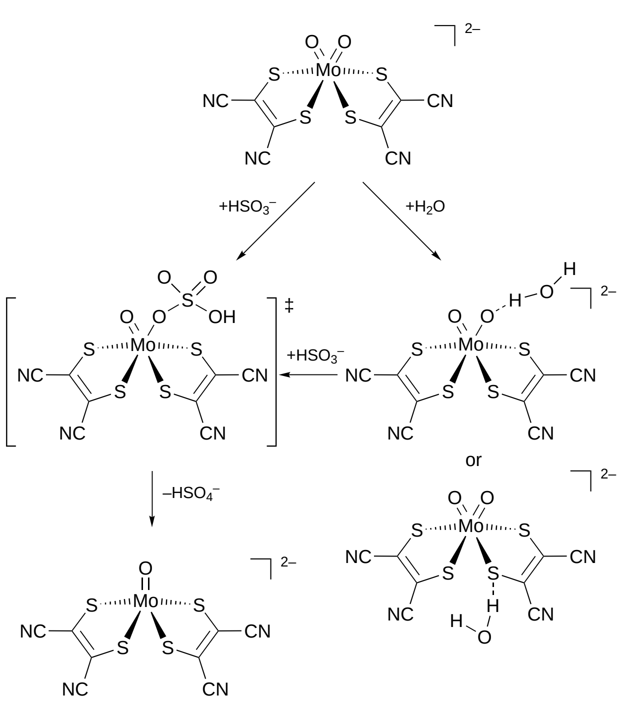


Fig. 6 The UV/VIS absorption spectra of complex **1** (– – –) and spectral variation for reaction between **1** and water in acetonitrile (——). Conditions: $[\mathbf{1}] = 3 \times 10^{-4}$, $[H_2O] = 27.8$ mol dm^{-3}, 25 °C. Time between scans 100 s, first scan obtained *ca.* 10 s after mixing

less susceptible to oxygen transfer. On the other hand, hydrogen bonding to one of the oxo ligands should weaken the Mo–O bond and may thus enhance the reactivity of the complex.

Another reaction that is consistent with the observed independence of rates on free mnt is the formation of a seven-co-ordinate complex, $[MoO_2(H_2O)(mnt)_2]^{2-}$, analogous to the intermediate in the reaction of **1** with hydrogensulfite that has been proposed by Das and co-workers[16] (Scheme 2). Seven-co-ordinate molybdenum[26,27] and tungsten[9] oxo complexes are known, but are not common. To our knowledge, there are no reports of a seven-co-ordinate molybdenum complex containing two oxo ligands, although the molybdenum(VI) dioxo form of the active site of dmso reductase may contain a seven-co-ordinate molybdenum atom.[28] While charge repulsion does not favour the formation of the proposed $[MoO_2(HSO_3)(mnt)_2]^{3-}$ complex, the kinetics indicates that such an intermediate may be formed. However, an alternative form of this intermediate is a six-co-ordinate complex in which the hydrogensulfite co-ordinates to one of the molybdenum oxo ligands *via* the central sulfur atom (Scheme 3). Such an intermediate is analogous to the proposed intermediates in the phosphine oxidation reactions (*cf.* Scheme 1) and in the deoxygenation of $[MoO_2(sap)(EtOH)]$ [sap = 2-(salicylideneamino)phenolate(2−)] by thionyl chloride.[29] It is apparent that the observed products, $[MoO(mnt)_2]^{2-}$ and HSO_4^-, may be formed from this proposed intermediate by concomitant electron transfer and metal–oxo bond cleavage. Further investigations are needed in order to clarify the reactions of **1** with water; at present, we believe that hydrogen bonding is more likely to be a part of the overall mechanism than the formation of a seven-co-ordinate molybdenum complex.



Scheme 3 Possible intermediates formed in the reactions of complex **1** with H_2O and/or HSO_3^-

Oxidation of sulfite by $[MoO_2(mnt)_2]^{2-}$ 1 in the absence of water

Reaction of **1** with excess hydrogensulfite in dry acetonitrile was studied by use of the acetonitrile-soluble salt $[NBu^n_4][HSO_3]$ (Table 3). The spectral variation for the reaction of **1** with $[NBu^n_4][HSO_3]$ in acetonitrile exhibits four well defined isosbestic points at 247, 280, 355 and 375 nm (Fig. 7). The observed pseudo-first-order rate constants are independent of the concentration of complex **1**. As in the case of the reaction of **1** with $NaHSO_3$ in water, saturation kinetics is observed at high concentrations of hydrogensulfite. A plot of k_{obs} *vs.* $[HSO_3^-]$ is shown in Fig. 8; the Michaelis–Menten equation may be fitted to these data, but a better fit is achieved when equation (5) is used. The latter rate law is consistent with a

$$k_{obs} = \frac{k_X + k_2K_1[HSO_3^-]}{1 + K_1[HSO_3^-]} = \frac{k_X/K_1 + k_2[HSO_3^-]}{1/K_1 + [HSO_3^-]} \quad (5)$$

mechanism in which the starting material, $[MoO_2(mnt)_2]^{2-}$ **1**, is involved in two competitive equilibria (Scheme 4); one equilibrium leads to the formation of an intermediate, possibly

Table 3 Observed and derived rate constants for the reaction between hydrogensulfite and $[MoO_2(mnt)_2]^{2-}$ in acetonitrile at 298.2 K

$[HSO_3^-]$/mmol dm^{-3}	$10^2k_{obs}{}^a$/s^{-1}	k_2/s^{-1}	K_1/M	$k_X{}^b$/s^{-1}
0.50	0.748 ± 0.09	0.0317 ± 0.001	62 ± 9	0.00674 ± 0.0004
1.25	0.879 ± 0.08			
2.5	0.992 ± 0.06			
5.0	1.21 ± 0.09			
10.0	1.70 ± 0.1			
25.0	2.16 ± 0.2			
40.0	2.43 ± 0.2			
50.0	2.59 ± 0.2			

[a] Standard deviations (σ) are given. [b] X is the unknown species.

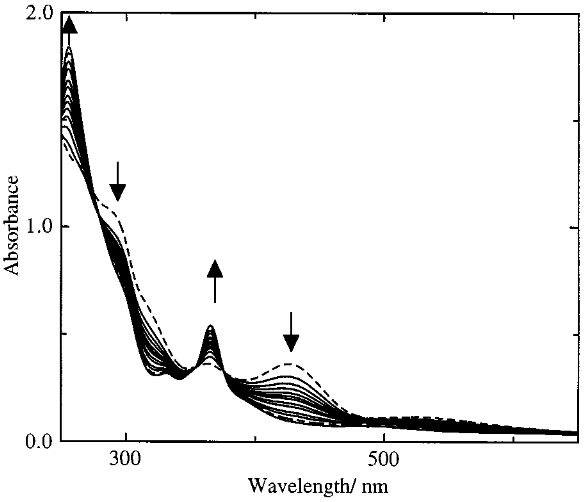


Fig. 7 The UV/VIS absorption spectra of complex **1** (– – –) and spectral variation for the oxo transfer reaction from **1** to hydrogensulfite in acetonitrile (——). Conditions: $[\mathbf{1}] = 5 \times 10^{-5}$, $[HSO_3^-] = 5 \times 10^{-2}$ mol dm^{-3}, 25 °C. Time between scans 20 s, first scan obtained *ca.* 10 s after mixing

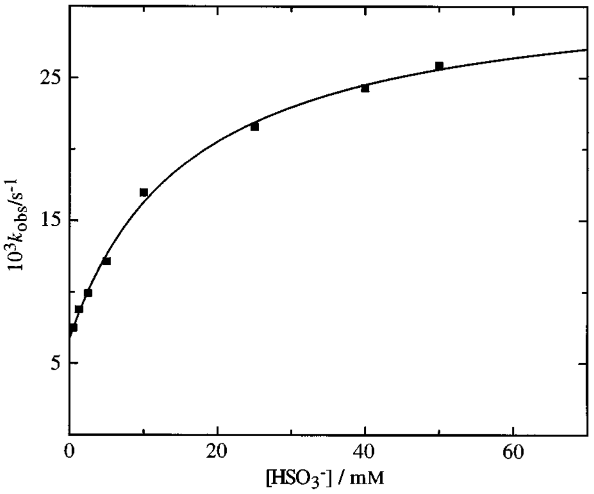
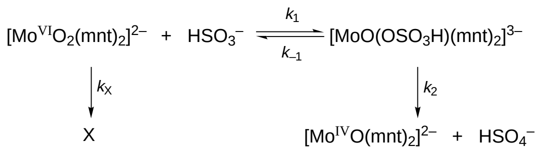


Fig. 8 Rate constants for the reaction between complex **1** and hydrogensulfite *vs.* $[HSO_3^-]$ in dry acetonitrile at 25 °C

the six-co-ordinate $[MoO(OSO_3H)(mnt)_2]^{3-}$, and subsequent oxo transfer, while the second equilibrium is a 'dead-end' equilibrium in which an unknown species (X) is formed. Alternatively, the second equilibrium may be replaced by an irreversible decomposition reaction. Fitting of equation (5) to the data gives $K_1 = 62 \pm 9$ M^{-1}, $k_2 = (3.2 \pm 0.1) \times 10^{-2}$ s^{-1} and $k_X = (6.7 \pm 0.4) \times 10^{-3}$ s^{-1}.

As a control experiment, the reaction of **1** with $[NBu^n_4][HSO_3]$ in the presence of water was studied. This reaction is considerably faster; in acetonitrile–water solution (3 : 1, v/v), the observed rate constant is 18 times larger than that for the corresponding reaction in pure acetonitrile. The presence of water affects the pH and the solvation properties of the reaction medium and it may be that the pH change affects the rate of the oxo transfer reaction. The trend of the experiments in acetonitrile is unexpected, because the rate of the overall reactions in the presence of water is faster than that in the absence of water. It is possible that the presence of water leads to the formation of a new, more reactive, intermediate complex containing a co-ordinated water molecule. One possibility is that the proposed complex '$[MoO_2(mnt)_2]^{2-}\cdot H_2O$' where the water is co-ordinated to one oxo ligand (see above and Scheme 3) is such a reactive intermediate. This proposed intermediate may be more susceptible towards co-ordination of HSO_3^- than $[MoO_2(mnt)_2]^{2-}$ itself. Another, perhaps more likely, explanation is that a small, but significant, amount of SO_3^{2-} is present in the acetonitrile–water mixtures. It has been shown that SO_3^{2-} is considerably more reactive than HSO_3^- towards electron transfer/oxidation to S^{VI}; for example, second-order rate constants for the oxidation of SO_3^{2-} by certain Pt^{IV} or Au^{III} complexes are up to five magnitudes larger than the corresponding rates for oxidation of HSO_3^-.[30] Thus, the presence of SO_3^{2-} may speed up the reaction considerably, even though charge repulsion does not favour the formation of a complex between **1** and the sulfite dianion.



Scheme 4 Proposed mechanism for the oxidation of hydrogensulfite by complex **1** in pure acetonitrile

Oxidation of hydrogensulfite by $[WO_2(mnt)_2]^{2-}$ 2

In contrast to **1**, its tungsten analogue, $[WO_2(mnt)_2]^{2-}$ **2**, does not react with sodium hydrogensulfite in $CH_3CN–H_2O$. However, we do observe a reaction between $[NBu_4]_2[WO_2(mnt)_2]$ and $[NBu_4][HSO_3]$ in acetonitrile at 36 °C. The UV/VIS spectrum shifts within 5 s after mixing of the reactants, revealing the formation of a new species with absorption maxima at λ = 275, 315 and 420 nm. This reaction is followed by a clean reaction for which isosbestic points at 350 and 395 nm are observed. We postulate that the latter reaction is an oxo transfer reaction that leads to the formation of $[WO(mnt)_2]^{2-}$ and HSO_4^-; this would mean that the tungsten dioxo moiety of this reaction system is able to mimic sulfite oxidase. Further investigations of this reaction are currently in progress.§

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§ *Note added at proof.* In a recent publication Kisker *et al.*[31] proposed that oxidation of sulfite by the enzyme sulfite oxidase occurs *via* attack of the substrate on one of the oxygens of the MoO_2 moiety.

Conclusion

The kinetics of oxidation of phosphines by $[MoO_2(mnt)_2]^{2-}$ **1** is consistent with the mechanism depicted in Scheme 1. No saturation behaviour has been observed in our studies of these reactions. The rate of phosphine oxidation may be correlated to the relative basicity of the phosphine; the more basic the phosphine, the larger is the rate of oxygen transfer.

The Michaelis–Menten type of kinetics that is observed for the oxidation of hydrogen sulfite by **1**, regardless of the presence of water, shows that the oxygen transfer is the rate-determining step in this case. The nature of the intermediate in the oxidation of hydrogensulfite is unclear, possible structures are depicted in Scheme 3. We propose that the intermediate is '$[MoO(OSO_3H)(mnt)_2]^{3-}$' with a structure analogous to that of '$[MoO(OPR_3)(mnt)_2]^{2-}$' (Scheme 3). If this is true, then the mechanisms for oxidation of phosphines and hydrogensulfite by **1** are essentially identical.

The rate of oxidation of hydrogensulfite is higher in acetonitrile–water mixtures than in pure acetonitrile. We have found that complex **1** reacts with water in three relatively slow reactions of unknown nature. The increased oxidation rate may be due to the formation of a new, more reactive molybdenum–oxo species in the presence of water, or the presence of the highly reactive sulfite dianion. Further investigations of the reactivity of **1** and related compounds towards biological substrates may clarify whether the observed reactivity is relevant to that of Moco.

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