Catalytic Air and Amine *N*-Oxide Oxidation of *p*-Substituted Benzoin by Molybdenum(VI) Complexes. Identification of the Deactivation Process by Dioxygen

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The catalytic oxidation of benzoin and two *p*-substituted benzoins, *e.g.* 4,4′-dimethoxy- and 4,4′-dichloro derivatives, by dioxygen or pyridine *N*-oxide, in the presence of [MoO_2(cysS-OMe)$_2$] (cysS-OMe = S-deprotonated cysteinate methyl ester) and [$MoO_2(S_2CNEt_2)_2$] was studied kinetically. The catalytic oxidation rates indicate a trend, MeO > H > Cl, which is related to the ease in apparent hydride release from the C–H group of benzoin derivatives. The stoicheiometric oxidation indicates a similar oxo-transfer reactivity of the above complexes towards the three *p*-substituted benzoins. Only one ^{18}O atom from [^{18}O] dioxygen was found in one of the benzil carbonyl groups. The catalytic dioxygen oxidation by [$MoO_2(S_2CNEt_2)_2$] suffers from deactivation through the formation of [$Mo^{V}O(S_2CNEt_2)_2$] formed by a one-electron-transfer reaction from [$Mo^{IV}O(S_2CNEt_2)_2$] to dioxygen.

Dioxomolybdenum complexes have been utilized as catalysts for molybdo-oxidase model oxo-transfer reactions[1] such as the stoicheiometric oxidation of triphenylphosphine by [$MoO_2(S_2CNR_2)_2$][2] or [MoO_2(cysS-OR)$_2$] (cysS-OR = S-deprotonated L-cysteinate alkyl ester, R = Me, Et, or Pr^i).[3,4] Recently, the catalytic oxidation of thiol by [MoO_2L] [L = pyridine-2,6-bis(1′,1′-diphenylethanethiolate)] has been reported.[5] We have reported the catalytic air oxidation of benzoin in the presence of [MoO_2(cysS-OMe)$_2$] and [MoO_2(cysS-NHC$_{10}$H$_{21}$)$_2$] as a model reaction for C–H activation similar to the biological oxidations of xanthine (3,7-dihydro-1*H*-purine-2,6-dione) or aldehyde by the corresponding oxidases.[6] These enzymes are known to utilize water as a source of oxygen atoms and dioxygen can be used as an oxidant.[7] Air oxidation of C–H groups is important not only in biological energy transduction, but also in applications to organic synthesis.

Our previous study showed that [MoO_2(cysS-OR)$_2$] is involved in a smooth catalytic cycle with dioxygen but the related complex [$MoO_2(S_2CNEt_2)_2$] shows slow deactivation of the catalyst.[6] Further to investigate this deactivation process, the oxidation of three benzoin derivatives by two types of oxidants, dioxygen and amine *N*-oxides, have now been examined. One-electron transfer or one- or two-oxygen-atom transfer with dioxygen is known for various metal complexes.[8] The influence of the nature of the ligands around MoO_2^{2+} was studied as previously it has been shown that side reactions occur with sulphur ligands such as S_2CNEt_2 and it was hoped these may be avoided by the use of mixed sulphur–nitrogen ligands such as cysS-OR.

In this paper, we also examine the rate of oxidation of the methine group using *p*-substituted benzoin. Involvement of dioxygen in the catalytic process is also studied using ^{18}O-enriched dioxygen.

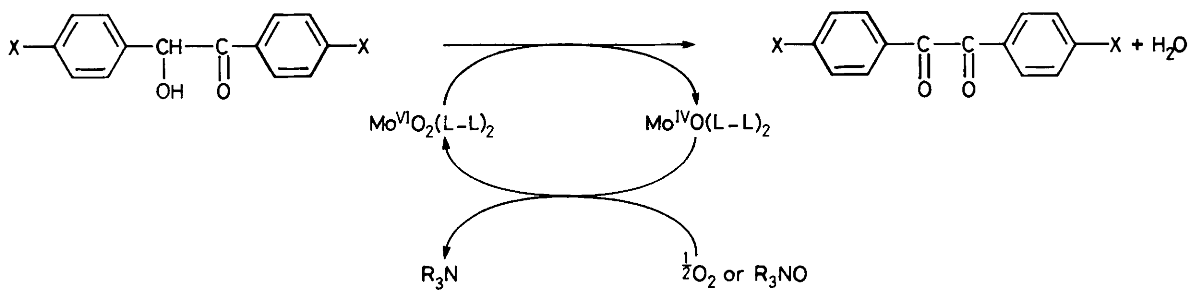
Experimental

Dimethylformamide (dmf) and acetonitrile were purified by distillation. 4,4′-Dimethoxybenzoin and benzoin were purchased from Nakarai Chemical Co. The complexes [MoO_2(cysS-OMe)$_2$] (**1**),[9] [$MoO_2(S_2CNEt_2)_2$] (**2**),[10] [Mo_2O_3(cysS-OMe)$_4$] (**3**),[11] [$Mo_2O_3(S_2CNEt_2)_4$] (**4**),[10] and 2,2′-bipyridine *N*-oxide[12] were synthesized by literature procedures. 50% ^{18}O-Enriched dioxygen was obtained from Nakarai Chemical Co.

4,4′-Dichlorobenzoin.—This compound was prepared by a modification of the literature method.[13] To a solution of *p*-chlorobenzaldehyde (5.6 g, 39.8 mmol) in methanol (10 cm^3) was added an aqueous solution (10 cm^3) of potassium cyanide (0.6 g, 9.3 mmol) at room temperature. The mixture was refluxed for 2 h. Cooling in an ice-bath gave a yellow precipitate which was collected by filtration and then dissolved in diethyl ether (200 cm^3). The ether solution was washed with an aqueous solution (20%) of $NaHSO_3$ and dried over sodium sulphate. Concentration of this solution under reduced pressure gave colourless crystals. The crude material was recrystallized from ether–light petroleum (Found: C, 59.50; H, 3.65. Calc. for $C_{14}H_{10}Cl_2O_2$: C, 59.40; H, 3.60%).

Catalytic Oxidation of p-*Substituted Benzoin.*—A dmf solution (1 cm^3) of benzoin (0.05 mmol), 4,4′-dimethoxybenzoin, or 4,4′-dichlorobenzoin was added to a dmf solution (1 cm^3) of a molybdenum(VI) complex (0.0025 mmol) with vigorous stirring at 30 °C under an argon atmosphere. Catalytic air oxidation was carried out by exposing the solution to air, while in the case of catalytic amine *N*-oxide oxidation a dmf solution (0.5 cm^3) of amine *N*-oxide (0.05 mmol) was added to a dmf solution (0.5 cm^3) of benzoin (0.05 mmol) with stirring at 30 °C. The same procedure was employed for the determination of benzil as described in the previous paper.[6] The observed initial rates of both the stoicheiometric reaction and the catalytic pyridine *N*-oxide oxidation were determined from the yield of benzil or *p*-substituted benzil.

Catalytic Oxidation of Benzoin by ^{18}O*-Enriched Dioxygen.*—To a dmf solution (20 cm^3) of benzoin (14 mmol) and [MoO_2(cysS-OMe)$_2$] (0.2 mmol) was introduced 50% ^{18}O-enriched dioxygen gas (10 mmol) *in vacuo*. The solution was stirred at 40 °C for 20 h. Water was collected with dmf as the benzene azeotrope under reduced pressure. About 0.18 cm^3 was obtained. Benzil was extracted with water–diethyl ether (1:1). The ether layer was concentrated and the addition of n-hexane gave a crude material which was recrystallized from hot hexane. Chromatographically pure benzil was obtained.



Scheme 1. X = Cl, H, or MeOH; L–L = cysS-OMe or S_2CNEt_2

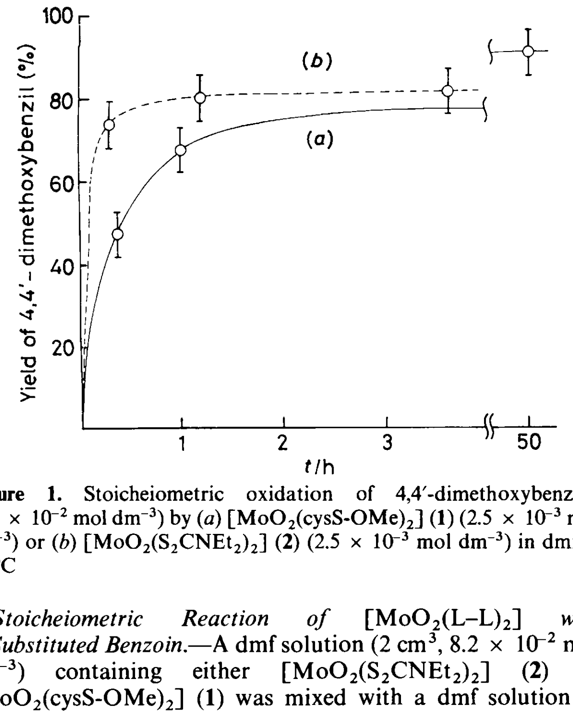


Figure 1. Stoicheiometric oxidation of 4,4′-dimethoxybenzoin (2.5×10^{-2} mol dm^{-3}) by (*a*) $[MoO_2(cysS\text{-}OMe)_2]$ (**1**) (2.5×10^{-3} mol dm^{-3}) or (*b*) $[MoO_2(S_2CNEt_2)_2]$ (**2**) (2.5×10^{-3} mol dm^{-3}) in dmf at 25 °C

Stoicheiometric Reaction of $[MoO_2(L\text{–}L)_2]$ *with* p-*Substituted Benzoin.*—A dmf solution (2 cm^3, 8.2×10^{-2} mol dm^{-3}) containing either $[MoO_2(S_2CNEt_2)_2]$ (**2**) or $[MoO_2(cysS\text{-}OMe)_2]$ (**1**) was mixed with a dmf solution (2 cm^3, 8.2×10^{-2} mol dm^{-3}) of the *p*-substituted benzoin at 20, 30, and 40 °C under an argon atmosphere. The yield of the *p*-substituted benzil was determined by h.p.l.c. using a μ-Bondapack C_{18} column (length 30 cm, inside diameter 0.39 cm).

Stoicheiometric dioxygen or pyridine *N*-oxide (0.0025 mol dm^{-3}) oxidation of μ-oxo binuclear molybdenum(v) complexes (0.0025 mol dm^{-3}) in acetonitrile at 25 °C was monitored by visible spectrophotometry. The yield of molybdenum(vi) complexes was determined by the measurement of absorption maxima at 350 nm for (**1**) and at 374 nm for (**2**) after the complete disappearance of absorption maxima at 500—510 nm due to the μ-oxo binuclear molybdenum-(v) and -(iv) complexes. Apparent oxidation rates were obtained from the decay of the absorption maxima at 500 nm for (**3**) and at 509 nm for (**4**) at 25 °C.

The attempted isolation of molybdenum(iv) species obtained upon the reduction of $[MoO_2(cysS\text{-}OMe)_2]$ by 4,4′-dimethoxybenzoin at 60 °C was unsuccessful. Only a dmf-insoluble golden precipitate was obtained which was identified as a polymeric molybdenum species (Found: C, 25.35; H, 4.20; N, 5.95. $C_8H_{16}MoN_2O_5S_2$ requires C, 25.25; H, 4.25; N, 7.35%). Raman: $\nu_{max.}$(Mo–O–Mo) 756vs; $\nu_{max.}$(Mo=O) 945 (sh) cm^{-1} (solid).

Air and Pyridine N-*Oxide Oxidations of* $[Mo^{V}{}_2O_3(L\text{–}L)_4]$.—An acetonitrile solution (4 cm^3) of $[Mo^{V}{}_2O_3(L\text{–}L)_4]$ (L–L = cysS-OMe or S_2CNEt_2) (0.04 mmol) was prepared in a 1-mm cell under an argon atmosphere and placed in a cell for electronic spectroscopic measurements. Air was bubbled into the solution at 30 °C. To another solution at 30 °C was added an acetonitrile solution (2 cm^3) of pyridine *N*-oxide (0.04 mmol).

Physical Measurements.—The visible spectrum of the solution containing the molybdenum(vi) complex was recorded on a Jasco Uvidic 5A instrument at room temperature. The cyclic voltammograms were taken on a Yanaco 1100 with a three-electrode system consisting of a glassy carbon working electrode, a platinum-wire auxiliary electrode, and a saturated calomel compartment. Solutions for the electrochemical measurement were 0.002 mol dm^{-3} in Mo^{VI} and a solution of tetra-n-butylammonium perchlorate (0.1 mol dm^{-3}) was employed as supporting electrolyte. The e.s.r. spectrum of a reaction mixture of $[Mo_2O_3(cysS\text{-}OMe)_4]$ (0.02 mmol) or $[Mo_2O_3(S_2CNEt_2)_2]$ (0.02 mmol) with excess of air (dioxygen, 0.04 mmol) in dmf (5 cm^3) was recorded on a JES-FE 1X spectrometer at 25 °C. High-resolution mass spectra were taken on a JEOL JEX-303 mass spectrometer.

Results and Discussion

Stoicheiometric Reaction of $[MoO_2(cysS\text{-}OMe)_2]$ *with* p-*Substituted Benzoin.*—The oxidizing ability of two different types of $[Mo^{VI}O_2(L\text{–}L)_2]$ complexes, $[MoO_2(cysS\text{-}OMe)_2]$ (**1**) and $[MoO_2(S_2CNEt_2)_2]$ (**2**), towards benzoin was examined under an argon atmosphere. Figure 1 shows the time dependence of the formation of 4,4′-dimethoxybenzil in the stoicheiometric reaction between (**1**) or (**2**) and 4,4′-dimethoxybenzoin (1:1). The higher reactivity of 4,4′-dimethoxybenzoin compared with benzoin results in over 50% yield of 4,4′-dimethoxybenzil and probably in the formation of '$[Mo^{IV}O(cysS\text{-}OMe)_2]$' although isolation of $[Mo^{IV}O(cysS\text{-}OMe)_2]$ was unsuccessful because of conversion into a Mo–O–Mo polymeric complex owing to the instability of the molybdenum(iv) species. The polymeric complex is inert to air. The 2:1 or 1:1 reaction between complex (**1**) and benzoin quantitatively gave $[Mo^{V}{}_2O_3(cysS\text{-}OMe)_4]$ which has a visible or circular dichroism (c.d.) extremum at 510 nm as described previously.[6] The binuclear molybdenum(v) complex has also been found on reduction of (**1**) with triphenylphosphine.[4] The consumption of over 90% of 4,4′-dimethoxybenzoin in the 1:1 reaction indicates a two-electron transfer with formation of *p*-substituted benzil accompanied by oxo transfer from the dioxomolybdenum(vi) to the mono-oxomolybdenum(iv) complex. This is supported by the lack of an e.s.r. signal attributable to a mono-oxomolybdenum(v) species.[6]

Table 1 lists the observed rates ($k_{obs.}$) of the stoicheiometric reaction between $[MoO_2(cysS\text{-}OMe)_2]$ and *p*-substituted benzoin. The similar results for different benzoins with both (**1**) and (**2**) indicate the lack of a *p*-substituent effect on the rates. In the present case, proton abstraction from the methine group is the rate-determining step and this induces a typically ionic reaction, *i.e.* proton and electron release from benzoin. The

Table 1. Stoicheiometric oxidation rates ($k_{obs.}$) of *p*-substituted benzoins (0.0082 mol dm^{-3}) by molybdenum(VI) complexes (0.0082 mol dm^{-3}) in dmf at 30 °C

	$10^6k_{obs.}/s^{-1}$	
	$[MoO_2(cysS\text{-}OMe)_2]$	$[MoO_2(S_2CNEt_2)_2]$
4,4′-Dichlorobenzoin	12 ± 2	150 ± 14
Benzoin	11 ± 1	190 ± 17
4,4′-Dimethoxybenzoin	12 ± 2	120 ± 11

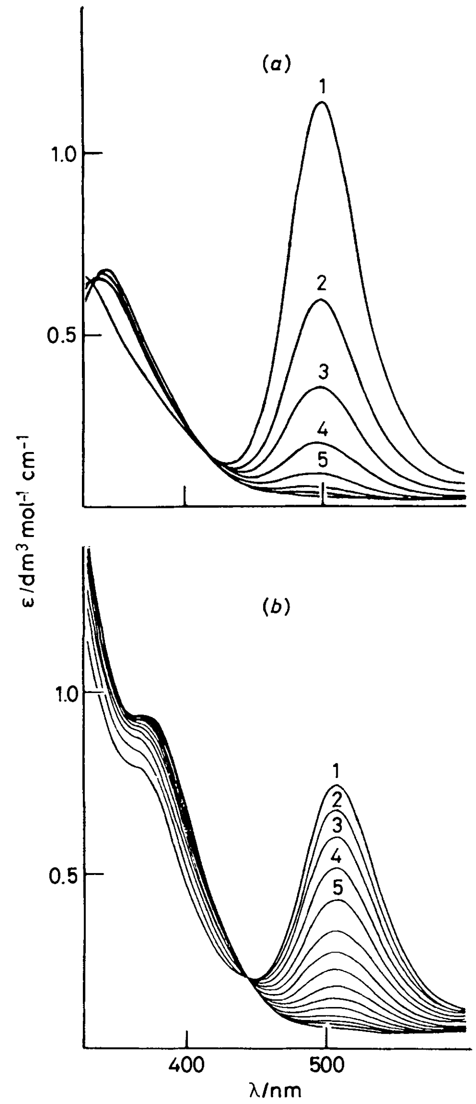


Figure 2. Variation of the visible spectra with time in the stoicheiometric reaction between μ-oxo binuclear molybdenum(V) complex [(*a*) (3) or (*b*) (4)] (0.0082 mol dm^{-3}) and air (dioxygen, 0.0082 mol dm^{-3}) in acetonitrile at room temperature. (1) Spectrum of a solution of (3) or (4); (2)—(5) refer to the spectra of the reaction mixtures after 5, 10, 15, and 20 min, respectively

higher stoicheiometric oxidation rate for (**2**) than (**1**) appears to result from a faster catalytic oxidation of (**2**), as described later. A considerable substituent effect on the rate has been reported in the oxidation of *p*-substituted benzoins by osmium tetraoxide[14] or nickel(II) acetate.[15] Hammond and Wu[15] reported that the relative rates of the stoicheiometric oxidation of benzoin, 4,4′-dichloro- and 4,4′-dimethoxybenzoin with nickel(II) acetate were 1.0, 2.4, and 0.21, respectively. In their study, the electron-withdrawing substituent at the *p* positions was found to accelerate the oxidation by $Ni(O_2CMe)_2/O_2$ products. On the contrary, Misra *et al.*[14] have reported the catalytic oxidation of *p*-substituted benzoin by alkaline hexacyanoferrate(III) in the presence of osmium tetraoxide. Their oxidation system showed a higher oxidation rate with the electron-donating group in the *p* position. Their results suggested the absence of proton elimination by OH$^-$ in the rate-determining step.

Stoicheiometric Reoxidation Reaction from $[Mo^V{}_2O_3(L\text{-}L)_4]$ *to* $[Mo^{VI}O_2(L\text{-}L)_2]$ *by Air or Pyridine* N-*Oxide.*—Although the synthesis of $[Mo^{IV}O(S_2CNEt_2)_2]$ has been established,[3] there is no report for the synthesis of pure $[Mo^{IV}O(cysS\text{-}OMe)_2]$ because of its thermal instability. μ-Oxo binuclear molybdenum(V) complexes, $[Mo^V{}_2O_3(cysS\text{-}OMe)_4]$ (**3**) and $[Mo^V{}_2O_3(S_2CNEt_2)_2]$ (**4**), are available as alternatives for the reduced species of (**1**) or (**2**). These binuclear complexes are thought to be in a resting state of the catalytic oxidation since there is a ready disproportionation equilibrium (1) (L–L = cysS-OMe or S_2CNEt_2) to give the corresponding molybdenum-(VI) and -(IV) complexes which are participating in the catalytic oxidation.[2]

$$[Mo^V{}_2O_3(L\text{-}L)_4] \overset{K}{\rightleftharpoons} [Mo^{IV}O(L\text{-}L)_2] + [Mo^{VI}O_2(L\text{-}L)_2] \quad (1)$$

The ease of oxidation of the molybdenum(IV) complex can be estimated from the oxidation with the corresponding μ-oxo binuclear molybdenum(V) complexes. Oxygen-atom transfer from Me_3CONO_2 or amine *N*-oxide to $[Mo^{IV}O(S_2CNEt_2)_2]$ has been confirmed.[16] The equilibrium constant (K) for the disproportionation of (**4**) in equation (1) has been reported to be 2.0×10^{-3} dm^3 mol^{-1} in dichloromethane.[17] Although no data for complex (**3**) have been reported, the equilibrium constant seems to be similar to that of (**4**).

The change observed in u.v.–visible spectra in the presence of complex (**3**) during the air oxidation is depicted in Figure 2. At the initial stage of the reoxidation, the rate using either dioxygen or pyridine *N*-oxide in dmf can be determined by monitoring the characteristic absorption maximum at 500 nm for (**3**). The apparent initial rate of oxidation using pyridine *N*-oxide or air was $(2.4 \pm 0.1) \times 10^{-3}$ or $(2.9 \pm 0.1) \times 10^{-3}$ s^{-1} respectively for (**3**). These observed rates can be discussed only at the initial stage since the presence of a disproportionation equilibrium prevents the accurate estimation of reoxidation rates. When the reduction of complex (**1**) by benzoin is analysed by visible spectroscopy the overlap of the absorption maxima for μ-oxo binuclear ($\lambda_{max.}$ 509 nm) and mononuclear molybdenum(V) complexes ($\lambda_{max.}$ 503 nm) complicates the estimation. Table 2 lists the yields of molybdenum(VI) complexes determined from the absorption maximum at 350 nm for (**1**) which is characteristic for a dioxomolybdenum(VI) complex. These data were obtained after the disappearance of peaks due to the μ-oxo binuclear molybdenum(V) species (**3**).

A simple oxidation process with oxo transfer was observed for (**3**). The e.s.r. spectrum of a dmf solution of this complex after air oxidation provides support for equation (1). No e.s.r. signal was observed from an air-oxidized solution of (**3**) at room temperature. The results suggest that a mononuclear molybdenum(V) species is not involved in the air oxidation.

Figure 2 also shows the change of the visible spectra of complex (**4**) in dmf. The rate at the initial stage determined by monitoring the absorption maximum at 509 nm for (**4**) is $(1.5 \pm 0.2) \times 10^{-3}$ s^{-1} in the presence of pyridine *N*-oxide. Reliable data were not obtained for air oxidation of (**4**) because

Table 2. Stoicheiometric dioxygen or pyridine *N*-oxide oxidation of μ-oxo binuclear molybdenum(V) complexes (0.0025 mol dm^{-3}) in acetonitrile at 25 °C

Complex	Oxidant	Reaction time (min)^a	Yield (%)^b of (1) or (2)
$[\mathrm{Mo_2O_3(cysS\text{-}OMe)_4}]$	Pyridine *N*-oxide	50	76
	Air	30	56
	Excess of dioxygen	30	40
$[\mathrm{Mo_2O_3(S_2CNEt_2)_4}]$	Pyridine *N*-oxide	10	56
	Air	75	55
	Excess of dioxygen	12	10

^{a} The reaction times refer to the complete disappearance of absorption *maxima* at 500—510 nm due to μ-oxo binuclear molybdenum(V) and mono-oxomolybdenum(IV) complexes. ^{b} The yields were obtained by monitoring the absorption maxima at 350 nm for $[\mathrm{Mo_2O_3(cysS\text{-}OMe)_4}]$ and at 374 nm for $[\mathrm{Mo_2O_3(S_2CNEt_2)_4}]$.

Table 3. Effect of addition of pyridine on the air oxidation of benzoin (0.05 mol dm^{-3}) in the presence of $[\mathrm{MoO_2(cysS\text{-}OMe)_2}]$ (0.0025 mol dm^{-3}) in dmf at 30 °C

Pyridine	Time (h)	Yield of benzil (%)
None	0.5	8 ± 1
	2	26 ± 2
0.0025 mol dm^{-3}	0.5	9 ± 1
	2	19 ± 2
0.025 mol dm^{-3}	0.5	11 ± 1
	2	23 ± 3

of concurrent formation of a mononuclear molybdenum(V) complex by one-electron transfer.

Tables 2 lists the yields of complex (**2**) from (**4**) determined from an absorption maximum at 374 nm. Although a simple oxidation process with oxo transfer from dioxygen to the molybdenum(IV) species was observed for (**3**), the air oxidation of (**4**) results in the formation of a new complex with an absorption maximum at 503 nm, which slowly decays with time. This unexpected reaction was suggested to be due to the formation of a mononuclear molybdenum(V) species, $[\mathrm{Mo^VO(S_2CNEt_2)_2}]^+$, formed by an outer-sphere one-electron transfer to dioxygen as shown in equation (2). The e.s.r.

$$[\mathrm{Mo^{IV}O(S_2CNEt_2)_2}] + \mathrm{O_2} \longrightarrow [\mathrm{Mo^{V}O(S_2CNEt_2)_2}]^+ + \mathrm{O_2^{\bullet -}} \quad (2)$$

spectrum of a dmf solution of complex (**4**) upon air oxidation provides support for equation (2). A clear e.s.r. signal for (**4**) under the above conditions was found at $g_{\mathrm{av.}} = 1.977$ at room temperature, in contrast to the results for the air oxidation of (**3**). No signal due to the superoxide anion was detected at room temperature.

Such e.s.r. signals due to the formation of mono-oxomolybdenum(V) species have been detected in the air oxidation of $[\mathrm{Mo^{IV}O(SCH_2CH_2S)_2}]^{2-}$.[18] No definite conversion from mononuclear molybdenum(V) to dioxo molybdenum(VI) complexes by air has been detected. The mononuclear complex $[\mathrm{Mo^VO(SPh)_4}]^-$ is known to give $[\mathrm{Mo^V{}_2O_2(SPh)_6(MeCN)}]$ upon electrochemical oxidation in acetonitrile.[19] Spontaneous decomposition of $[\mathrm{Mo^VO(L\text{–}L)_2}]^+$ (L–L = aminocyclopent-1-ene-1-carbodithioate) to a seven-co-ordinate complex, $[\mathrm{Mo^VO(L\text{–}L)_3}]$, has been reported.[20] A similar dithiocarbamato complex, $[\mathrm{Mo^VO(S_2CNEt_2)_2}]^+$, was found to decompose slowly to give $[\mathrm{Mo^V{}_2O_4(S_2CNEt_2)_2}]$ as an inert complex.[10] Thus, the difficulties experienced in forming a dioxomolybdenum(VI) complex from the corresponding mononuclear molybdenum(V) complex are well known.

Cyclic Voltammograms of Dioxomolybdenum(VI) *and Binuclear Molybdenum*(V) *Complexes*.—The electrochemical properties of complexes (**1**)—(**4**) were examined in dmf as shown in Figure 3. An irreversible reduction peak of (**1**) at $E_{\mathrm{pc}} = -1.25$ V *vs.* saturated calomel electrode (s.c.e.) is assignable to the $\mathrm{Mo^{VI}O_2{}^{2+}}$–$\mathrm{Mo^VO_2{}^+}$ couple followed by an irreversible reduction to a $\mathrm{Mo^{IV}O^{2+}}$ species. The redox behaviour of complex (**2**) was re-examined and compared to those of the μ-mono-oxo binuclear molybdenum(V) complexes. Complex (**2**) exhibits a reduction peak at $E_{\mathrm{pc}} = -0.87$ V *vs.* s.c.e. ($\mathrm{Mo^{VI}O_2{}^{2+}}$–$\mathrm{Mo^VO_2{}^+}$) with the first scan similar to that reported by DeHayes *et al.*[21] The $\mathrm{Mo^VO_2{}^+}$ species thus formed is converted rapidly into a $\mathrm{Mo^{IV}O^{2+}}$ species. Therefore, the lowering of these $\mathrm{Mo^{VI}O_2{}^{2+}}$–$\mathrm{Mo^VO_2{}^+}$ redox potentials reflects the ease of the oxo- transfer reactions with benzoin. A new reduction peak due to $\mathrm{Mo^VO^{3+}}$–$\mathrm{Mo^{IV}O^{2+}}$ probably appears at -0.85 V *vs.* s.c.e. which is overlapped by the reduction peak of $\mathrm{Mo^{VI}O_2{}^{2+}}$–$\mathrm{Mo^VO_2{}^+}$. An irreversible oxidation peak for (**2**) was observed at $+0.15$ V *vs.* s.c.e. due to the redox couple $\mathrm{Mo^{VI}O^{4+}}$–$\mathrm{Mo^VO^{3+}}$ when the scanning was carried out over -1.30 v *vs.* s.c.e. This is followed by formation of $\mathrm{Mo^{IV}O^{2+}}$ species with oxo transfer. Complex (**3**) exhibits a reduction peak at $E_{\mathrm{pc}} = -1.30$ V *vs.* s.c.e. which corresponds to $\mathrm{Mo^{VI}O_2{}^{2+}}$–$\mathrm{Mo^VO_2{}^+}$ of (**1**) formed from (**3**) by the disproportionation reaction (1). A dmf solution of (**4**) at 27 °C showed a reduction peak at $E_{\mathrm{pc}} = -0.87$ V due to $\mathrm{Mo^{VI}O_2{}^{2+}}$–$\mathrm{Mo^VO_2{}^+}$ of (**2**). This peak disappears at 0 °C because of the absence of (**2**) through the temperature-dependent equilibrium (2). A clear peak of (**4**) at -1.10 V is probably due to the couple $\mathrm{Mo^V{}_2O_3{}^{4+}}$–$\mathrm{Mo^VMo^{IV}O_3{}^{3+}}$. No such peaks could be recognized for (**3**).

Since the redox potential for $\mathrm{O_2}$–$\mathrm{O_2^-}$ had been reported as -0.6 V *vs.* s.c.e. in dmf,[22] both reduced $\mathrm{Mo^{IV}O^{2+}}$ species of (**1**) and (**2**) are capable of a one-electron transfer to dioxygen although such a reduction of dioxygen is not a favourable reaction for transition-metal complexes in general.

Catalytic Oxidation of Benzoin by Various Oxidants in the Presence of $[\mathrm{MoO_2(cysS\text{-}OMe)_2}]$.—Possible perturbation of the reaction through accumulation of amine generated from amine *N*-oxide was examined by addition of pyridine to the catalytic system (Table 3). Only a slight increase of the yield was observed upon addition of even 10 molar equivalents of pyridine to the molybdenum(VI) complex. In basic solutions, *e.g.* in the presence of formylflavin, air oxidation of benzoin is accelerated.[23] Actually, in the case of molybdenum(VI) oxidation, proton elimination from the methine group of benzoin by base somewhat promotes the oxidation.

Table 4 lists the yields of benzil from the non-catalytic and the catalytic amine *N*-oxide oxidation. Trimethylamine *N*-oxide provides the highest oxidation rates but it also has some activity in the control experiment. During oxidation by pyridine *N*-oxide or 2,2′-bipyridyl *N*-oxide the solution exhibits a purple colour which is ascribed to the presence of $[\mathrm{Mo_2O_3(cysS\text{-}OMe)_4}]$. In this catalytic system, the observed oxidation rate is limited by the reoxidation from $\mathrm{Mo^{IV}}$ to $\mathrm{Mo^{VI}}$. In the air oxidation, complex (**1**) exhibited almost the same oxidation activity as in the pyridine *N*-oxide oxidation. Amine *N*-oxide has been reported to be reduced by liver aldehyde oxidase which is known to contain a dioxomolybdenum(VI) active site.[24] Recently, *Escherichia coli* triethylamine *N*-oxide reductase has been established to be a molybdoenzyme.[25] Generally, amine *N*-oxides are known to be oxidants for molybdenum(IV) complexes. For example, oxo transfer from pyridine *N*-oxide to

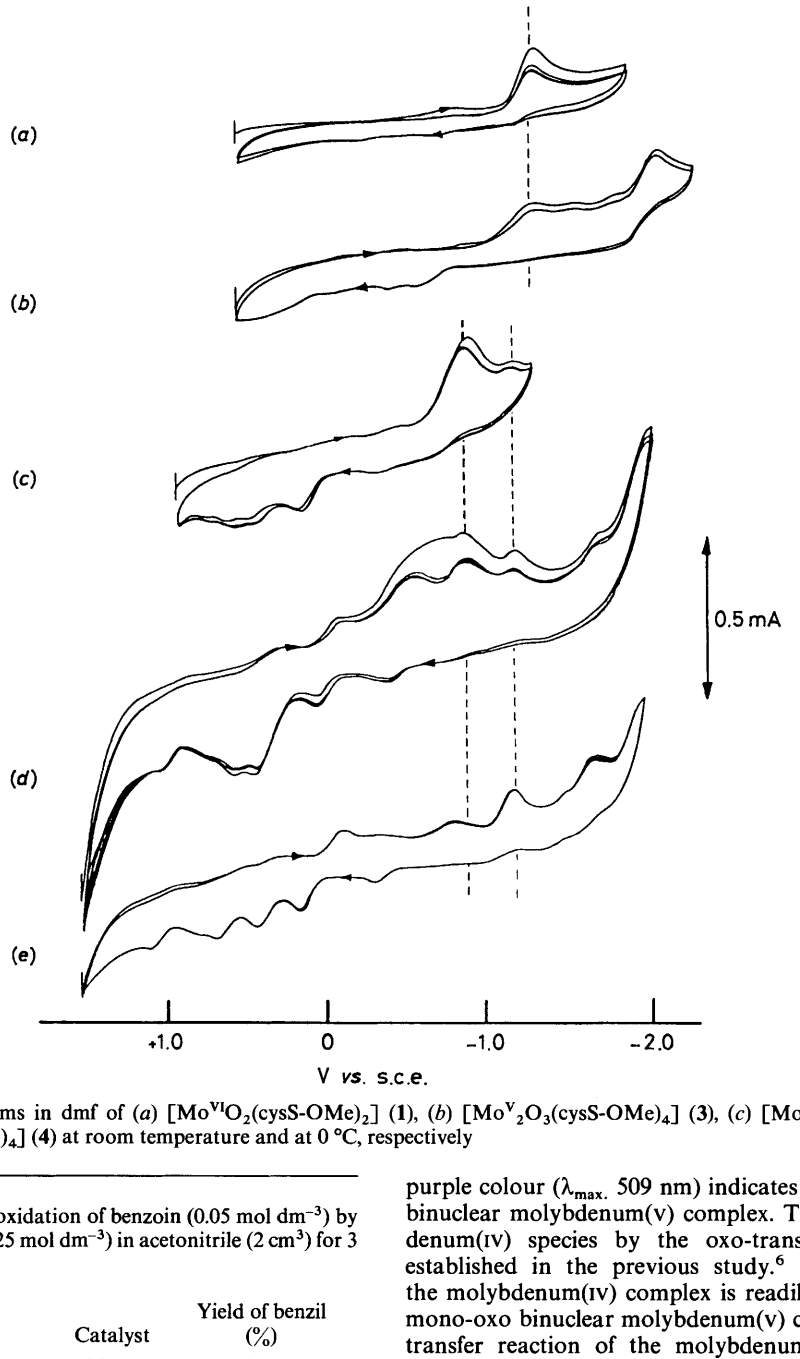


Figure 3. Cyclic voltammograms in dmf of (*a*) $[Mo^{VI}O_2(cysS\text{-}OMe)_2]$ (1), (*b*) $[Mo^{V}{}_2O_3(cysS\text{-}OMe)_4]$ (3), (*c*) $[Mo^{VI}O_2(S_2CNEt_2)_2]$ (2), and (*d*) and (*e*) $[Mo^{V}{}_2O_3(S_2CNEt_2)_4]$ (4) at room temperature and at 0 °C, respectively

Table 4. Air or amine *N*-oxide oxidation of benzoin (0.05 mol dm^{-3}) by $[MoO_2(cysS\text{-}OMe)_2]$ (1) (0.0025 mol dm^{-3}) in acetonitrile (2 cm^3) for 3 h at 30 °C

Oxidant	Catalyst	Yield of benzil (%)
Trimethylamine *N*-oxide	None	6 ± 1
(0.05 mol dm^{-3})	1	88 ± 5
Pyridine *N*-oxide	None	0
(0.05 mol dm^{-3})	1	21 ± 2
2,2′-Bipyridyl *N*-oxide	None	0
(0.05 mol dm^{-3})	1	9 ± 2
Air	None	0
(>0.05 mol dm^{-3})	1	21 ± 3

$[Mo^{IV}O(L)(dmf)]$ [L = pyridine-2,6-bis(1′,1′-diphenylethanethiolate)] has been reported.[26]

Catalytic Oxidation of p-*Substituted Benzoin*.—A reaction mixture containing benzoin and $[MoO_2(cysS\text{-}OMe)_2]$ gave a yellow solution during the catalytic air oxidation, while a purple solution results on catalysis by $[MoO_2(S_2CNEt_2)_2]$.[6] The purple colour ($\lambda_{max.}$ 509 nm) indicates the presence of a μ-oxo binuclear molybdenum(V) complex. The formation of molybdenum(IV) species by the oxo-transfer reaction has been established in the previous study.[6] At high concentration, the molybdenum(IV) complex is readily converted into the μ-mono-oxo binuclear molybdenum(V) complex. When the oxo-transfer reaction of the molybdenum(VI) complex is faster than the reoxidation step, the solution develops a purple colour due to the formation of a μ-mono-oxo binuclear molybdenum(V) complex. The oxidation and the reoxidation rates were controlled using various *p*-substituted benzoins and various oxidants, respectively. There is no oxidation of *p*-substituted benzoin in the absence of the molybdenum(VI) complex.

The presence of a disproportionation equilibrium between molybdenum(VI), μ-oxo binuclear molybdenum(V), and molybdenum(IV) species hinders any attempt to obtain reliable oxidation rates, since the value of the corresponding equilibrium constant varies with temperature and concentration.[10] This disproportionation has been studied in detail for $[Mo^{V}{}_2O_3(S_2CNEt_2)_4]$ in benzene solutions.[10] In the case of the catalytic oxidation, the rate-determining step of the molybdenum(VI) oxidation probably is the apparent hydride release that is associated with the proton and electron elimination from

Table 5. Catalytic pyridine *N*-oxide (0.025 mol dm^{-3}) oxidation rates of *p*-substituted benzoins (0.025 mol dm^{-3}) in the presence of [MoO_2(cysS-OMe)$_2$] (0.001 25 mol dm^{-3}) in dmf at 30 °C

	$10^6k_{obs.}/s^{-1}$
4,4'-Dichlorobenzoin	12 ± 2
Benzoin	46 ± 5
4,4'-Dimethoxybenzoin	96 ± 9

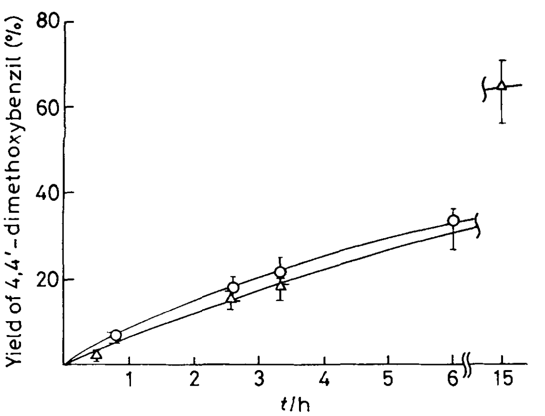


Figure 4. Time *vs.* conversion curves of the catalytic air (○) or pyridine *N*-oxide (△) oxidation of 4,4'-dimethoxybenzoin (5 × 10^{-2} mol dm^{-3}) by [MoO_2(cysS-OMe)$_2$] (**1**) (2.5 × 10^{-3} mol dm^{-3}) in dmf at 30 °C

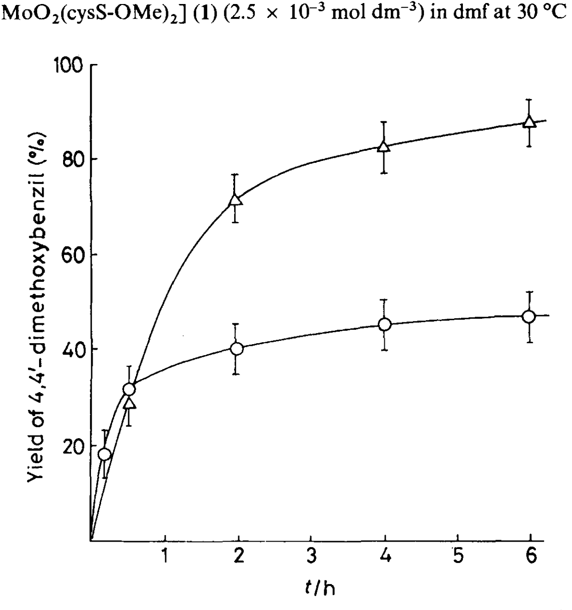


Figure 5. Time *vs.* conversion curves of the catalytic air (○) or pyridine *N*-oxide (△) oxidation of 4,4'-dimethoxybenzoin (5 × 10^{-2} mol dm^{-3}) by [$MoO_2(S_2CNEt_2)_2$] (**2**) (2.5 × 10^{-3} mol dm^{-3}) in dmf at 30 °C

the C–H group of benzoin. The high proton affinity of 4,4'-dimethoxybenzoin as a solvent increases the proton release rate in the competition between proton and electron releases. It is likely that, in the catalytic system, the presence of a large amount of electron-donating solvent facilitates the proton release and makes the electron release the rate-determining step. The value of the stoicheiometric oxidation rate [(1.1 ± 1) × 10^{-5} s^{-1} for complex (**1**) and benzoin] is much smaller than that of the reoxidation rate [(2.4 ± 0.1) × 10^{-3} s^{-1} for (**3**) by pyridine *N*-oxide] as described later. Therefore, the oxidation of benzoin is clearly a rate-determining step in the catalytic oxidation. Thus, the proton abstraction competes with the successively occurring electron release from the alcoholic C–O group. Protonation of a moiety Mo=O with alcoholic OH has previously been examined by ^{1}H n.m.r. measurements of the peak due to the OH proton of diphenylmethanol in the presence of [MoO_2(cysS-OEt)$_2$], revealing a rapid exchange.[6]

Catalytic Air and Pyridine N-*Oxide Oxidation of* 4,4'-*Dimethoxybenzoin.*—Figure 4 shows the formation of 4,4'-dimethoxybenzil with time in the catalytic oxidation by [MoO_2(cysS-OMe)$_2$]. The oxidation using pyridine *N*-oxide in the presence of complex (**1**) exhibits the same tendency as the oxidation by air. The results indicate that the reoxidation rates of Mo^{IV} to Mo^{VI} by the two oxidants are almost the same under these conditions. Furthermore, almost no deactivation was observed during the catalytic oxidation by (**1**). For example, the yield of 4,4'-dimethoxybenzil with air or pyridine *N*-oxide in the presence of (**1**) attains 1 760% catalyst yield (turnover number 18) after 3 d.

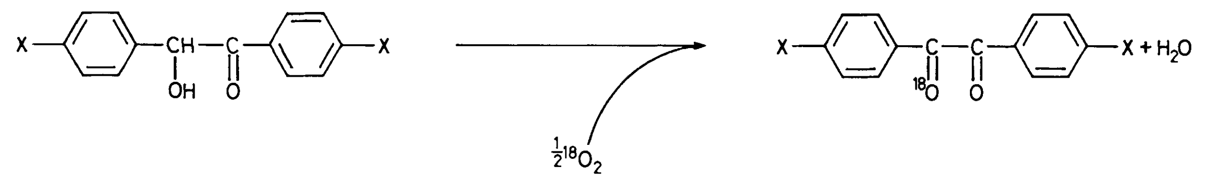
Table 5 shows the substituent effect on the corresponding yield of benzil in the catalytic oxidation. The observed rates of the catalytic reaction indicate a trend MeO > H > Cl which is similar to that reported for the oxidation by osmium tetraoxide under alkaline conditions.[14] The difference from the tendency in the stoicheiometric reaction suggests the presence of two pathways for the benzoin oxidation.

Figure 5 shows the rate of formation of 4,4'-dimethoxybenzil in air and pyridine *N*-oxide oxidation of 4,4'-dimethoxybenzoin by complex (**2**). At the initial stage the observed rate in the presence of air is higher than that in the presence of pyridine *N*-oxide. The presence of air results in deactivation of the catalyst after *ca.* 30 min in the catalytic cycle as previously described for the air oxidation of benzoin.[6] The higher rates by dioxygen than by pyridine *N*-oxide at the initial stage show the ease of oxo transfer by (**2**). Similar behaviour was found in the air oxidation of 4,4'-dichlorobenzoin by (**2**). The difference in the catalytic cycles between complexes (**1**) and (**2**) is due to the one-electron transfer reaction of (**2**) with dioxygen as demonstrated by the air oxidation of [$Mo^{V}_2O_3(S_2CNEt_2)_2$]. The e.s.r. results indicate that the deactivation of the catalyst in the presence of (**2**) is caused by the formation of a mononuclear molybdenum(v) species during the oxidation cycle. This species probably dimerizes slowly to a more inert di-μ-oxo binuclear molybdenum(v) species.

Incorporation of ^{18}O *from* ^{18}O-*Enriched Dioxygen to Benzil.*—The catalytic oxidation of benzoin by 50% ^{18}O-enriched dioxygen in the presence of [$Mo^{VI}O_2$(cysS-OMe)$_2$] was continued up to 5 000% catalytic yield of benzil. Water and benzil isolated separately were analysed by mass spectroscopy which, unexpectedly, showed the absence of ^{18}O atom in water; the formation of water was also confirmed by ^{1}H n.m.r. spectroscopy.

Incorporation of an ^{18}O atom from ^{18}O-enriched dioxygen into benzil was established by high-resolution mass spectroscopic analysis. Two main peaks were observed at *m*/*z* 212.071 ± 0.001 and 107.039 ± 0.001. These correspond to ^{18}O-enriched benzil, $^{12}C_{14}H_{10}{}^{16}O^{18}O$ (calculated *m*/*z* 212.0723) and one of the fragments, $^{12}C_7H_5{}^{18}O$ (calculated *m*/*z* 107.0383). The oxygen-18 content in benzil was determined from the peak intensities of $C_{14}H_{10}{}^{16}O^{18}$ and $C_{14}H_{10}{}^{16}O_2$. The benzil obtained in the oxidation contained 20 ± 2% of ^{18}O. Since 50% ^{18}O-enriched dioxygen was employed, almost all the dioxygen was incorporated into the benzil, but not in water (Scheme 2). This result suggests the possible involvement of peroxide co-ordinating in a side-on manner to Mo^{VI} or in a bridging mode between two molybdenum(vi) ions.

Our preliminary results obtained using $^{18}O_2$ and *p*-substituted benzoins suggest that two types of benzoin oxidations are involved. One is an oxo-transfer oxidation by



Scheme 2.

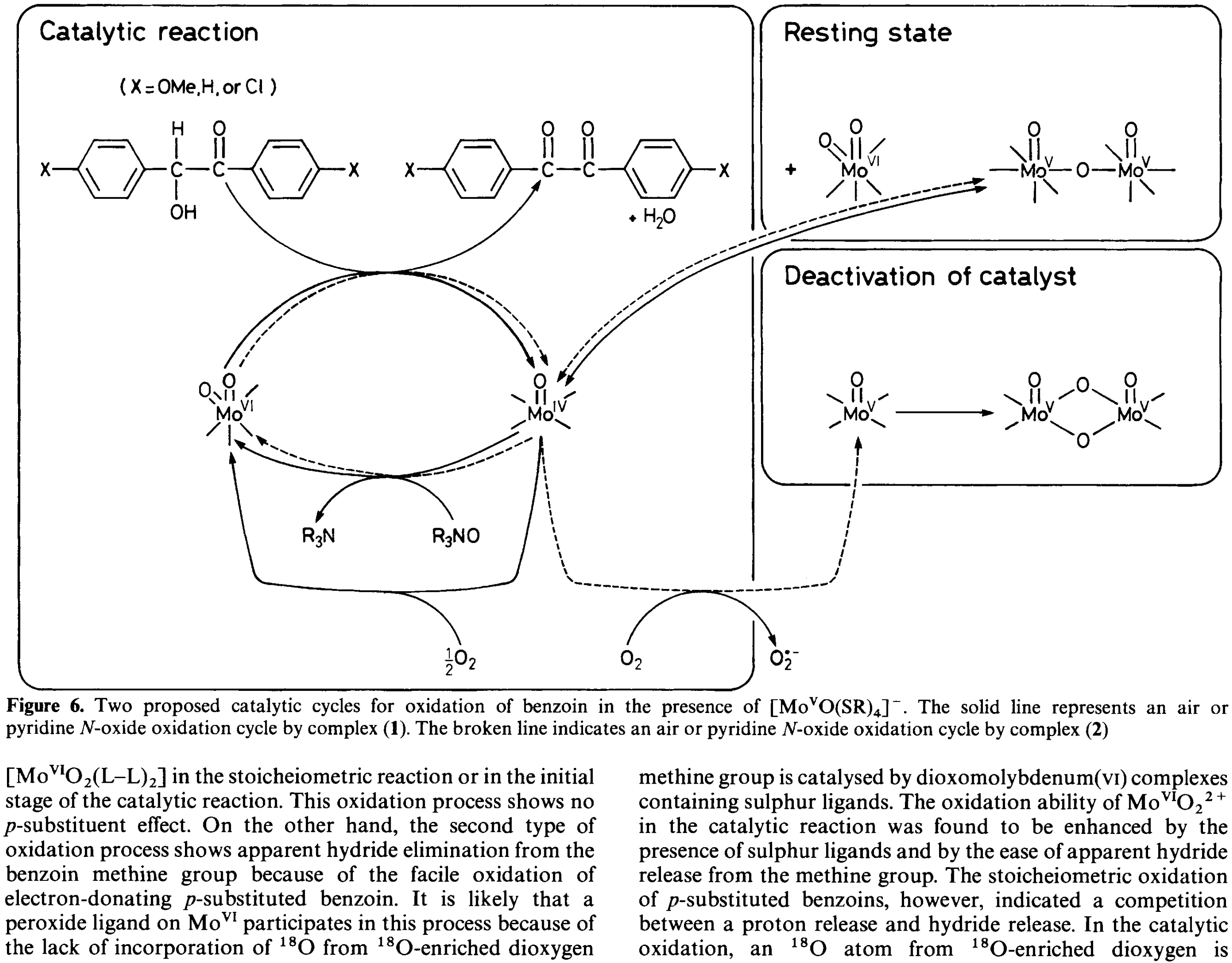


Figure 6. Two proposed catalytic cycles for oxidation of benzoin in the presence of $[Mo^{V}O(SR)_4]^-$. The solid line represents an air or pyridine *N*-oxide oxidation cycle by complex (**1**). The broken line indicates an air or pyridine *N*-oxide oxidation cycle by complex (**2**)

$[Mo^{VI}O_2(L\text{–}L)_2]$ in the stoicheiometric reaction or in the initial stage of the catalytic reaction. This oxidation process shows no *p*-substituent effect. On the other hand, the second type of oxidation process shows apparent hydride elimination from the benzoin methine group because of the facile oxidation of electron-donating *p*-substituted benzoin. It is likely that a peroxide ligand on Mo^{VI} participates in this process because of the lack of incorporation of ^{18}O from ^{18}O-enriched dioxygen into the water formed. In the case of dioxygen reoxidation of the reduced molybdenum(IV) species, σ-type co-ordination of dioxygen to Mo^{IV} is presumed during the catalytic oxidation. It is likely that two molecules of a molybdenum(IV) species are involved in the formation of a μ-peroxo species such as Mo–O–O–Mo as an intermediate. The cleavage of the μ-peroxo group subsequently occurs yielding species involving $Mo(=O)_2$ or peroxo molybdenum(VI) moieties with net two-electron transfer. Formation of such a μ-peroxo complex is well documented, *e.g.* for μ-peroxo binuclear cobalt complexes.[27] The involvement of two tris(ethylenediamine)ruthenium(II) ions in the reaction with dioxygen has also been reported based on a kinetic study.[28] Recently, a new dioxygen complex, $[Cu_2(O_2)L]^{2+}$ [L = tris(2-pyridylmethyl)amine] has been isolated from a reaction between $[CuL(RCN)]^+$ and dioxygen.[29]

Conclusions

A new catalytic air or amine *N*-oxide oxidation of the alcoholic methine group is catalysed by dioxomolybdenum(VI) complexes containing sulphur ligands. The oxidation ability of $Mo^{VI}O_2^{2+}$ in the catalytic reaction was found to be enhanced by the presence of sulphur ligands and by the ease of apparent hydride release from the methine group. The stoicheiometric oxidation of *p*-substituted benzoins, however, indicated a competition between a proton release and hydride release. In the catalytic oxidation, an ^{18}O atom from ^{18}O-enriched dioxygen is incorporated into the benzil carbonyl group, but not into water. Deactivation of the catalytic air oxidation of benzoin in the presence of $[MoO_2(S_2CNEt_2)_2]$ is caused by a one-electron transfer from the reduced mono-oxomolybdenum(IV) species to dioxygen. The chelating structure of the sulphur ligands is thus highly important for this type of air oxidation (Figure 6).

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