# 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 <sup>18</sup>O atom from [<sup>18</sup>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  $[Mo^vO(S_2CNEt_2)_2]$  formed by a one-electron-transfer reaction from  $[Mo^{1v}O(S_2CNEt_2)_2]$  to dioxygen.

Dioxomolybdenum complexes have been utilized as catalysts for molybdo-oxidase model oxo-transfer reactions<sup>1</sup> such as the stoicheiometric oxidation of triphenylphosphine by  $[MoO_2(S_2CNR_2)_2]^2$  or  $[MoO_2(cysS-OR)_2]$  (cysS-OR = Sdeprotonated L-cysteinate alkyl ester, R = Me, Et, or  $Pr^{i}$ ).<sup>3,4</sup> Recently, the catalytic oxidation of thiol by  $[MoO_2L]$  [L = pyridine-2,6-bis(1',1'-diphenylethanethiolate)] has been reported.<sup>5</sup> We have reported the catalytic air oxidation of benzoin in the presence of [MoO<sub>2</sub>(cysS-OMe)<sub>2</sub>] and [MoO<sub>2</sub>-(cysS-NHC<sub>10</sub>H<sub>21</sub>)<sub>2</sub>] as a model reaction for C-H activation similar to the biological oxidations of xanthine (3,7-dihydro-1H-purine-2,6-dione) or aldehyde by the corresponding oxidases.<sup>6</sup> These enzymes are known to utilize water as a source of oxygen atoms and dioxygen can be used as an oxidant.<sup>7</sup> 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.<sup>6</sup> 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.<sup>8</sup> 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 <sup>18</sup>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),<sup>9</sup>  $[MoO_2(S_2CNEt_2)_2]$  (2),<sup>10</sup>  $[Mo_2O_3(cysS-OMe)_4]$  (3),<sup>11</sup>  $[Mo_2O_3(S_2CNEt_2)_4]$  (4),<sup>10</sup> and 2,2'-bipyridine

*N*-oxide<sup>12</sup> were synthesized by literature procedures. 50%<sup>18</sup>O-Enriched dioxygen was obtained from Nakarai Chemical Co.

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4,4'-Dichlorobenzoin.—This compound was prepared by a modification of the literature method.<sup>13</sup> To a solution of *p*-chlorobenzaldehyde (5.6 g, 39.8 mmol) in methanol (10 cm<sup>3</sup>) was added an aqueous solution (10 cm<sup>3</sup>) 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<sup>3</sup>). The ether solution was washed with an aqueous solution (20%) of NaHSO<sub>3</sub> 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<sub>14</sub>H<sub>10</sub>Cl<sub>2</sub>O<sub>2</sub>: C, 59.40; H, 3.60%).

Catalytic Oxidation of p-Substituted Benzoin.—A dmf solution  $(1 \text{ cm}^3)$  of benzoin (0.05 mmol), 4,4'-dimethoxybenzoin, or 4,4'-dichlorobenzoin was added to a dmf solution  $(1 \text{ cm}^3)$  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  $(0.5 \text{ cm}^3)$  of amine N-oxide (0.05 mmol) was added to a dmf solution  $(0.5 \text{ cm}^3)$  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.<sup>6</sup> 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 <sup>18</sup>O-Enriched Dioxygen.— To a dmf solution (20 cm<sup>3</sup>) of benzoin (14 mmol) and  $[MoO_2-(cysS-OMe)_2]$  (0.2 mmol) was introduced 50% <sup>18</sup>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<sup>3</sup> 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<sub>2</sub>CNEt<sub>2</sub>



Figure 1. Stoicheiometric oxidation of 4,4'-dimethoxybenzoin  $(2.5 \times 10^{-2} \text{ mol dm}^{-3})$  by (a) [MoO<sub>2</sub>(cysS-OMe)<sub>2</sub>] (1)  $(2.5 \times 10^{-3} \text{ mol dm}^{-3})$  or (b) [MoO<sub>2</sub>(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>] (2)  $(2.5 \times 10^{-3} \text{ mol dm}^{-3})$  in dmf at 25 °C

Stoicheiometric Reaction of  $[MoO_2(L-L)_2]$  with p-Substituted Benzoin.—A dmf solution  $(2 \text{ cm}^3, 8.2 \times 10^{-2} \text{ mol} \text{ dm}^{-3})$  containing either  $[MoO_2(S_2CNEt_2)_2]$  (2) or  $[MoO_2(cysS-OMe)_2]$  (1) was mixed with a dmf solution (2 cm<sup>3</sup>, 8.2 × 10<sup>-2</sup> mol dm<sup>-3</sup>) 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<sub>18</sub> column (length 30 cm, inside diameter 0.39 cm).

Stoicheiometric dioxygen or pyridine N-oxide (0.0025 mol dm<sup>-3</sup>) oxidation of  $\mu$ -oxo binuclear molybdenum(v) complexes (0.0025 mol dm<sup>-3</sup>) in acetonitrile at 25 °C was monitored by visible spectrophotometry. The yield of molybdenum(v1) 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  $\mu$ -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  $[MoO_2(cysS-OMe)_2]$  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:  $v_{max.}(Mo-O-Mo)$  756vs;  $v_{max.}(Mo=O)$  945 (sh) cm<sup>-1</sup> (solid).

Air and Pyridine N-Oxide Oxidations of  $[Mo^{V}_{2}O_{3}(L-L)_{4}]$ .— An acetonitrile solution (4 cm<sup>3</sup>) of  $[Mo^{V}_{2}O_{3}(L-L)_{4}]$  (L-L = cysS-OMe or S<sub>2</sub>CNEt<sub>2</sub>) (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  $(2 \text{ cm}^3)$  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<sup>-3</sup> in Mo<sup>VI</sup> and a solution of tetra-n-butylammonium perchlorate (0.1 mol dm<sup>-3</sup>) was employed as supporting electrolyte. The e.s.r. spectrum of a reaction mixture of  $[Mo_2O_3(cysS-OMe)_4]$  (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<sup>3</sup>) 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<sub>2</sub>(cysS-OMe)<sub>2</sub>] with p-Substituted Benzoin.-The oxidizing ability of two different types of  $[Mo^{VI}O_2(L-L)_2]$  complexes,  $[MoO_2(cysS-OMe)_2]$  (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<sup>IV</sup>O(cysS-OMe)<sub>2</sub>]' although isolation of [Mo<sup>IV</sup>O(cysS-OMe)<sub>2</sub>] 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  $[Mo_2^VO_3(cysS-OMe)_4]$  which has a visible or circular dichroism (c.d.) extremum at 510 nm as described previously.<sup>6</sup> The binuclear molybdenum(v) complex has also been found on reduction of (1) with triphenylphosphine.<sup>4</sup> 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.<sup>6</sup>

Table 1 lists the observed rates  $(k_{obs.})$  of the stoicheiometric reaction between  $[MoO_2(cysS-OMe)_2]$  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<sup>-3</sup>) by molybdenum(v1) complexes (0.0082 mol dm<sup>-3</sup>) in dmf at 30 °C

	$10^6 k_{\text{obs.}} / \text{s}^{-1}$		
	$[MoO_2(cysS-OMe)_2]$	[MoO <sub>2</sub> (S <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub> ]	
4,4'-Dichlorobenzoin	$12 \pm 2$	$150 \pm 14$	
Benzoin	$11 \pm 1$	$190 \pm 17$	
4,4'-Dimethoxy- benzoin	$12 \pm 2$	$120 \pm 11$	



Figure 2. Variation of the visible spectra with time in the stoicheiometric reaction between  $\mu$ -oxo binuclear molybdenum(v) complex [(a) (3) or (b) (4)] (0.0082 mol dm<sup>-3</sup>) and air (dioxygen, 0.0082 mol dm<sup>-3</sup>) 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<sup>14</sup> or nickel(II) acetate.<sup>15</sup> Hammond and Wu<sup>15</sup> reported that the relative rates of the stoicheiometric oxidation 389

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<sub>2</sub>CMe)<sub>2</sub>/O<sub>2</sub> products. On the contrary, Misra *et al.*<sup>14</sup> 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<sup>-</sup> in the rate-determining step.

Stoicheiometric Reoxidation Reaction from  $[Mo^V_2O_3(L-L)_4]$ to  $[Mo^{VI}O_2(L-L)_2]$  by Air or Pyridine N-Oxide.—Although the synthesis of  $[Mo^{IV}O(S_2CNEt_2)_2]$  has been established,<sup>3</sup> there is no report for the synthesis of pure  $[Mo^{IV}O(cysS-OMe)_2]$ because of its thermal instability.  $\mu$ -Oxo binuclear molybdenum(v) complexes,  $[Mo^V_2O_3(cysS-OMe)_4]$  (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.<sup>2</sup>

$$[Mo^{V}_{2}O_{3}(L-L)_{4}] \stackrel{K}{\longleftrightarrow} [Mo^{IV}O(L-L)_{2}] + [Mo^{VI}O_{2}(L-L)_{2}]$$
(1)

The ease of oxidation of the molybdenum(IV) complex can be estimated from the oxidation with the corresponding  $\mu$ -oxo binuclear molybdenum(V) complexes. Oxygen-atom transfer from Me<sub>3</sub>CONO<sub>2</sub> or amine *N*-oxide to [Mo<sup>IV</sup>O(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>] has been confirmed.<sup>16</sup> The equilibrium constant (*K*) for the disproportionation of (4) in equation (1) has been reported to be  $2.0 \times 10^{-3}$  dm<sup>3</sup> mol<sup>-1</sup> in dichloromethane.<sup>17</sup> 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<sup>-1</sup> 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(v1) 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  $(1.5 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$  in the presence of pyridine *N*-oxide. Reliable data were not obtained for air oxidation of (4) because

Complex	Oxidant	Reaction time (min) <sup>a</sup>	Yield (%) <sup>b</sup> of (1) or (2)
$[Mo_2O_3(cysS-OMe)_4]$	Pyridine N-oxide	50	76
	Air	30	56
	Excess of dioxygen	30	40
[Mo <sub>2</sub> O <sub>3</sub> (S <sub>2</sub> CNEt <sub>2</sub> ) <sub>4</sub> ]	Pyridine N-oxide	10	56
	Air	75	55
	Excess of dioxygen	12	10

<sup>a</sup> The reaction times refer to the complete disappearance of absorption maxima at 500—510 nm due to  $\mu$ -oxo binuclear molybdenum(v) and mono-oxomolybdenum(v) complexes. <sup>b</sup> The yields were obtained by monitoring the absorption maxima at 350 nm for [Mo<sub>2</sub>O<sub>3</sub>(cysS-OMe)<sub>4</sub>] and at 374 nm for [Mo<sub>2</sub>O<sub>3</sub>(S<sub>2</sub>CNEt<sub>2</sub>)<sub>4</sub>].

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

Pyridine	Time (h)	Yield of benzil (%)
None	0.5	$8 \pm 1$
	2	$26 \pm 2$
0.0025 mol dm <sup>-3</sup>	0.5	9 <u>+</u> 1
	2	$19 \pm 2$
0.025 mol dm <sup>-3</sup>	0.5	$11 \pm 1$
	2	$23 \pm 3$

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,  $[Mo^VO(S_2CNEt_2)_2]^+$ , formed by an outer-sphere one-electron transfer to dioxygen as shown in equation (2). The e.s.r.

$$[Mo^{IV}O(S_2CNEt_2)_2] + O_2 \longrightarrow [Mo^{V}O(S_2CNEt_2)_2]^+ + O_2^{\bullet^-}$$
(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  $g_{av.} = 1.977$  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  $[Mo^{IV}O(SCH_2CH_2S)_2]^{2^-.18}$  No definite conversion from mononuclear molybdenum(v) to dioxo molybdenum(vi) complexes by air has been detected. The mononuclear complex  $[Mo^{V}O(SPh)_4]^-$  is known to give  $[Mo^{V}_2O_2(SPh)_6(MeCN)]$ upon electrochemical oxidation in acetonitrile.<sup>19</sup> Spontaneous decomposition of  $[Mo^{V}O(L-L)_2]^+$  (L-L = aminocyclopent-1ene-1-carbodithioate) to a seven-co-ordinate complex,  $[Mo^{V}O(L-L)_3]$ , has been reported.<sup>20</sup> A similar dithiocarbamato complex,  $[Mo^{V}O(S_2CNEt_2)_2]^+$ , was found to decompose slowly to give  $[Mo^{V}_2O_4(S_2CNEt_2)_2]$  as an inert complex.<sup>10</sup> Thus, the difficulties experienced in forming a dioxomolybdenum(VI) complex from the corresponding mono-nuclear 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  $E_{pc} =$ -1.25 V vs. saturated calomel electrode (s.c.e.) is assignable to the  $Mo^{VI}O_2^{2+}-Mo^{V}O_2^{+}$  couple followed by an irreversible reduction to a  $Mo^{IV}O^{2+}$  species. The redox behaviour of complex (2) was re-examined and compared to those of the  $\mu$ mono-oxo binuclear molybdenum(v) complexes. Complex (2) exhibits a reduction peak at  $E_{pc} = -0.87 \text{ V} vs. \text{ s.c.e.} (\text{Mo}^{VI}\text{O}_2^2)$  $-Mo^{V}O_{2}^{+})$  with the first scan similar to that reported by DeHayes *et al.*<sup>21</sup> The Mo<sup>V</sup>O<sub>2</sub><sup>+</sup> species thus formed is converted rapidly into a  $Mo^{IV}O_2^{2+}$  species. Therefore, the lowering of these  $Mo^{VI}O_2^{2+}-Mo^{V}O_2^{+}$  redox potentials reflects the ease of the oxo- transfer reactions with benzoin. A new reduction peak due to  $Mo^{V}O^{3+}-Mo^{IV}O^{2+}$  probably appears at -0.85 V vs. s.c.e. which is overlapped by the reduction peak of  $Mo^{VI}O_2^{2+}$  $-Mo^{V}O_{2}^{+}$ . An irreversible oxidation peak for (2) was observed at +0.15 V vs. s.c.e. due to the redox couple  $Mo^{VI}O^{4+}-Mo^{V}O^{3+}$  when the scanning was carried out over -1.30 v vs. s.c.e. This is followed by formation of Mo<sup>IV</sup>O<sup>2+</sup> species with oxo transfer. Complex (3) exhibits a reduction peak at  $E_{pc} = -1.30$  V vs. s.c.e. which corresponds to Mo<sup>V1</sup>O<sub>2</sub><sup>2+</sup> -Mo<sup>V</sup>O<sub>2</sub><sup>+</sup> of (1) formed from (3) by the disproportionation reaction (1). A dmf solution of (4) at 27 °C showed a reduction peak at  $E_{pc} = -0.87$  V due to Mo<sup>VI</sup>O<sub>2</sub><sup>2+</sup>-Mo<sup>V</sup>O<sub>2</sub><sup>+</sup> 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  $Mo_{2}^{V}O_{3}^{4+}-Mo^{V}Mo^{IV}O_{3}^{3+}$ . No such peaks could be recognized for (3).

Since the redox potential for  $O_2-O_2^-$  had been reported as -0.6 V vs. s.c.e. in dmf,<sup>22</sup> both reduced Mo<sup>IV</sup>O<sup>2+</sup> 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  $[MoO_2(cysS-OMe)_2]$ .—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(v1) complex. In basic solutions, e.g. in the presence of formylflavin, air oxidation of benzoin is accelerated.<sup>23</sup> Actually, in the case of molybdenum(v1) 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 Noxide or 2,2'-bipyridyl N-oxide the solution exhibits a purple colour which is ascribed to the presence of [Mo<sub>2</sub>O<sub>3</sub>(cysS-OMe)<sub>4</sub>]. In this catalytic system, the observed oxidation rate is limited by the reoxidation from Mo<sup>IV</sup> to Mo<sup>VI</sup>. 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.<sup>24</sup> Recently, Escherichia coli triethylamine N-oxide reductase has been established to be a molybdoenzyme.<sup>25</sup> Generally, amine Noxides 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)  $[Mo^{VI}O_2(cysS-OMe)_2]$  (1), (b)  $[Mo^{V_2}O_3(cysS-OMe)_4]$  (3), (c)  $[Mo^{VI}O_2(S_2CNEt_2)_2]$  (2), and (d) and (e)  $[Mo^{V_2}O_3(S_2CNEt_2)_4]$  (4) at room temperature and at 0 °C, respectively

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

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

 $[Mo^{IV}O(L)(dmf)]$  [L = pyridine-2,6-bis(1',1'-diphenylethane-thiolate)] has been reported.<sup>26</sup>

Catalytic Oxidation of p-Substituted Benzoin.—A reaction mixture containing benzoin and  $[MoO_2(cysS-OMe)_2]$  gave a yellow solution during the catalytic air oxidation, while a purple solution results on catalysis by  $[MoO_2(S_2CNEt_2)_2]$ .<sup>6</sup> The purple colour ( $\lambda_{max}$ . 509 nm) indicates the presence of a  $\mu$ -oxo binuclear molybdenum(v) complex. The formation of molybdenum(iv) species by the oxo-transfer reaction has been established in the previous study.<sup>6</sup> At high concentration, the molybdenum(iv) complex is readily converted into the  $\mu$ -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  $\mu$ -mono-oxo binuclear molybdenum(v) complex is faster than the reoxidation step, the solution 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),  $\mu$ -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.<sup>10</sup> This disproportionation has been studied in detail for [Mo<sup>V</sup><sub>2</sub>O<sub>3</sub>(S<sub>2</sub>CNEt<sub>2</sub>)<sub>4</sub>] in benzene solutions.<sup>10</sup> 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<sup>-3</sup>) oxidation rates of *p*-substituted benzoins (0.025 mol dm<sup>-3</sup>) in the presence of  $[MoO_2(cysS-OMe)_2]$  (0.001 25 mol dm<sup>-3</sup>) in dmf at 30 °C

	$10^6 k_{\rm obs.}/{\rm s}^{-1}$
4,4'-Dichlorobenzoin	$12 \pm 2$
Benzoin	46 <u>+</u> 5
4,4'-Dimethoxybenzoin	96 ± 9



**Figure 4.** Time vs. conversion curves of the catalytic air ( $\bigcirc$ ) or pyridine N-oxide ( $\triangle$ ) oxidation of 4,4'-dimethoxybenzoin (5 × 10<sup>-2</sup> mol dm<sup>-3</sup>) by [MoO<sub>2</sub>(cysS-OMe)<sub>2</sub>] (1) (2.5 × 10<sup>-3</sup> mol dm<sup>-3</sup>) in dmf at 30 °C



Figure 5. Time vs. conversion curves of the catalytic air ( $\bigcirc$ ) or pyridine N-oxide ( $\triangle$ ) oxidation of 4,4'-dimethoxybenzoin (5 × 10<sup>-2</sup> mol dm<sup>-3</sup>) by [MoO<sub>2</sub>(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>] (2) (2.5 × 10<sup>-3</sup> mol dm<sup>-3</sup>) 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  $[(1.1 \pm 1) \times 10^{-5} \text{ s}^{-1}$  for complex (1) and benzoin] is much smaller than that of the reoxidation rate  $[(2.4 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$ 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 <sup>1</sup>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.<sup>6</sup>

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<sup>IV</sup> to Mo<sup>VI</sup> 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.<sup>14</sup> 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.<sup>6</sup> 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  $[Mo_2^VO_3(S_2CNEt_2)_2]$ . 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 <sup>18</sup>O from <sup>18</sup>O-Enriched Dioxygen to Benzil.—The catalytic oxidation of benzoin by  $50\%^{-18}$ Oenriched dioxygen in the presence of [Mo<sup>VI</sup>O<sub>2</sub>(cysS-OMe)<sub>2</sub>] 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 <sup>18</sup>O atom in water; the formation of water was also confirmed by <sup>1</sup>H n.m.r. spectroscopy.

Incorporation of an <sup>18</sup>O atom from <sup>18</sup>O-enriched dioxygen into benzil was established by high-resolution mass spectroscopic analysis. Two main peaks were observed at m/z212.071  $\pm$  0.001 and 107.039  $\pm$  0.001. These correspond to <sup>18</sup>O-enriched benzil, <sup>12</sup>C<sub>14</sub>H<sub>10</sub><sup>16</sup>O<sup>18</sup>O (calculated m/z212.0723) and one of the fragments, <sup>12</sup>C<sub>7</sub>H<sub>5</sub><sup>18</sup>O (calculated m/z107.0383). The oxygen-18 content in benzil was determined from the peak intensities of C<sub>14</sub>H<sub>10</sub><sup>16</sup>O<sup>18</sup> and C<sub>14</sub>H<sub>10</sub><sup>16</sup>O<sub>2</sub>. The benzil obtained in the oxidation contained 20  $\pm$  2% of <sup>18</sup>O. Since 50% <sup>18</sup>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<sup>VI</sup> 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



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)

**O**<sub>2</sub>

 $[Mo^{VI}O_2(L-L)_2]$  in the stoicheometric 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<sup>VI</sup> participates in this process because of the lack of incorporation of <sup>18</sup>O from <sup>18</sup>O-enriched dioxygen into the water formed. In the case of dioxygen reoxidation of the reduced molybdenum(IV) species,  $\sigma$ -type co-ordination of dioxygen to Mo<sup>IV</sup> 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.<sup>27</sup> The involvement of two tris(ethylenediamine)ruthenium(II) ions in the reaction with dioxygen has also been reported based on a kinetic study.<sup>28</sup> 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)]<sup>+</sup> and dioxygen.29

R<sub>3</sub>N

R<sub>3</sub>NO

 $\frac{1}{2}O_{2}$ 

# 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  $M0^{Vi}O_2^{2+}$ 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 <sup>18</sup>O atom from <sup>18</sup>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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