Catalytic Air Oxidation of Benzoin in the Presence of Dioxomolybdenum(VI) Complexes with Sulphur Chelate Ligands

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Catalytic air oxidation of benzoin to benzil in *N,N*-dimethylformamide (dmf) occurred in the presence of [MoO_2(cysS-OR)$_2$] [cysS-OR = S-deprotonated cysteine alkyl ester; R = Me (**1**) or Et (**2**)], [$MoO_2(S_2CNEt_2)_2$] (**3**) or [MoO_2(cysS-NHC$_{10}$H$_{21}$)$_2$] (**4**) (cysS-NCH$_{10}$H$_{21}$ = S-deprotonated cysteine n-decylamide), [Mo_2O_3(cysS-OMe)$_4$] (**5**), or [$Mo_2O_3(S_2CNEt_2)_4$] (**6**) with conversions of 1 500, 1 200, 1 000, 1 800, 1 300, and 900% ([Mo]/[benzoin] = 1/20, 20 h, 30 °C), respectively. The initial first-order rate constants ranged from 0.012 to 0.048 s^{-1} (per mol of catalyst). Slow deactivation of the catalysis by complexes (**1**)—(**3**) was observed due to the formation of di-μ-oxo binuclear molybdenum(V) complexes from μ-oxo binuclear molybdenum(V) complexes. The oxidation in the presence of (**4**) proceeds without deactivation. In the stoicheiometric reduction of complex (**2**) with benzoin the absence of any e.s.r. signal due to a mononuclear molybdenum(V) species indicates that a molybdenum(IV) species formed by a two-electron transfer process is aerobically converted into a μ-oxo binuclear molybdenum(V) complex. An ^{1}H n.m.r. study showed that the initial proton transfer from the benzoin OH group to Mo=O is followed by elimination of a proton from the benzoin methine group to form a carbonyl group.

The air oxidation of benzoin to benzil has been shown to occur in the presence of compounds such as $Cu(OCOCH_3)_2$,[1] NiO_2,[2] or $Yb(NO_3)_3$.[3] Under alkaline conditions, flavin derivatives are also effective for this oxidation in which the enediol form PhC(OH)=C(OH)Ph was proposed as an intermediate.[4]

The catalysis by some molybdenum complexes of the air oxidation of triphenylphosphine has been studied using [$MoO_2(S_2CNR_2)_2$] (R = Et or Pr^i)[5] and [MoO_2(cysS-OEt)$_2$][6] (cysS-OEt = S-deprotonated ethyl cysteinate) in *N,N*-dimethylformamide (dmf). In a previous paper we reported that the mechanism of oxidation of triphenylphosphine catalyzed by [MoO_2(cysS-OR)$_2$] [R = Me (**1**) or Et (**2**)] differs from that with [$MoO_2(S_2CNEt_2)_2$] (**3**) and that it requires a large amount of water.[7]

Since we have found that complex (**3**) has a weak oxidizing ability for primary or secondary alcohols, in this study benzoin, PhCOCH(OH)Ph, was chosen as a substrate for air oxidation catalyzed by dioxomolybdenum(VI) complexes under mild conditions.

Experimental

Materials.—Dimethylformamide, tetrahydrofuran (thf), and diethyl ether were purified by distillation just before use. Isobutyl chloroformate was of commercial grade. Benzoin, mandelic acid ethyl ester, PhCOCH(OEt)Ph, and diphenylmethanol were purified by recrystallization. Chloro(porphyrinato)iron(III) (hemin) was of commercial grade. 10-Formylmethyl-7,8-dimethylisoalloxazine (formylflavin) was prepared by the method of Fall and Petering.[8]

Preparation of Molybdenum(VI) *Complexes.*—Complexes (**1**) and (**2**) were prepared according to the procedure of Kay and Mitchell;[9] (**3**), [Mo_2O_3(cysS-OMe)$_4$] (**5**), and [$Mo_2O_3(S_2CNEt_2)_4$] (**6**) were synthesized by literature methods.[10,11]

Synthesis of [MoO_2(cysS-NHC$_{10}$H$_{21}$)$_2$] (**4**).—*S*-Acetamidomethyl-*N*-t-butyloxycarbonylcysteine n-decylamide was synthesised by the mixed anhydride method.[12] To a solution (150 cm^3) of the corresponding N,S-substituted cysteine (15 g, 0.055 mol) was added triethylamine (7.7 cm^3, 0.055 mol) and isobutyl chloroformate (7.2 cm^3, 0.055 mol) at −15 °C. After 15 min n-decylamine (11 cm^3, 0.055 mol) was added at −15 °C. The mixture was stirred for 30 min at −15 °C and then allowed to stand overnight at room temperature. The solution was concentrated under reduced pressure. The crude material obtained by addition of water to the residue was dissolved in ethyl acetate (400 cm^3). The organic layer was washed with 4% aqueous $NaHCO_3$, water, 10% aqueous citric acid, and water. It was then concentrated under reduced pressure and dried over Na_2SO_4. A semisolid was obtained by washing with light petroleum (b.p. 35—80 °C) (Found: C, 58.65; H, 9.7; N, 9.70. Calc. for $C_{21}H_{41}N_3O_4S$: C, 58.4; H, 9.55; N, 9.80%).

S-Acetamidomethylcysteine n-decylamide hydrochloride was prepared by removing the t-butyloxycarbonyl group in an ethyl acetate solution saturated with HCl gas. Yield 74.8%. The corresponding *S*-chloromercurio-derivative was synthesized by the addition of water to a mixture of the above hydrochloride (2.4 g, 6.5 mmol) and $HgCl_2$ (3.5 g, 13 mmol) in dmf (5 cm^3). Yield 91%. Cysteine n-decylamide hydrochloride was prepared by bubbling hydrogen sulphide gas through a dispersion of the corresponding *S*-acetamidomethyl peptide in methanol and was obtained as a white powder by concentration of the solution.

Complex (**4**) was synthesized by the reaction of Na_2MoO_4 (0.54 g, 2.2 mmol) and cysteine n-decylamide hydrochloride (1.48 g, 5 mmol) in water. The yellow product was purified by reprecipitation from diethyl ether–n-hexane (Found: C, 47.85; H, 8.40; N, 8.35. Calc. for $C_{26}H_{54}MoN_4O_4S_2$: C, 48.45; H, 8.15; N, 8.70%). I.r.: 891 and 913 cm^{-1}, ν(Mo=O). N.m.r. in $(CD_3)_2SO$: $NHCH_2C_9H_{19}$, 0.87; SCH_2, 1.28; NH, 8.72 p.p.m. C.d. in Me_2SO: 413 (Δε = +2.6), 364 (Δε = −2.4), and 286 nm (Δε = −21.0 dm^3 mol^{-1} cm^{-1}).

Catalytic Air Oxidation of Benzoin.—To a dmf solution (1 cm^3) of a molybdenum(VI) complex (0.0025 mmol), a dmf solution (1 cm^3) of benzoin (0.050 mmol) was added with vigorous stirring. The solution was allowed to stand at 30 °C for a given period. Diethyl ether (1 cm^3) and water (5 cm^3) were added in order to collect benzil and unreacted benzoin in an ether layer. The conversion of benzoin and the yield of benzil were determined by using h.p.l.c. with a μ-Bondapack C_{18} column (30 cm × 3.9 mm inside diameter).

E.S.R., ^1H and ^{13}C N.M.R., and C.D. Studies of the Stoicheiometric Reaction of Molybdenum(VI) *Complexes with Benzoin.*—The e.s.r. spectrum of a dmf solution (1 cm^3) of complex (**1**) (0.025 mmol) and benzoin (0.050 mmol) under anaerobic conditions was recorded on a JES-FE 1X spectrometer at 298 and 77 K. Proton n.m.r. spectra of a $(CD_3)_2SO$ solution (0.5 cm^3) of complex (**1**) (0.013 mmol) and of a $CDCl_3$ solution (0.5 cm^3) of (**2**) (0.013 mmol) containing benzoin were taken on a Varian XL-100 spectrometer. Carbon-13 n.m.r. spectra of a $CDCl_3$ solution (0.5 cm^3) of complex (**2**) (0.025 mmol) with benzoin (0.025 mmol) were obtained on a JEOL FX-90Q spectrometer with a long time delay (3.0 s) in order to monitor the time dependence of the ^{13}C signal intensity. The c.d. spectrum of a mixture of complex (**1**) (0.005 mmol) and benzoin (0.010 mmol) in dmf (1 cm^3) was obtained with a JASCO J-40 spectrometer.

Results

Catalytic Air Oxidation of Benzoin.—We have examined the catalytic activity of dioxomolybdenum(VI) complexes containing chelating thiolate or dithiocarbamate ligands, *i.e.* (**1**), (**2**), or (**4**) with S,N ligands and (**3**) with S,S ligands, for the air oxidation of benzoin in dmf at 30 °C. Figure 1 shows the time dependence of the conversion of benzoin. Initially, the observed oxidation rates with all of the catalysts were proportional to the concentration of the complexes (Figure 2). Table 1 lists initial rate constants, $k_{obs.}/s^{-1}$. The $1/k_{obs.}$ values when plotted against the reciprocal of the initial concentrations of benzoin gave a straight line with a small intercept. An apparent retardation in the catalysis by complexes (**1**)—(**3**) ensued after 1 h at conversions of 15, 12, and 8%, respectively; complex (**3**) exhibits a relatively high catalytic activity only at the initial stage. Such retardations may be due to the reaction of the molybdenum(VI) complexes with water generated by dehydrogenation of benzoin. With the complex having long alkyl chains, $[MoO_2(cysS\text{-}NHC_{10}H_{21})_2]$ (**4**), the conversion exhibits first-order kinetics depending only on the concentration of catalyst even after 1 h, as shown in Figure 1. After 20 h the yield (relative to that in the absence of catalyst) of benzil from benzoin was 1 500, 1 200, 1 000, and 1 800% and in the presence of complexes (**1**)—(**4**) ($[Mo^{VI}]/[benzoin] = 1/20$ in dmf at 30 °C). Formylflavin was not oxidized under these mild conditions.

Table 2 lists the observed rate constants of the initial stages with the incremental addition of water. Most molybdenum(VI) complexes having S,N ligands are known to be susceptible to water.[13] When $[H_2O]/[Mo^{VI}] < 17$, no significant inhibition was observed with complexes (**1**)—(**3**). Up to the ratio $[H_2O]/[Mo^{VI}] = 110$, the rate of the reaction catalyzed by (**1**) or (**2**) decreased. However, complex (**3**) still retained activity at this ratio. The results indicate that the decomposition of these molybdenum(VI) complexes involving a direct reaction with water is not a significant factor in the observed retardations.

The results of the air oxidation of benzoin in the presence of the binuclear molybdenum(V) complexes, $[Mo_2O_3(cysS\text{-}OMe)_4]$ (**5**) and $[Mo_2O_3(S_2CNEt_2)_4]$ (**6**), are given in Table 1. Both complexes exhibited the almost same catalytic activity as the corresponding mononuclear molybdenum(VI) complexes: 1 300 and 900% conversion respectively ($[Mo^V]/[benzoin] = 1/20$) in dmf for 20 h at 30 °C. Usually μ-oxo binuclear molybdenum(V) complexes exist in equilibrium between molybdenum-(VI) and -(IV) complexes. This results in a similar situation as with the mononuclear molybdenum(VI) complexes and therefore the formation of the μ-oxo binuclear molybdenum(V) complex from the latter is not a factor in the retardation.

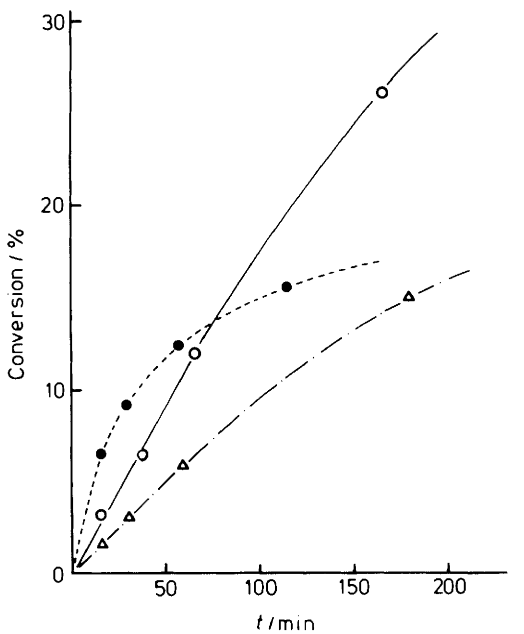


Figure 1. Time dependence of the air oxidation of benzoin (5×10^{-2} mol dm^{-3}) catalysed by (△) $[MoO_2(cysS\text{-}OMe)_2]$, (●) $[MoO_2(S_2CNEt_2)_2]$, and (○) $[MoO_2(cysS\text{-}NHC_{10}H_{21})_2]$ ($[Mo^{VI}] = 2.5 \times 10^{-3}$ mol dm^{-3}) in dmf at 30 °C

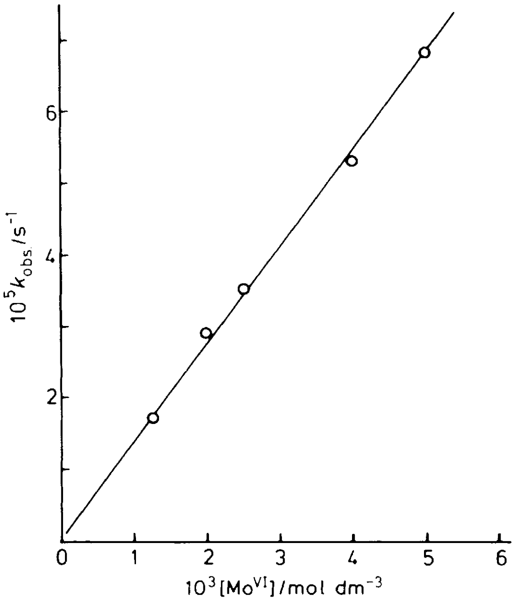


Figure 2. Dependence on the concentration of $[MoO_2(cysS\text{-}OMe)_2]$ for the observed initial rate constants for the air oxidation of benzoin (2.5×10^{-2} mol dm^{-3}) in dmf at 30 °C

Complexes (**1**)—(**4**) did not exhibit any catalytic activity for mandelic acid ethyl ester or benzoin ethyl ether in dmf at 30 °C.

Stoicheiometric Reaction of $[MoO_2(cysS\text{-}OR)_2]$ *with Benzoin.*—A dmf solution of complex (**2**) containing 2 equivalents of benzoin at room temperature and 77 K under anaerobic conditions was examined by e.s.r. spectroscopy. The absence of mononuclear molybdenum(V) species was confirmed. In the case of PPh_3 as substrate, the formation of such species was

Table 1. Observed initial first-order rate constants for the catalytic air oxidation of benzoin (5×10^{-2} mol dm^{-3}) by [$MoO_2(L-L)_2$] in dmf at 30 °C

Catalyst	$10^2k_{obs.}/s^{-1}$
None	0
[MoO_2(cysS-OMe)$_2$] (**1**)	1.4
[MoO_2(cysS-OMe)$_2$]-hemin (1 : 1)	1.3
[MoO_2(cysS-OEt)$_2$] (**2**)	1.9
[MoO_2(cysS-$NHC_{10}H_{21}$)$_2$] (**4**)	2.5
[$MoO_2(S_2CNEt_2)_2$] (**3**)	4.8
[Mo_2O_3(cysS-OMe)$_4$] (**5**)	1.2
[$Mo_2O_3(S_2CNEt_2)_4$] (**6**)	3.1
Formylflavin	0

Table 2. Dependence of observed initial first-order rate constants upon the addition of water in the oxidation of benzoin (2.5×10^{-2} mol dm^{-3}) catalysed by molybdenum(VI) complexes (1.25×10^{-3} mol dm^{-3}) in dmf at 30 °C

Complexes	[H_2O]/[Mo^{VI}]	$10^2k_{obs.}/s^{-1}$
(**1**) [MoO_2(cysS-OMe)$_2$]	0	1.4
	17	1.1
	110	0.46
	440	0.16
(**2**) [MoO_2(cysS-OEt)$_2$]	0	1.6
	17	1.2
	110	0.62
(**3**) [$MoO_2(S_2CNEt_2)_2$]	0	4.2
	17	3.4
	110	2.8
	440	0.62

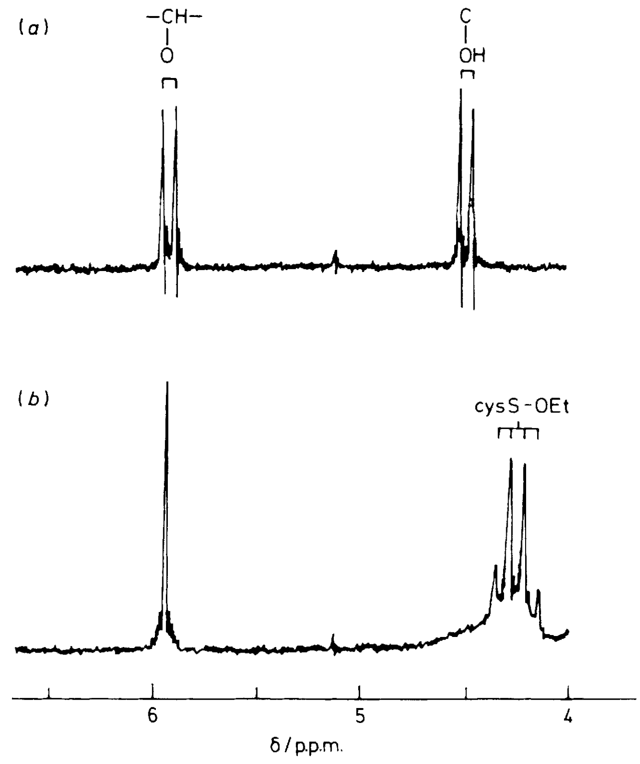


Figure 3. Proton n.m.r. spectra of (*a*) benzoin and (*b*) a mixture of benzoin (2.5×10^{-2} mol dm^{-3}) and [MoO_2(cysS-OEt)$_2$] (2.5×10^{-2} mol dm^{-3}) in $CDCl_3$

found by e.s.r. spectroscopy in dmf–water (1 : 0.15).[14] Therefore, in the course of the oxidation of benzoin, molybdenum(IV) and binuclear molybdenum(V) complexes exist in equilibrium. A similar situation has been observed in the reduction of [$MoO_2(S_2CNR_2)_2$] with PPh_3.[5] Upon addition of benzoin the c.d. spectrum of complex (**2**) remained unaltered for 20 min ([Mo^{VI}] 5×10^{-3}, [benzoin] 1.0×10^{-2} mol dm^{-3}). These results suggest the absence of a stable complex formed between (**2**) and benzoin. After 20 min a trough gradually appeared in the spectrum at 510 nm. The complete reduction of complex (**2**) in dmf was observed after 2 h. The c.d. spectrum of the reduced species [a characteristic extremum at 510 nm ($\Delta\varepsilon$ −6.0 dm^3 mol^{-1} cm^{-1})] indicates the predominant formation of complex (**5**); an authentic sample exhibited a c.d. trough at 510 nm ($\Delta\varepsilon$ −6.2 dm^3 mol^{-1} cm^{-1}) in dmf. The similar $\Delta\varepsilon$ values indicate that [Mo_2O_3(cysS-OMe)$_4$] is formed quantitatively in a solution of complex (**1**) and benzoin.

Figure 3 shows the partial ^1H n.m.r. spectrum of the reaction mixture of complex (**2**) and benzoin (1 : 1 molar ratio). The resonance of the OH proton of benzoin disappears immediately upon addition of (**2**). The formation of alkoxide anion from benzoin was indicated by the change in the resonance of the methine proton of benzoin from a doublet to a singlet. The methine proton signal gradually decreased with the formation of benzil which has characteristic phenyl proton signals around 7.5—7.8 p.p.m. Benzoin has phenyl signals at different field (7.2—7.5 p.p.m.) and is readily recognizable.

In order to examine the interaction between alcoholic OH and MoO_2^{2+} species the ^1H n.m.r. spectrum of a solution of diphenylmethanol and complex (**2**) was obtained in $CDCl_3$. The OH proton resonance of diphenylmethanol was a broad peak at 2.30 p.p.m. on addition of (**2**), but it was observed at 2.18 p.p.m. in the absence of (**2**). The broad peak at 2.30 p.p.m., which is probably associated with rapidly exchanging protons of water, the alcoholic OH, and $Mo{=}\overset{+}{O}H$, shifts to 3.05 p.p.m. at −50 °C. The results suggest that the equilibrium between the alcoholic OH and $Mo{=}\overset{+}{O}H$ lies to the left [see equation (1)]. The

$$[MoO_2(\text{cysS-OEt})_2] + PhCH(OH)Ph \rightleftharpoons [MoO(\overset{+}{O}H)(\text{cysS-OEt})_2] + PhCH(O^-)Ph \quad (1)$$

corresponding c.d. spectrum suggests that free [MoO_2(cysS-OEt)$_2$] is predominant. This is also supported by the low catalytic activity of this complex in the benzoin oxidation as mentioned above.

The gradual formation of benzil was also followed by a ^{13}C n.m.r. spectroscopy. Figure 4 shows the spectra of a mixture of benzoin and complex (**2**) (2 : 1 mol ratio) in $CDCl_3$. The assignments of the peaks due to benzoin, benzil, (**2**), and [Mo_2O_3(cysS-OEt)$_4$] were made by reference to the spectra of authentic samples. The addition of complex (**2**) results in a shift of the methine proton resonance of benzoin from 76.29 to 76.07 p.p.m. due to the partial formation of a benzoin alkoxide anion by proton transfer to the [$MoO_2(L-L)_2$] species. Figure 5(*a*) and (*b*) show the time dependence of the relative intensities of the ^{13}C signals of the methine and ester carbons of (**2**) during this reaction. The relative intensities were estimated from the signal of $CDCl_3$ as an internal reference. The formation of benzil as monitored from the methine signal at 76.07 p.p.m. clearly corresponds to the rate of consumption of benzoin as monitored by one of its phenyl signals at 134.74 p.p.m. [Figure 5(*a*)]. On the other hand, the decrease in intensity of the ester carbon signal of (**2**) is accompanied by the appearance of two signals of the unequivalent ester carbons of [Mo_2O_3(cysS-OEt)$_4$] at 173.91 and 171.20 p.p.m. as shown in Figure 5(*b*). The quantitative formation of the binuclear complex was supported by the results of the c.d. spectral study mentioned above.

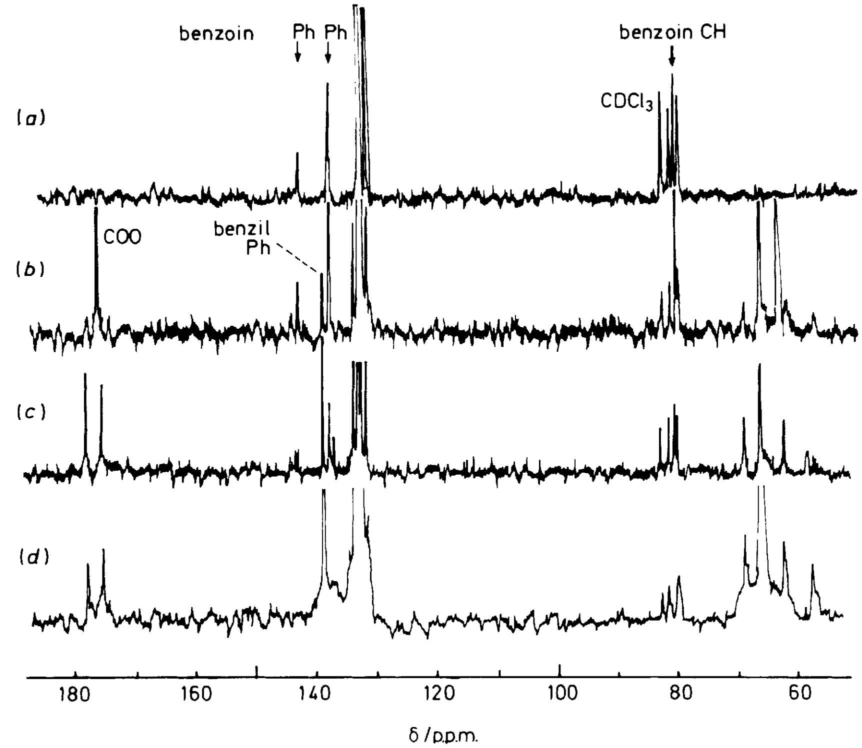


Figure 4. ^{13}C N.m.r. spectra of (*a*) benzoin, (*b*) a mixture of benzoin (5×10^{-2} mol dm^{-3}) and [MoO_2(cysS-OEt)$_2$] (5×10^{-2} mol dm^{-3}) after 0.5 h, (*c*) after 1.5 h, and (*d*) after 24 h in $CDCl_3$ at room temperature

Discussion

Stoicheiometric Reaction of Molybdenum(VI) *Complexes with Benzoin.*—We have investigated the stoicheiometric reaction by spectroscopic means. It is now clear that the stoicheiometric reduction of [MoO_2(cysS-OR)$_2$] with benzoin results in the formation of molybdenum(IV) species. The absence of an e.s.r. signal has been confirmed in the case of the reduction of [$MoO_2(S_2CNR_2)_2$] with triphenylphosphine and the formation of [$Mo^{IV}O(S_2CNR_2)_2$] has been established.[5] The $\Delta\varepsilon$ value of the c.d. trough at 510 nm observed in the stoicheiometric reduction ([Mo^{VI}]/[benzoin] = 1/1) is indicative of the quantitative formation of [Mo_2O_3(cysS-OR)$_4$] as shown in equations (2) and (3).

$$[\mathrm{Mo^{VI}O_2(cysS\text{-}OR)_2}] + \mathrm{PhCH(OH)COPh} \longrightarrow [\mathrm{Mo^{IV}O(cysS\text{-}OR)_2}] + \mathrm{H_2O} + \mathrm{PhCOCOPh} \quad (2)$$

$$[\mathrm{MoO(cysS\text{-}OR)_2}] + [\mathrm{MoO_2(cysS\text{-}OR)_2}] \rightleftharpoons [\mathrm{Mo_2O_3(cysS\text{-}OR)_4}] \quad (3)$$

The ^{1}H n.m.r. analysis of the stoicheiometric reaction indicates that an equilibrium between benzoin and [MoO_2(cysS-OR)$_2$] exists, while a Mo–OH group probably forms by proton transfer from benzoin similar to the situation shown in equation (1). The CH–O–Mo bonding is important for the activation of benzoin for the oxidation. Benzoin ethyl ether is not oxidized in the presence of complexes (**1**)—(**4**). The results of the ^{13}C n.m.r. spectral study indicate that the formation of benzil occurs slowly, by the elimination of the methine proton of benzoin. A molybdenum(IV) species appears rapidly after the transfer of the methine proton and formation of the Mo–OH group.

Catalytic Oxidation of Benzoin.—The catalytic activity in the air oxidation of benzoin was found to be limited to dioxomolybdenum(VI) complexes having S,N or S,S ligands. This is not very surprising. Molybdenum oxidases, *e.g.* xanthine oxidase, are known to exhibit a weak activity for air oxidation of ethylene glycol.[15] The active site of the enzyme has been shown by extended *X*-ray absorption fine structure[16] and e.s.r.[17] analysis to have a Mo(=S)(=O)$^{2+}$ moiety surrounded by some thiolate ligands.

In the initial stage, the molybdenum(VI) complex (**3**) containing S,S ligands exhibits a higher activity ($k_{obs.} = 0.048$ s^{-1}) than [MoO_2(cysS-OR)$_2$] having S,N ligands {$k_{obs.} = 0.014$ s^{-1} for [MoO_2(cysS-OMe)$_2$]} in the oxidation of benzoin as well as of triphenylphosphine. The activation of the M=O group was ascribed to the higher electron-donating effect of the S,S chelate than that of the S,N chelate. The absence of a reaction with ethyl mandelate indicates that the catalytic activity of the present molybdenum(VI) complexes is too weak for primary alcohols.

There are some remarkable differences between the oxidation of triphenylphosphine and benzoin. The first is the inhibition of the oxidation of benzoin by water as mentioned earlier, whereas the catalytic oxidation of triphenylphosphine requires prescribed amounts of water, although a large excess of water decomposes the catalytically active species. The second is the absence of an accelerating effect of hemin or formylflavin in the case of benzoin. With triphenylphosphine, the addition of hemin or riboflavin to [MoO_2(cysS-OMe)$_2$] remarkably increases the rate of reaction.[18] This difference is ascribed to the difference in the oxidation state of the molybdenum species during the turnover. Thus, it is plausible that the species reduced by benzoin is Mo^{IV}, but that reduced by triphenylphosphine is Mo^V.

Most of the molybdenum(VI) complexes are decomposed by water generated by the dehydrogenation of benzoin. A spontaneous decomposition occurs when [MoO_2(cysS-O-peg)$_2$] [peg = $(CH_2CH_2O)_n$ – H, M = 2 200] having a water-soluble group in peg was dissolved in water.[13] However, the

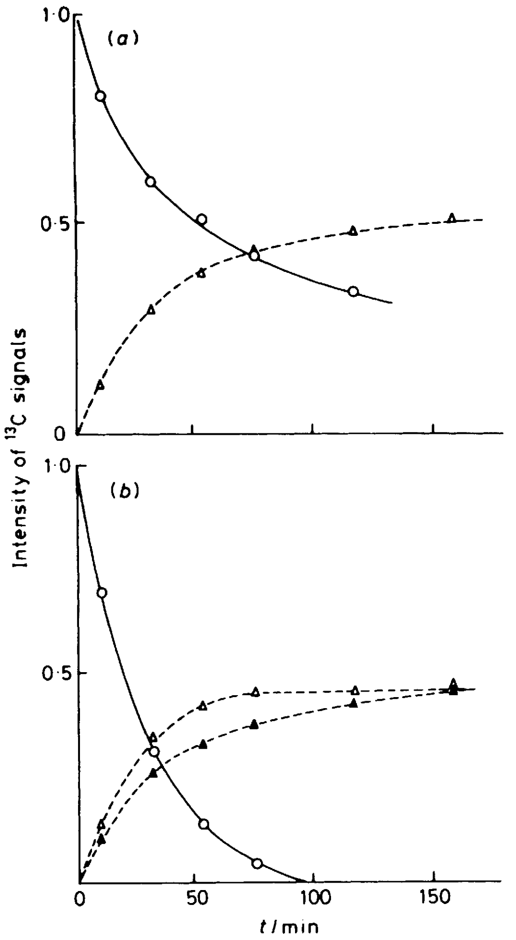
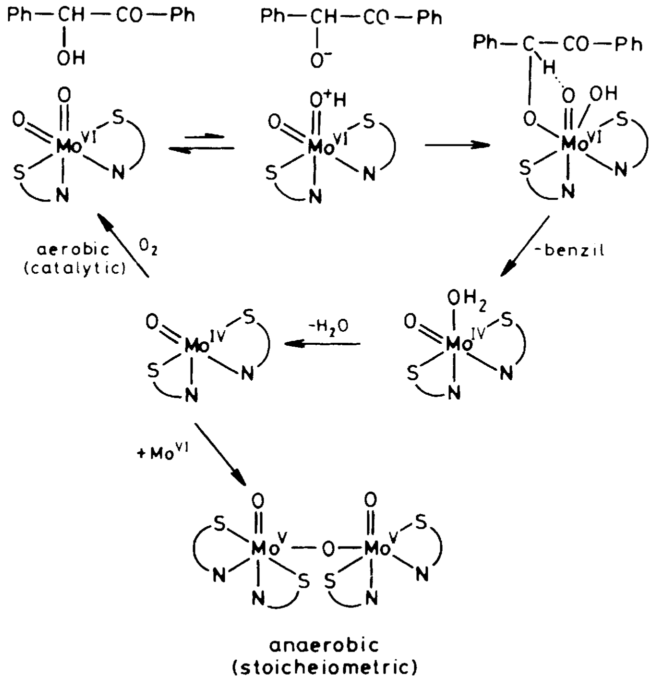


Figure 5. Time dependence of the relative intensities of ^{13}C n.m.r. signals in the stoicheiometric reaction of benzoin and $[MoO_2(cysS\text{-}OEt)_2]$: (*a*) relative intensities of the methine carbon signals of benzoin (○) and of the phenyl carbon signals of benzil (△); (*b*) relative intensities of the ester carbon signal of $[MoO_2(cysS\text{-}OEt)_2]$ (○) and of the ester carbon signals of $[Mo_2O_3(cysS\text{-}OEt)_4]$ (△, ▲)

deactivation commenced when water (more than 17 equivalents) was added to the oxidation system in the presence of the molybdenum(VI) complex. Water does not seriously deactivate the catalyst when it is generated from the oxidation reaction within four or five turnovers.

On the other hand, the long hydrophobic alkyl chains of complex (**4**) protect the active species from deactivation, probably by preventing the reduced species from forming a μ-oxo binuclear molybdenum(V) complex and its subsequent conversion into a di-μ-oxo binuclear molybdenum(V) complex. The rapid deactivation of complex (**3**) is suggested to be caused by the rapid formation of $[Mo_2O_4(S_2CNEt_2)_2]$ from (**6**). This is supported by the rapid formation of $[Mo_2O_4(cysS\text{-}O\text{-}peg)_2]$ from $[MoO_2(cysS\text{-}O\text{-}peg)_2]$ in the presence of water.[13] Di-μ-oxo-molybdenum(V) complexes having S,N ligands, *e.g.* $Na_2[Mo_2O_4(cysO)_2]$ (cysO = cysteinate),[9] are known to be kinetically stable to dissociation or hydrolysis.

The proposed mechanism for the air oxidation of benzoin in the presence of $[MoO_2(cysS\text{-}OR)_2]$ or $[MoO_2(S_2CNR_2)_2]$ is shown in the Scheme. An electron transfer from co-ordinated benzoin anion to $MoO(OH)^{2+}$ causes release of H_2O from Mo–OH. Thus, the formation of benzil, water, and molybdenum(IV) species occurs rapidly after the transfer of the methine proton to the Mo=O group. The rate-determining step is thus formation of the molybdenum(IV) species as found in the stoicheiometric reactions. This species is rapidly oxidized by dioxygen to regenerate the original molybdenum(VI) complex. The retardation probably occurs through the formation of a μ-dioxo-molybdenum(V) complex from the μ-oxo-molybdenum(V) complex by reaction with dioxygen or water.



Scheme.

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