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Molybdenum(VI) Complexes as Oxidants

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Molybdenum has been identified as an essential constituent of the xanthine, aldehyde, and sulphite oxidases [1] and electron spin resonance studies [2] have indicated that the conversion of these substrates is accomplished in the immediate vicinity of this metal. The net effect of each of these enzymic catalyses is the addition of an oxygen atom to the substrate. So far chemists have failed to develop simple molybdenum-containing systems which can oxidise xanthines, aldehydes, or sulphite, even though these oxidations are fairly readily accomplished by other oxidants. Spence [3] has noted that *cis*-MoO_2(ethyl-L-cysteinate)$_2$, dissolved DMF or DMSO, is capable of oxidising aldehydes to carboxylic acids, although we have been unable to confirm this observation (*vide infra*). Molybdenum(VI) has, however, been shown capable of oxidising thiols [4], hydrazine [5] and polyketones [6] and this metal is included as a component in certain [7] solid phase oxidation catalysts. Presently, the best characterised [8, 9] oxidation accomplished by a molybdenum(VI) complex is the oxygen atom transfer between *cis*-$MoO_2(S_2CNR_2)_2$ (R = Et, Pr^n or Bu^i) and tertiary phosphines. In fact, this type of molybdenum centre is capable of catalysing the oxidation, by dioxygen, of a tertiary phosphine to the corresponding phosphine oxide. We have attempted to develop oxygen transfer reactions from molybdenum(VI) complexes to biological substrates.

Experimental

The most detailed studies were undertaken for homogeneous systems in non-aqueous media under an atmosphere of purified dinitrogen, where hydrolysis of the metal and hydroxide/oxide precipitation were minimised. All manipulations were carried out under an atmosphere of purified dinitrogen using freshly dried and distilled solvents, transfers being effected using serum cap and syringe techniques. Blank solutions were run in parallel for each set of experiments. The complexes chosen for these studies included the *cis*-dioxomolybdenum(VI) complexes MoO_2L_2 (where L = diethyldithiocarbamate [10] (*A*), ethyl-L-cysteinate [11] (*B*), acetylacetonate [12] (*C*) and *o*-salicylaldehyde [13] (*D*). Benzaldehyde was purified by washing several times with a 10% solution of $NaHCO_3$, dried over $MgSO_4$, before distillation under a reduced pressure. Oxidations of aqueous solutions of sulphite and xanthine were also attempted using the complexes (*A*)–(*D*) suspended in a polystyrene matrix as described by Wang [14]. Polarographic measurements were recorded for the complexes (*A*)–(*D*) dissolved in DMF with Ph_4AsCl as the carrier electrolyte.

Results and Discussion

The potentials (*vs.* S.C.E.) at which polarographic reduction was identified varied, for these molybdenum complexes as, (*A*) –0.95v, (*B*) –1.14v, (*C*) –1.66v and (*D*) *ca.* –1.9v, the first of these values comparing favourably with that (–0.98v) reported by Sawyer *et al.* [15] for this complex in MeCN and DMF solutions. These indications of relative oxidising abilities were found to be consistent with their chemical behaviour. Whereas all of these complexes were reduced by $NaBH_4$ (in methanol), $Na_2S_2O_4$ (in aqueous DMF), and Ph_3P (in MeCN), only (*A*) and (*B*) were capable of oxidising ethyl-L-cysteine·HCl (in DMF) and showed any evidence of reduction in the presence of aldehydes (*vide infra*). When polystyrene suspensions of these complexes were immersed in an aqueous solution of xanthine or sulphite, only in the case of (*B*) was any reduction of the molybdenum(VI) centre characterised.

No reaction was observed between benzaldehyde and (*B*) in CH_2Cl_2, $CHCl_3$, MeCN, or toluene solution. However, in DMF, a number of changes occurred over a period of several hours. The initial yellow solution became pink and the appearance of an absorption at 504 nm suggested [16] that Mo_2O_3(ethyl-L-cysteinate)$_4$ had been formed. The solution then became progressively paler in colour and a white powder, subsequently characterised as diethylcystine, precipitated. No evidence was obtained for the formation of benzoic acid, following spectroscopic studies and the attempted preparation [17] of its *S*-benzyl thiouronium salt. This reaction is therefore suggested to be a consequence of the partial displacement of ethylcysteine by DMF, thus allowing the remaining complex (*B*) to oxidise this free ligand, as described earlier.

In contrast to these observations, the only solvents, in which appreciable colour changes were produced by (*A*) and benzaldehyde, were CH_2Cl_2 and $CHCl_3$. In both media a deep red colour (λ_{max} = 508 nm) was produced. Further investigations, initiated to clarify the apparent inconsistency in the rate at which this colour developed, showed that the reaction was photolytic and subsequent studies were accomplished using a 1 litre Hanovia Photochemical

Reactor. CH_2Cl_2 or $CHCl_3$ solutions containing (*A*) (10^{-3} *M*) and benzaldehyde (1*M*) showed clear evidence for reaction after an incubation time of *ca.* 75 sec with no further increase in the absorption at λ_{max} = 508 nm being noted after *ca.* 10 min. The spectral (i.r.; u.v./vis.) data of the coloured material were consistent with its formation [18] as $MoO(S_2CNEt_2)_2$. Infra-red studies indicated the formation of a carboxylic acid function and the production of benzoic acid was confirmed by the isolation [17] and characterisation of *S*-benzyl thiouronium benzoate (m.p. 163 °C). The recovery of 8×10^{-4} mol of this salt suggests that a 1:1 oxygen atom transfer between *cis*-$[MoO_2(S_2CNEt_2)_2]$ and benzaldehyde had been accomplished. However, this oxidation represents only a modest improvement in the development of model reactions for the molybdenum-containing oxidases, particularly in view of the reliance on photolysis and chlorinated solvents.

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