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Oxo Transfer Reactions of Mo(VI) Complexes to Phosphines and Phosphites

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The oxygenation reactions of aldehydes, tertiary phosphines and phosphites catalyzed by the cis-*dioxomolybdenum(VI)–ethyl-L-cysteinate complex were studied. The reaction with aldehydes seems to have a radical character and that with phosphines and phosphites involves an oxo transfer from molybdenum to trivalent phosphorus. Some attempts were made to find a correlation between reactivity and structure of the substrates.*

Introduction

Molybdenum has been found to be an essential constituent in the active centres of the aldehyde, sulphite and xanthine oxidases [1]. These enzymes belong to the group of mono-oxygenases where the net effect of the enzymatic catalysis is the addition of one oxygen atom to the substrate. Attempts have been made to develop simple molybdenum containing systems which can oxidize aldehydes, sulphite and xanthine [2, 3]. Molybdenum(VI) complexes have been found to oxidize thiols [4], hydrazine [5], polyketones [6], and tertiary phosphines [7–11]. Spence [12] has reported that *cis*-MoO_2(ethyl-L-cysteinate)$_2$, dissolved in DMSO or DMF, is capable of oxidizing aldehydes to carboxylic acids but recently Garner *et al.* [13] have been unable to confirm this observation. We have also attempted to develop oxygen transfer reactions from Mo(VI) oxo-complexes to biological substrates, tertiary phosphines and phosphites in order to learn more about the features and mechanistic implications of the oxo abstraction.

Experimental

The complexes *cis*-MoO_2(ethyl-L-cysteinate)$_2$ [12] and *cis*-$MoO_2(S_2CNPr^n)_2$ [13], PMe_2Ph [14], $PEtPh_2$ [15], and $P(CH_2OH)_3$ [16] were synthesised by known methods. $P(OMe)_3$, $P(OEt)_3$, $P(OBu)_3$, PPh_3, PBu_3, $P(C_6H_{11})_3$, and $Ph_2PCH_2CH_2PPh_2$ were of reagent grade (Strem Chemicals) and used without further purification. Benzaldehyde and propionaldehyde were purified by washing with a 10% solution of $NaHCO_3$, dried over $MgSO_4$ and distilled under argon before use. All manipulations were carried out under an atmosphere of purified argon using dry and distilled solvents. The oxygenation reactions were carried out in thermostatted reaction vessels connected to a thermostatted gas buret. The IR and UV–VIS spectra were recorded on Specord 75 IR and Specord UV–VIS instruments (Carl Zeiss, Jena).

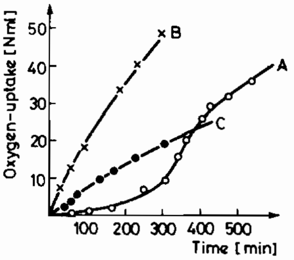


Figure 1. The oxygenation of benzaldehyde in DMF in the presence of *cis*-MoO_2(ethyl-L-cysteinate)$_2$. A) Catalyst conc.: 1.26×10^{-2} *M*; benzaldehyde conc.: 2.97 *M*; total volume 10 ml; temp. 60 °C. B) Conditions of A plus 340 mg benzoic acid. C) Conditions of B without molybdenum catalyst.

Results and Discussion

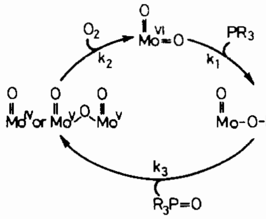
Repeating the work of Spence [12] we tried to oxygenate propionaldehyde and benzaldehyde to the corresponding carboxylic acids in DMF and DMSO in the presence of *cis*-MoO_2(ethyl-L-cysteinate)$_2$ and *cis*-MoO_2(dipropyldithiocarbamate)$_2$. At room temperature no reaction occurred at all for 48 h. On raising the temperature to 60 °C the colour of the reaction mixture containing *cis*-MoO_2(dipropyldithiocarbamate)$_2$ changed from yellow to green but no oxygen consumption could be observed. *cis*-MoO_2(ethyl-L-cysteinate)$_2$ behaved differently. The results can be seen on Fig. 1.

The oxygenation of benzaldehyde in DMF in the presence of *cis*-MoO_2(ethyl-L-cysteinate)$_2$ at 60 °C starts slowly with an induction period; the curve usually takes the form (A). If the same reaction is carried out in the presence of added benzoic acid the induction period disappears and the rate of the reaction is faster (B). Curve (C) shows autoxidation of benzaldehyde in DMF at 60 °C without added molybdenum catalyst.

In no case did the original yellow colour of the molybdenum(VI) complex turn to pink or red which would point to molybdenum(V) and -(IV) species as a result of oxo abstraction. The results clearly indicate that the oxygenation of benzaldehyde to benzoic acid in the presence of the *cis*-dioxomolybdenum(VI)–ethyl-L-cysteinate complex has a radical character. The benzoic acid formed during the reaction catalyzes the decomposition of the perbenzoic acid as usually found in such autocatalytic processes. The comparison of the curves A and C suggests that the *cis*-MoO_2(ethyl-L-cysteinate)$_2$ has some activity in catalyzing some step(s) of the radical reaction.

Extending the oxygenation reaction to tertiary phosphines and phosphites we were interested to know how the structure of the substrates influences the rate and character of the reaction and whether a correlation between structure and reaction rate can be found.

Garner *et al.* [8] have already reported on the rates of the oxygen transfer reactions from different *cis*-dioxymolybdenum(VI) dialkyldithiocarbamate complexes to phosphines. Comparing the oxygenation of triphenylphosphines catalyzed by *cis*-MoO_2(ethyl-L-cysteinate)$_2$ and *cis*-MoO_2(dipropyldithiocarbamate)$_2$ in DMF it could be observed that the colour of the solution in the first case remained yellow but in the latter turned to intense pink. This suggests that most of the molybdenum is in the form of *cis*-MoO_2(ethyl-L-cysteinate)$_2$ (absorption band at 360 nm in the VIS spectrum) and Mo_2O_3(dipropyldithiocarbamate)$_4$ or MoO(dipropyldithiocarbamate)$_2$ (λ_{max} at 514 nm), respectively. From this fact the conclusion may be drawn that in the oxygenation reaction which involves the transfer of the oxo ligand to the phosphine and the uptake of oxygen yielding the dioxo complex, different steps are rate-determining for the two types of catalysts (see Scheme 1; k_1 and k_2): for *cis*-MoO_2(ethyl-L-cysteinate)$_2$ it is the transfer of the oxo group to the phosphine and for *cis*-MoO_2(dipropyldithiocarbamate)$_2$ the reoxidation of the Mo(V) or Mo(IV) species which should be rate-determining. Preliminary kinetic data of the oxygenation of different alkyl phosphines with *cis*-MoO_2(ethyl-L-cysteinate)$_2$ suggest, however, that k_1 and k_2 in Scheme 1 are of the same order of magnitude. With phosphines having low pK_a values, $k_1 < k_2$ and in the case of strongly basic phosphines $k_1 > k_2$ at least in some solvents.



(ethyl-L-cysteinato ligands omitted)

Scheme 1. The catalytic cycle for the oxygenation of tertiary phosphines catalyzed by *cis*-dioxo-molybdenum-(ethyl-L-cysteinate)$_2$.

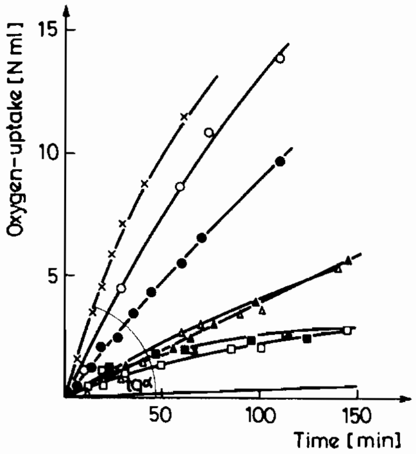


Figure 2. The oxygenation of phosphines and phosphites in DMF in the presence of *cis*-MoO_2(ethyl-L-cysteinate)$_2$. Catalyst conc.: 1.77 × 10^{-2} *M*; phosphine or phosphite conc.: 0.38 *M*; total volume 5 ml; temp.: 50 °C. × PBu_3; ○ PMe_2Ph; ● $Ph_2PCH_2CH_2PPh_2$; △ $PEtPh_2$; ▲ PPh_3; ■ $P(OMe)_3$; ▪ $P(OEt)_3$; □ $P(OBu)_3$; — PBu_3 without the catalyst.

In order to study the effect of the structure of tertiary phosphines and phosphites we investigated the oxygenations catalyzed by *cis*-MoO_2(ethyl-L-cysteinate)$_2$. The results depicted in Fig. 2 clearly show that the initial rates of oxygenations vary depending on the substituents of the trivalent phosphorus. Tricyclohexylphosphine and trihydroxymethylphosphine autoxidized very quickly under the

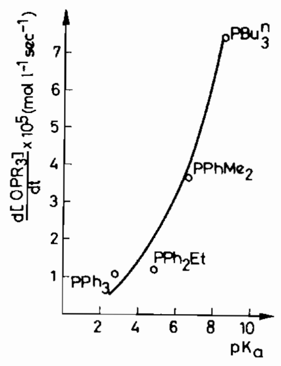


Figure 3. The initial rates of oxygen uptake of phosphines in DMF in the presence of *cis*-MoO_2(ethyl-L-cysteinate)$_2$ against their basicities. Conditions were the same as given for Fig. 2.

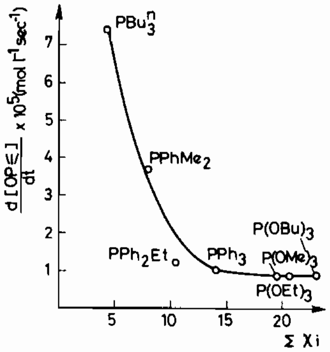


Figure 4. The initial rates of oxygenation of phosphines and phosphites in DMF in the presence of *cis*-MoO_2(ethyl-L-cysteinate)$_2$ against Tolman's χ_R and χ_{OR} values [17]. Conditions as in Fig. 2.

conditions so that the catalytic effect of *cis*-MoO_2-(ethyl-L-cysteinate)$_2$ could not be measured. The results suggest that the more basic alkyl phosphines are oxygenated faster than the arylphosphines and the phosphites. Fig. 3 shows the initial reaction rates of the oxygenation of the different phosphines against their pK_a values. The basicity of the phosphine may not be the only factor influencing the reactivity in this reaction.

Tolman [17] has found that the electron donor and acceptor properties of phosphorous ligands can be determined rapidly and conveniently by measuring the A_1 carbonyl stretching frequency of Ni-$(CO)_3L$ complexes in CH_2Cl_2. Using this substituent contribution parameter the correlation shown in Fig. 4 was obtained with the slopes of initial oxygen-uptake.

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References

1 R. C. Bray and J. C. Swan, "Structure and Bonding", Springer-Verlag (Berlin) *11*, 107 (1972).
2 R. A. D. Wentworth, *Coord. Chem. Rev., 18,* 1 (1976).
3 F. L. Bowden, in "Techniques and Topics in Inorganic Chemistry", Ed. C. A. McAuliffe, MacMillan, London, pp. 207–267 (1975).
4 L. S. Meriwether, W. F. Marzluff and W. G. Hodgon, *Nature (London), 212,* 465 (1966).
5 T. Huang and J. T. Spence, *J. Phys. Chem., 72,* 4198, 4573 (1968).
6 J.-F. Verchere and M.-B. Fleury, *Bull. Soc. Chim. France,* 2611 (1972).
7 R. Barral, C. Bocard, I. Sérée de Roch and L. Sajus, *Tetrahedron Letters,* 1693 (1972).
8 R. Durant, C. D. Garner, M. R. Hyde and F. E. Mabbs, *J. Chem. Soc. Dalton,* 955 (1977).
9 C. D. Garner, R. Durant and F. E. Mabbs, *Inorg. Chim. Acta Letters, 24,* L29–L30 (1977).
10 D. B. McDonald and J. I. Shulman, *Analyt. Chem., 47,* 2023 (1975).
11 G. J.-J. Chen, J. W. McDonald and W. E. Newton, *Inorg. Chem., 15,* 2612 (1976).
12 J. T. Spence and P. Kronek, *J. Less-Comm. Metals, 36,* 465 (1974).
13 W. E. Newton, J. L. Corbin, D. C. Bravard, J. E. Searles and J. W. McDonald, *Inorg. Chem., 13,* 1100 (1974).
14 J. Meisenheimer, J. Caspar, M. Höning, W. Lauter, L. Lichlenstad and W. Samuel, *Ann. Chem., 449,* 227 (1926).
15 H. Goetz and S. Domin, *Ann. Chem., 704,* 1 (1967).
16 E. I. Grinshtein, A. B. Bruker and L. Z. Soborovskii, *Dokl. Akad. Nauk SSSR, 139,* 1359 (1961); *C.A., 56,* 1475g (1962).
17 C. A. Tolman, *J. Am. Chem. Soc., 92,* 2953 (1970).