Metal Catalysis in Oxidation by Peroxides. Part 7.[1] Ligand Exchange and Catalytic Activity of Molybdenum(VI) Species in the Oxidation of Organic Sulphides by t-Butyl Hydroperoxide

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The oxidation of di-n-butyl sulphide by t-butyl hydroperoxide catalysed by bis(acetylacetonato)dioxomolybdenum(VI) [$MoO_2(acac)_2$] has been studied in MeOH, EtOH, and Pr^{i}OH at 25°. The oxidation rates depend on the nature of the alcoholic solvent with the reactivity order Pr^{i}OH > EtOH > MeOH. Evidence, based on ^1H n.m.r. and kinetic analysis, is given to show that the acetylacetone ligands in $MoO_2(acac)_2$ are displaced by solvent alcohol and that two molybdenum(VI) species, with zero and one diketonate ligands bonded to the metal, respectively, are formed. The original bis(diketone) complex appears to be devoid of any catalytic activity, whereas the two intermediate Mo^{VI} species have similar efficiency as catalysts. In agreement with this observation it was found that added acetylacetone inhibits the oxidation. The precursor complex bis(dipivaloylmethanato)dioxomolybdenum(VI) was observed to have lower reactivity than $MoO_2(acac)_2$. A change of the hydroperoxide to Bu^{n}OOH in the $MoO_2(acac)_2$ catalysed oxidation has a negligible effect on the rate. The nature of the catalytic complexes and the mechanism of the oxygen-transfer process are discussed.

HOMOGENEOUS catalysis by compounds of molybdenum and vanadium is recognized as one of the most efficient means of achieving selective oxidation of organic substrates (alkenes, amines, sulphides, *etc.*) *via* oxygen transfer from hydroperoxides.[2] Several investigators have agreed that the metal catalyst should function so as to activate the peroxide O–O bond *via* co-ordination, thus promoting nucleophilic attack by the substrate on the peroxide.

However, in spite of the technical interest in these oxidation systems, which is well documented by the patent literature,[2] some relevant questions concerning the reaction mechanism have remained unanswered. In particular, practically all the mechanisms advanced so far give no details as to the co-ordination sphere surrounding the metal ion.[3]

Several pieces of evidence indicate that metal species commonly employed, such as $MoO_2(acac)_2$, $Mo(CO)_6$, $VO(acac)_2$, *etc.*, as catalysts in these reactions should be considered as precursors of the true catalytic species.[3-7] For example Sheldon *et al.* observed that a number of molybdenum compounds have (except for the initial stage of the reaction) identical catalytic activity in the epoxidation of cyclohexene by t-butyl hydroperoxide in benzene, which suggests that all catalyst precursors are converted into the same active species under the reaction conditions.[5] Furthermore, the same dihydroxodioxomolybdenum(VI) complex could be isolated from these epoxidations regardless of the molybdenum compound initially added as catalyst.[6,7]

These oxidation systems increasingly find useful synthetic applications; these include attempts to achieve high enantioselectivity in oxidizing prochiral substrates by using optically active metal complexes.[8-10]

We feel, however, that no serious attempt to rationalize these processes can begin until data are obtained concerning the fate of the original ligand environment and the nature and number of catalytically active metal–ion species generated under the various reaction conditions.

In a previous paper [4] we pointed out the relevance of ligand exchange and acid–base equilibria involving vanadium(V) catalysts on the rates of oxidation of model substrates by t-butyl hydroperoxide. We now report our studies aimed at shedding some light into the nature of the Mo^{VI} active species which act as catalysts in the same oxidation processes.

RESULTS AND DISCUSSION

Effect of Protic Solvents.—The general features of the homogeneous catalysis by bis(acetylacetonato)dioxomolybdenum(VI) in the oxidation of di-n-butyl sulphide by Bu^{t}O$_2$H in ethanol have been reported.[11] The decomposition rate of Bu^{t}O$_2$H in the absence of the sulphide, in EtOH,[11] as well as in MeOH and Pr^{i}OH, at the catalyst concentration used throughout, is immeasurably slow. The stoicheiometry of the reaction in the three solvents was confirmed to be 1 : 1 by *ca.* 95% recovery of di-n-butyl sulphoxide as the only detectable product.

The rate law (1) was found to be obeyed at relatively low peroxide initial concentrations.† Within a narrow

$$v = k_{2,\mathrm{obs}}[\mathrm{Sulphide}][\mathrm{Bu^tO_2H}] \qquad (1)$$

range of low catalyst initial concentration a linear dependence of $k_{2,\mathrm{obs}}$ on $[MoO_2(acac)_2]_0$ was also observed indicating that equation (2) holds:

$$k_{2,\mathrm{obs}} = k_2{}^0 + k_3[\mathrm{MoO_2(acac)_2}]_0 \qquad (2)$$

In equation (2), $k_2{}^0$, the rate constant for the uncatalysed oxidation, which is very slow, may be neglected.[11] At higher initial catalyst concentrations a negative deviation from first-order dependence in

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† At higher peroxide ($>5 \times 10^{-2}$M) concentrations a definite trend toward lower order is observed, which is an indication that a saturation effect is operative.[11]

$[MoO_2(acac)_2]_0$ was observed. The occurrence of aggregation involving molybdenum species forming less effective catalysts was tentatively suggested as a rationale for this behaviour.[11]

Preliminary experiments showed that equation (1) is equally well obeyed in methanol and propan-2-ol. Also in these solvents, at high peroxide initial concentration, deviations from first-order dependence of rate on Bu^tO_2H were observed (see Table 1).

TABLE 1

Effect of changing initial hydroperoxide concentration on oxidation rates at constant sulphide and metal catalyst [a] in three alcoholic solvents, at 25.0 ± 0.05°

	$10^4 v_0$ [b]/mol l^{-1} s^{-1}		
$[Bu^tO_2H]_0$/M	EtOH [c]	MeOH	Pr^iOH
0.0147	0.0793		
0.0153			0.0885
0.0168		0.885	
0.0220		1.100	
0.0250	0.133		0.144
0.0438			0.251
0.0448		1.841	
0.0554	0.276		
0.0887		2.702	
0.0895			0.502
0.113	0.538		

[a] In all experiments $[Bu_2^nS]_0 = 0.5$M and $[MoO_2(acac)_2]_0 = 0.6 \times 10^{-5}$M. [b] Initial loss of peroxide from plots of $[Bu^tO_2H]$ *versus* time. [c] Data from ref. 11.

In Figure 1, the effect of changing the alcohol solvent from ethanol to methanol and propan-2-ol on the profile of $k_{2,obs}$ *versus* $[MoO_2(acac)_2]_0$ plots is shown. In the latter two solvents, for the concentration interval explored, no significant deviation from linearity occurs. The catalytic third-order constant values for propan-2-ol and methanol solvent are k_3 320 and 6 l^2 mol^{-2} s^{-1}, respectively. These values, together with the k_3 value of 162 l^2 mol^{-2} s^{-1} previously estimated for EtOH indicate the catalytic activity decreases in the alcohol solvents as $Pr^iOH > EtOH > MeOH$, which is opposite to that expected on basis of alcohol acidity, if the influence of the protic species was solely to assist O–O bond breaking in the transition state.[12] In the uncatalysed oxidation of Bu_2^nS by Bu^tO_2H, in fact, the relative rate constants are Pr^iOH, 1; EtOH, 1.4; and MeOH, 4. The same trend is also observed in the V^V catalysed oxidation of the same substrate by Bu^tO_2H,[13,14] where the observed rates decrease in the order $MeOH > EtOH > Pr^iOH$.

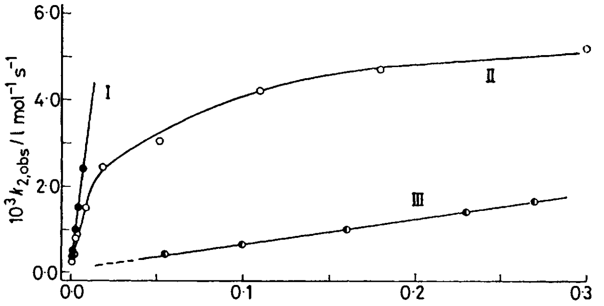


FIGURE 1 Effect of changing $MoO_2(acac)_2$ concentration on the rates of the di-n-butyl sulphide oxidation by t-butyl hydroperoxide at 25.00° in three alcohols: I, Pr^iOH; II, EtOH; III, MeOH. $[Bu_2^nS]_0$ 0.2—0.3M, $[Bu^tO_2H]_0$ 1.0×10^{-2}M

The results obtained for Mo^{VI}-catalysed oxidation seem therefore to suggest that the catalytic mechanism differs in some important detail from that of the vanadium species and that the alcoholic solvent is involved in the co-ordination sphere of the molybdenum ion. This suggestion is supported by the finding that $MoO_2(acac)_2$-catalysed oxidation by Bu^tO_2H of prochiral sulphides in hydrocarbon–chiral alcohol media results in measurable optical yields of chiral sulphoxides.[8]

^{1}H *N.M.R. Experiments.*—The observations above prompted us to seek direct spectroscopic evidence of changes taking place in the co-ordination sphere of catalyst precursors when dissolved in alcoholic solvents. In the methyl proton resonance region the ^{1}H n.m.r. spectra of $MoO_2(acac)_2$ dissolved in $[^2H_6]$ethanol exhibit three singlets (Figure 2) in an intensity ratio of *ca.* 6 : 8 : 1 at δ 2.01, 2.07, and 2.20, respectively. By comparison with the ^{1}H n.m.r. spectra of acetylacetone (acacH) in the same solvent, the first and third signals can be attributed to the CH_3 resonance of the enol and keto forms, respectively, of this compound; the signal at δ 2.07 can then be attributed to the CH_3 resonance of metal-bound acetylacetonate ligand. Upon varying the sample temperature from 28 to 56° the signals at δ 2.01 and 2.07 coalesce into one broad peak (δ 2.05). The ^{1}H n.m.r. spectra of $MoO_2(acac)_2$ in $[^2H_4]$methanol show features similar to these described above.

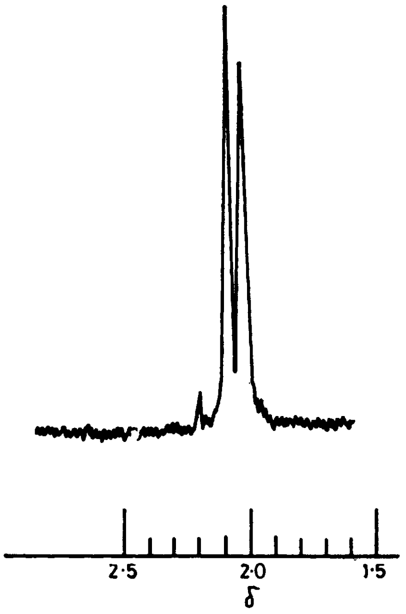
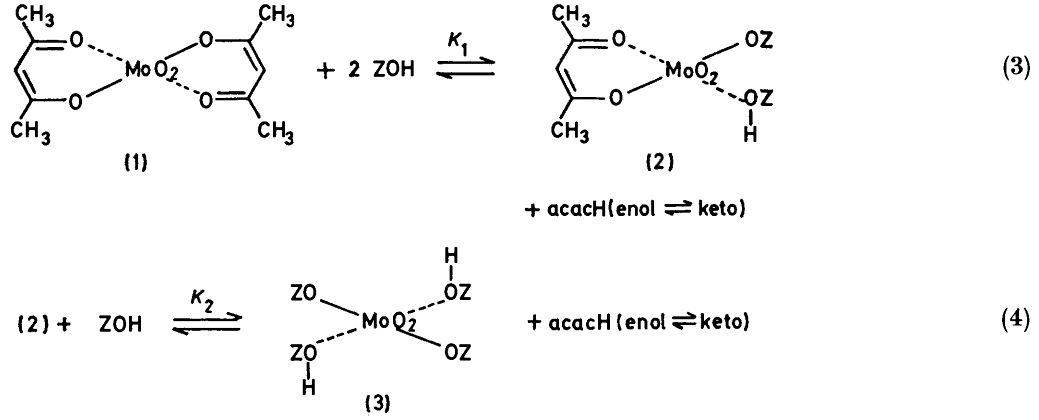


FIGURE 2 ^{1}H N.m.r. spectrum (90 MHz) of 0.01M-$MoO_2(acac)_2$ in $[^2H_6]$ethanol at 28.0°

We interpret these observations as indicating that dissolving $MoO_2(acac)_2$ in alcohols results in the equilibrium dissociation of one or more diketone ligands, to yield equilibria (3) and (4). As the concentrations of $MoO_2(acac)_2$ employed in the n.m.r. experiments (*ca.*

10^{-2}M) are vastly different from those in the rate experiments (10^{-5}M), no attempt was made to estimate the relative amounts of (1) to (2) to (3) present at equilibrium in the n.m.r. conditions.



(3)

(4)

Inhibition Experiments.—As equilibria (3) and (4) depend on the acetylacetone concentration, a study of the effect of the addition of acacH on the oxidation rates might provide useful data on the relative catalytic activity of species such as (1)—(3). In Table 2 the variation of the rate constant upon addition of increasing amounts of acacH is shown for two concentrations of $MoO_2(acac)_2$ and in two alcohols.

TABLE 2

Effect of the addition of acetylacetone (acacH) upon the rates of the molybdenum catalysed oxidation of di-n-butyl sulphide with t-butyl hydroperoxide in two alcohols at 25.00 ± 0.05 [a]

$10^5[\text{Cat}]_0$/M	$10^5[\text{acacH}]_{\text{st}}$ [b]/M	$10^3k_{2,\text{obs}}$ [c]/l mol^{-1} s^{-1}	
		EtOH	Pr^{i}OH
			0.008
0.39	0.78		1.26
0.39	20.8		0.228
0.39	101.0		0.079
0.39	501.0		0.017
		0.011	
1.00	2.00	1.31	
1.00	3.00	1.09	
1.00	4.00	1.00	
1.00	7.00	0.637	
1.00	15.3	0.325	
1.00	35.3	0.157	
1.00	48.6	0.115	
1.00	102.1	0.073	
1.00	202.1	0.049	
2.00	4.0	2.00	
2.00	6.3	1.70	
2.00	8.7	1.30	
2.00	13.3	0.881	
2.00	27.3	0.401	
2.00	51.0	0.261	
2.00	144.0	0.108	
2.00	237.7	0.065	

[a] In all experiments $[Bu_2^nS]_0 = 0.23$M and $[Bu^tO_2H] = 0.01$M. [b] Total concentration of acacH calculated as $2[MoO_2(acac)_2] + [\text{acacH}]$ added. [c] Estimated as $k_{1,\text{obs}}/[Bu_2^nS]_0$ from experiments under pseudo-first-order conditions.

As the amount of added acetylacetone is increased, the rates approach the value of the uncatalysed reaction. In fact, at [acacH] 2.0×10^{-3}M, with $[MoO_2(acac)_2]$ 1.0×10^{-5}M, the rate constant of the catalysed reaction in EtOH is only four times larger than that of the uncatalysed process; in the absence of added acacH the catalysed process is faster by a factor of *ca.* 100. The first conclusion which may be drawn from this result is that undissociated $MoO_2(acac)_2$, *i.e.* (1), is not the compound leading to the peroxide-containing catalytically active species, which is therefore likely to be produced through equilibria (3) and (4). In fact, the n.m.r. experiments indicate that both equilibria are likely to be involved.

If only equilibrium (3) is taken into account, the active catalyst would be (2) and hence the general rate equation is (5). Expressing [(2)] as a function of stoicheiometric

$$v = \{k_2^0 + k_3[(2)]\}[\text{sulphide}][Bu^tO_2H] \qquad (5)$$

molybdenum, $[\text{Mo}]_{\text{st}}$, and the appropriate equilibrium constant K_1, equation (5) becomes (6). Equation (6)

$$\frac{v}{[\text{sulphide}][Bu^tO_2H]} = k_{2,\text{obs}} = k_2^0 + \frac{k_3K_1[\text{Mo}]_{\text{st}}}{K1 + [\text{acacH}]} \qquad (6)$$

requires that a plot of $1/(k_{2,\text{obs}} - k_2^0)$ *versus* [acacH] be linear. However, this is not the case as some curvature of this plot is observed.

Therefore, both species (2) and (3) [equations (3) and (4)] must be assumed to be precursors of the oxidizing species and hence the kinetic equation (7) should be

$$\frac{v}{[\text{sulphide}][Bu^tO_2H]} = k_{2,\text{obs}} - k_2^0 = k_3'[(2)] + k_3''[(3)] \qquad (7)$$

observed. Taking into account the mass balance equations $\{i.e., [\text{Mo}]_{\text{st}} = [(1)] + [(2)] + [(3)]$ and $[\text{acacH}]_{\text{st}} = [\text{acacH}] + [(2)] + 2[(1)]\}$, the equilibrium concentration of (2) and (3) can be obtained as a function of $[\text{Mo}]_{\text{st}}$ and of the appropriate values of K_1 and K_2 defined as in equations (3) and (4).

Knowing the $k_{2,\text{obs}}$ and k_2^0 values, this would allow the k_3' and k_3'' values to be obtained from equation (7). A computer program was developed which, by an iteration procedure, sets the best K_1, K_2, k_3', and k_3'' values to fit the observed variation of $k_{2,\text{obs}}$ as a function of stoicheiometric acetylacetone. The computer analysis was run using two sets of $k_{2,\text{obs}}$ values independently obtained for two stoicheiometric concentrations of molybdenum, both in EtOH, covering in each case a wide range of acacH concentrations (Figure 3).

The values of kinetic and equilibrium constants obtained for the two sets of data (*i.e.*, k_3' $1.3 \pm 0.3 \times 10^2$, $1.1 \pm 0.1 \times 10^2$ l^2 mol^{-2} s^{-1}; k_3'' $1.6 \pm 0.7 \times 10^2$, $1.7 \pm 0.2 \times 10^2$ l^2 mol^{-2} s^{-1}; K_1 2.8 ± 1.1, 2.9 ± 1.2 mol l^{-1}; K_2 $0.27 \pm 0.09 \times 10^{-4}$, $0.43 \pm 0.02 \times 10^{-4}$ mol l^{-1}) are in close agreement, supporting the kinetic model advanced. It is noteworthy that, based on the k_3' and k_3'' values estimated, the Mo^{VI} species (2) and (3) seem to give rise to almost equally effective metal–hydroperoxide catalytic complexes.

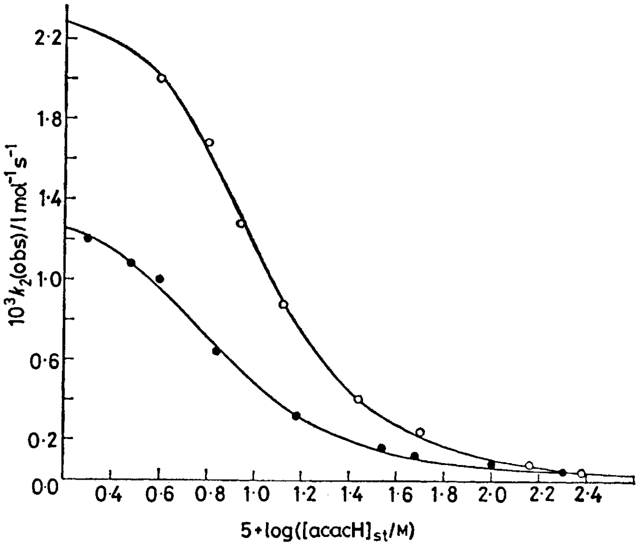


FIGURE 3 Calculated (see text) $k_{2,\text{obs}}$ values (oxidation of $Bu_2{}^nS$ by Bu^tO_2H), as a function of added acetylacetone for $[MoO_2(acac)_2]_0$ 1.0×10^{-5}M (lower curve) and 2.0×10^{-5}M (upper curve). The circles are experimental points (see Table 1)

The degree of dissociation of (1) to yield (2) and (3) depends, of course, on the $MoO_2(acac)_2$ initial concentration so that a decrease in the catalytic activity with increasing molybdenum concentration is expected and is, in fact, experimentally observed for EtOH (Figure 1). However, a comparison of the curve of $k_{2,\text{obs}}$ *versus* $[MoO_2(acac)_2]$, calculated by employing kinetic and equilibrium constants provided by the computer program, with that experimentally observed (see Figure 4) shows that in the latter the curvature is more pronounced. This, in turn, indicates that other factors, such as aggregation of molybdenum species, may be involved.

Effect of Changing Catalyst Precursor.—In Table 2 data are reported which illustrate the effect of changing the catalyst precursor from $MoO_2(acac)_2$ to bis(dipivaloylmethanato)dioxomolybdenum(VI), $MoO_2(dpm)_2$, in EtOH. In the Mo^{VI} concentration interval explored, the observed rates for $MoO_2(acac)_2$ catalysis are consistently faster than those for $MoO_2(dpm)_2$. Based on $k_{2,\text{obs}}$ *versus* catalyst concentration plots,[11] data in Table 3 allow an estimate of an apparent catalytic third-order constant of *ca.* 60 l^2 mol^{-2} s^{-1} for $MoO_2(dpm)_2$, which is *ca.* 2.7 times lower than that observed for $MoO_2(acac)_2$ catalyst precursor.[11] The difference in rates observed should depend at least on two factors: (a) the relative amounts of species (1)—(3) present at equilibrium and hence on the concentration of catalytic active species, and (b) the reactivity of (2). Both factors are related to the nature of the diketonate ligand.

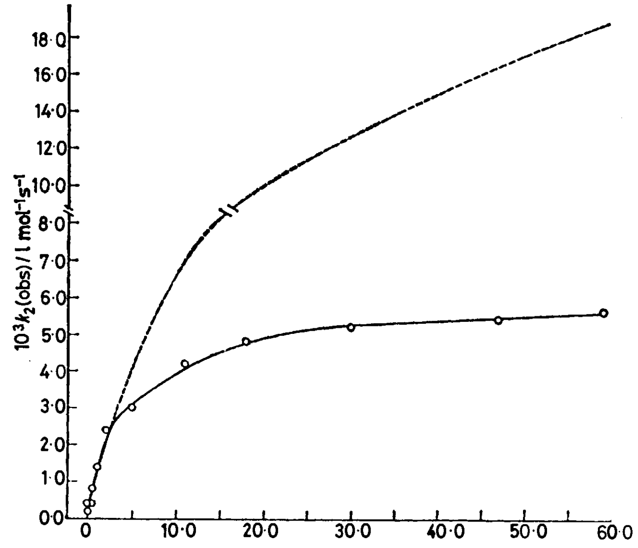


FIGURE 4 Calculated (upper curve) and experimental (lower curve) $k_{2,\text{obs}}$ values (oxidation of $Bu_2{}^nS$ by Bu^tO_2H) as a function of added $[MoO_2(acac)_2]_0$

This result is in apparent contradiction with the hypothesis advanced for closely related oxidizing systems (*e.g.* the molybdenum-catalysed cyclohexene epoxidation in hydrocarbon solvent at 60°) [3,5,6] that molybdenum-catalyst precursor complexes lose their original ligand environment entirely during reaction. However, it is likely that the different results depend on the different reaction conditions, *i.e.* that in the more severe conditions adopted by other authors,[5] a complete ligand displacement and concurrent oxidation of diketonate might occur.

TABLE 3

Dependence of rates on catalyst concentration in the oxidation of di-n-butyl sulphide by t-butyl hydroperoxide in the presence of $MoO_2(dpm)_2$ in ethanol at $25.00 \pm 0.05°$ [a]

$10^5[MoO_2(dpm)_2]$/M	$10^3k_{2,\text{obs}}$ [b]/l mol^{-1} s^{-1}
none	0.011
1.70	1.06
4.11	2.64
8.22	4.73
9.14	5.63

[a] In all experiments, $[Bu_2{}^nS]_0 = 0.24$M and $[Bu^tO_2H]_0 = 1.0 \times 10^{-2}$M. [b] As note *c*, Table 2.

Effect of Changing Hydroperoxide.—A few experiments were carried out using n-butyl hydroperoxide as oxidant instead of t-butyl hydroperoxide in the same system. Comparison of data collected in Table 4 with those previously obtained using Bu^tO_2H reveals that oxidation rates are not significantly affected by the change from Bu^t to Bu^n. This indicates that changes in leaving group or steric effects on going from Bu^n to Bu^t are not relevant; also, no alkyl group shift should occur at any stage of the reaction. Thus, nucleophilic attack by the sulphide on the O–O bond should occur at the hydroperoxide oxygen distal from the alkyl group (a common feature of hydroperoxide chemistry).[12]

Effect of Added Acid.—In a previous paper [11] we reported that methanesulphonic acid acts as an effective *inhibitor* of molybdenum-catalysed sulphide oxidation. For example, for 0.59×10^{-5}M-Mo^{VI}, addition of 1.3×10^{-4}M-$MeSO_3H$ depresses the oxidation rate by a factor of *ca.* 5.[11] In the light of the results reported in the present study, this should be taken as to indicate that equilibria involving formation of other Mo^{VI} species starting with $MoO_2(acac)_2$ in alcohol solvent are pH-dependent.

TABLE 4

Dependence of rates on catalyst concentration in the oxidation of di-n-butyl sulphide by n-butyl hydroperoxide in the presence of $MoO_2(acac)_2$ in ethanol at 25.00 ± 0.05° [a]

$10^5[MoO_2(acac)_2]$/M	$10^3 k_{2,obs}$ [b]/l mol^{-1} s^{-1}
0.29	0.482
1.18	1.92
1.80	2.97
4.60	6.70

[a] In all experiments $[Bu_2^nS]_0 = 0.20$M and $[Bu^nO_2H]_0 = 1.0 \times 10^{-2}$M. [b] As note *c*, Table 2.

To rationalize this one can envisage that complexes (2) and (3) behave as the conjugate acids of molybdate anions and undergo acid ionization equilibria (8) and (9) to yield (2′) and (3′).

$$MoO_2(acac)ZO(ZOH) \rightleftharpoons \underset{(2')}{[MoO_2(acac)(ZO)_2]^-} + H^+ \qquad (8)$$

$$MoO_2(ZO)_2(ZOH)_2 \rightleftharpoons \underset{(3')}{[MoO_2(ZO)_3ZOH]^-} + H^+ \qquad (9)$$

Solvolysis of $MoO_2(acac)_2$ should therefore depend on the acidity of the medium. In particular, as the activity of the proton in the solution is increased, both acid–base and solvolytic equilibria move to the left, the equilibrium concentrations of (2′) and (3′) decrease and undissociated $MoO_2(acac)_2$ increases. The overall effect should be, as is observed, a decrease of the catalytic efficiency of the system.

Obviously the observed dependence of the rate of the catalytic process upon medium acidity introduces one more complicating factor, which calls for more detailed studies on acid–base equilibria involving alkoxymolybdenum(VI) species generated upon dissolving bisdiketonatomolybdenum(VI) complexes in alcohols.

Conclusions.—The results reported here underline some of the complexities involved in the rationalisation of these processes, in that the metal–catalyst compound initially added may give rise to equilibrium formation of other catalyst species by changing totally or in part the original ligand environment. The balance among these species should depend upon (a) the reaction conditions, (b) the nature of the solvent, and (c) the tendency of the original ligand to remain more or less tightly bound to the metal ion. The chemical stability of the ligands under the reaction conditions is also relevant.

The nature of the alcoholic solvent should, in particular, play an important role in determining the rates of the oxidation process. The change from methanol to ethanol and to propan-2-ol may affect (a) the dissociation equilibria of acetylacetonate species, (b) the complexation to the metal of the peroxide, which competes with the alcohol solvent, and (c) the peroxide oxygen-transfer process to the substrate. The latter effect is usually small [12] and hence the other two factors should account for the overall kinetic behaviour. Increasing basicity of alcohols would result in an accelerating effect, according to (a) and a decelerating effect according to (b) and (c).

For the MoO_2^{2+}-acetylacetone type of complex it seems important that at least one ligand is displaced by the solvent if effective catalytic species are to be generated.[15] Akin to this suggestion is the observation that Mo^{VI} complexes such as MoO_3(diethylenetriamine) or $Na_4[Mo_2O_6(edta)]$, with ligands which are tightly held around the metal ion, are inefficient catalysts in the epoxidation of cyclohexane by hydroperoxides, whereas MoO_2(quinolin-8-ol)$_2$ and $MoO_2(acac)_2$ are found to behave satisfactorily.[16] Furthermore Michaelson *et al.* have reported that the *N*-phenyl-benzohydroxamate complex, $MoO_2[PhN(O)COPh]_2$, is almost inactive as a catalyst in the epoxidation of allylic alcohols by Bu^tO_2H under conditions (benzene solvent; 80°; 2 h) where $Mo(CO)_6$ or $MoO_2(acac)_2$ are efficient catalysts.[10] Furthermore, the same authors report that, under the reaction conditions given above, β-diketonato-ligands are rapidly destroyed ', whereas our results (rate inhibition by acetylacetone, effect of changing catalyst precursor, *etc.*) suggest that under the mild conditions adopted (alcohol solvents; 25°) the β-diketone is not oxidized.

Thus, an understanding of the modifications of the metal–catalyst species seems crucial to design oxidation systems giving maximum efficiency and selectivity. We feel the results reported here are a step in this direction.

EXPERIMENTAL

Materials.—Commercial di-n-butyl sulphide, t-butyl hydroperoxide, acetylacetone, and bis(acetylacetonato)dioxomolybdenum(VI) were purified as previously reported; [11] n-butyl hydroperoxide was prepared by solvolysis in basic hydrogen peroxide solution of the n-butyl methanesulphonate, according to a reported procedure.[17] Bis(dipivaloylmethanato)dioxomolybdenum(VI) was prepared and purified by a reported procedure.[18] Anhydrous alcohols were obtained by standard procedures starting from high purity commercial samples, and kept over 4A molecular sieves.

Spectroscopic Experiments.—^{1}H N.m.r. spectra were recorded on a Bruker HFX-10 instrument at 90 MHz with tetramethylsilane as internal standard, in $[^2H_6]$ethanol.

The chemical shifts were read to ±0.1 Hz with a frequency difference counter.

Kinetic Experiments.—All operations were performed under dry nitrogen with temperature control to better than ±0.050°, following the procedure previously reported.[11, 13]

Computer Calculations.—Combination of equations (5)—(7) gives the third-order equation (10) which is solved for

$$\frac{(\mathrm{acacH})^3}{K_1K_2} + \left\{\frac{2[\mathrm{Mo}]_{\mathrm{st}} - [\mathrm{acacH}]_{\mathrm{st}}}{K_2} + 1\right\}\frac{[\mathrm{acacH}]^2}{K_1} + \left\{\frac{[\mathrm{Mo}]_{\mathrm{st}} - [\mathrm{acacH}]_{\mathrm{st}}}{K_1} + 1\right\}[\mathrm{acacH}] = [\mathrm{acacH}]_{\mathrm{st}} \qquad (10)$$

[acacH] with standard numerical methods. The concentrations of (2) and (3) are then obtained from equations (7) and (10).

The equilibrium and kinetic constants K_1, K_2, k_3', and k_3'' were simultaneously obtained by means of a computer program adaption of the 'bit-mapping' least-squares method of Sillen.[19]

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