Metal Catalysis in Oxidation by Peroxides. Part 2.[1] Molybdenum Catalysed Oxidation of Organosulphur Compounds by t-Butyl Hydroperoxide

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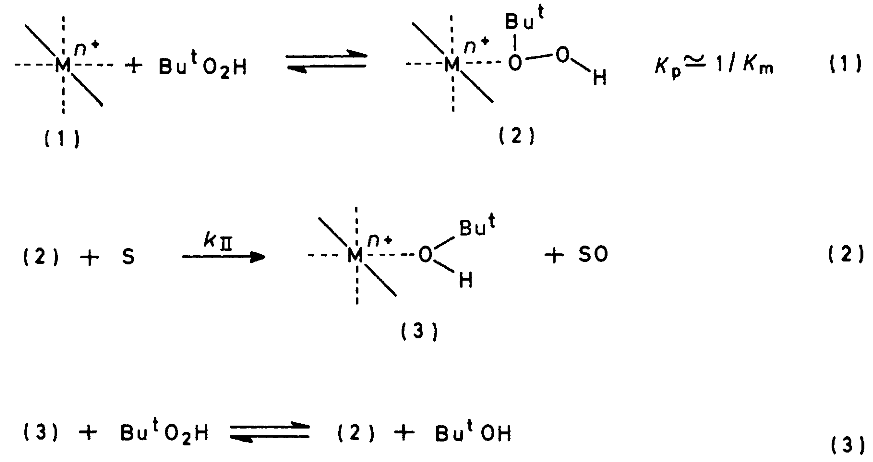
The reaction of di-n-butyl sulphide with t-butyl hydroperoxide in dry ethanol at 25°, catalysed by dioxomolybdenum-(VI) acetylacetonate, affords di-n-butyl sulphoxide in quantitative yield. The kinetics conform to a rate law which is first order in sulphide and hydroperoxide; in the range of catalyst concentrations from 1.0×10^{-7} to *ca.* 200×10^{-7}M, it is first order in the molydbdenum chelate, allowing a catalytic third-order rate constant (k_3) of 162 l^2 mol^{-2} s^{-1} to be estimated. This is *ca.* 2×10^4 highe1 than the k_3 value determined for catalysis by methanesulphonic acid, a typical strong protic acid, in the same solvent. At a given sulphide and metal catalyst concentration, dependence of rates on the initial concentration of Bu^tO_2H suggests that a Michaelis–Menten type rate law holds. A Lineweaver–Burk type treatment of data allows values of 0.56 mol l^{-1} for K' (a constant related to the dissociation constant of a postulated intermediate hydroperoxide–metal ion complex) and 103 l mol^{-1} s^{-1} for k_{II} (the limiting specific rate constant for rate-determining nucleophilic attack by the sulphide on the metal ion-activated peroxide molecule) to be estimated. The relative rates of oxidation of some representative substrates were found to decrease in the order Bu^n_2S (100) > Bu^n_2S=O (0.15) ≫ cyclohexene (0.01), indicating that the molybdenum-catalysed reaction is quite sensitive to substrate nucleophilicity.

THE use of molybdenum and vanadium catalysts for the epoxidation of olefins by hydroperoxides is well known.[2] Epoxidation of structurally simple alkenes by t-butyl hydroperoxide catalysed by dioxomolybdenum(VI) acetylacetonate and by a number of chelated diketonates of oxovanadium(IV) were found to be highly selective, yielding only the corresponding epoxides and t-butyl alcohol.[3] Although careful kinetic studies have indicated a heterolytic rather than free radical character of these reactions and have provided evidence of the intervention of a hydroperoxide–metal ion complex, questions are unanswered on the detailed mechanism.[2,3]



SCHEME

In a recent paper we reported on the general features of the homogeneous catalysis by bisacetylacetonato-oxovanadium(IV) in the oxidation of organic sulphides by Bu^tO_2H in ethanol, pointing out that these substrates can be successfully adopted as model compounds to investigate the characteristics of metal-ion catalysed oxygen-transfer reactions.[1] In fact, as for vanadium and molybdenum catalysed olefin epoxidation[3] and

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[1] Part 1, R. Curci, F. Di Furia, R. Testi, and G. Modena, *J.C.S. Perkin II*, 1974, 752.

[2] (*a*) R. Hiatt in 'Oxidation,' eds. R. L. Augustine and D. J. Trecker, Marcel Dekker, New York, vol. II, ch. 3, pp. 113*ff*; (*b*) A. R. Doumaux, jun., *ibid.*, ch. 4, pp. 141 *et seq*; (*c*) G. Sosnowasky and D. J. Rawlison in 'Organic Peroxides,' ed. D. Swern, Wiley-Interscience, New York, 1970, vol. I, chs. 9, 10; 1971, vol. II, chs. 2, 3; (*d*) M. N. Sheng and J. G. Zajacek in 'Oxidation of Organic Compounds,' Advances in Chemistry Series no. 76, American Chemical Society, Washington, 1968, vol. II, pp. 418*ff*; see also references quoted in these reviews.

[3] (*a*) C.-C. Su, J. W. Reed, and E. S. Gould, *Inorg. Chem.*, 1973, **12**, 337; (*b*) E. S. Gould, R. R. Hiatt, and K. C. Irwin, *J. Amer. Chem. Soc.*, 1968, **90**, 4573; see also references therein.

amine oxidation,[4] our data suggested sulphide oxidation occurs by means of nucleophilic attack by the substrate at the O–O bond of a hydroperoxide–metal ion complex (Scheme).

In the Scheme, where S is the substrate and SO the oxidized substrate, equation (2) is rate determining. Regeneration of the hydroperoxide–metal ion complex, which occurs in step (3), could be mediated by a nucleophilic solvent (*e.g.* ethanol) *via* the formation of species where the solvent takes the place of Bu^tOH or Bu^tO_2H in (2) or (1), respectively.[1]

Such species, of course, might also be involved in the equilibrium formation of the hydroperoxide–metal ion complex, as it is likely that, in alcoholic solvents, Bu^tO_2H has to displace at least one co-ordinated solvent molecule to form (1).[1]

According to the Scheme it would be expected that changing the nature of the metal ion should influence the reaction rate since both the steady-state concentration of the active complex (2) in equation (1) and the rate constant k_{II} of the rate-determining step (2) might vary.

In fact, it has been reported that, under similar conditions, epoxidation of cyclohexene by Bu^tO_2H catalysed by $MoO_2(acac)_2$ proceeds *ca.* 10^2 times as fast as that catalysed by vanadium chelates.[3] Wishing to verify this, and in the hope of gaining insight into the mechanism we decided to study the effect of changing the catalyst from $VO(acac)_2$ to $MoO_2(acac)_2$ in the oxidation of organic sulphides by Bu^tO_2H.

EXPERIMENTAL

Materials.—Di-n-butyl sulphide, di-n-butyl sulphoxide, commercial cyclohexene, and t-butyl hydroperoxide were purified as previously reported.[1] Dioxomolybdenum(VI) acetylacetonate was purified by crystallization dissolving the commercial product in warm acetylacetone, then adding ligroin; the precipitate, a yellow powder, collected by filtration and washed several times with ligroin, was dried and kept under nitrogen, m.p. (decomp.) 185°; $\nu_{max.}$ (Nujol) 940 and 910 cm^{-1} (Mo=O stretch). Anhydrous ethanol was obtained by standard procedures starting from high purity commercial samples, and kept over 4A molecular sieves (Linde).

Stoicheiometry.—Experiments to establish stoicheiometry, carried out as described previously[1] or by g.l.c. techniques, have shown that $Bu^n_2S{=}O$ is produced in $\geqslant 90\%$ yield in the reaction of Bu^n_2S with Bu^tO_2H catalysed by $MoO_2(acac)_2$. In a typical experiment, Bu^n_2S (0.846 g, 5.8 mmol) was oxidized with Bu^tO_2H (0.498 g, 5.7 mmol) and $MoO_2(acac)_2$ (0.081 g, 0.24 mmol) under nitrogen in anhydrous ethanol containing nonadecane (0.028M) as an internal g.l.c. standard. After *ca.* 2 h the reaction was complete (iodimetric titre), and analysis of g.l.c. data (column conditions given in ref. 1) showed that >98% $Bu^n_2S{=}O$ (identified by g.l.c. retention time and i.r. spectrum) had been produced.

U.v. Spectra.—The electronic spectrum of $MoO_2(acac)_2$ in dry ethanol shows two distinct maxima in the $\pi \longrightarrow \pi^*$ transitions region at 273 (ε *ca.* 20 000) and 318 nm (ε *ca.* 4 500). A slow decrease of the intensity occurs with standing and/or exposure of the solutions to atmospheric moisture. A marked decrease in band intensity was also observed upon increasing of water content from 0 to 10%.[4] In dry ethanol, addition of Bu^tO_2H also promotes changes in the intensity of these two transitions. With 6×10^{-5}M-$MoO_2(acac)_2$ and 5×10^{-2}M-Bu^tO_2H the band at 318 nm disappears, and the spectrum consists of just one band near 273 nm. Again, a slow decrease in the intensity of this band with time is observed. By way of contrast, addition of excess (up to *ca.* 0.5M) Bu^n_2S has practically no effect on the appearance of the u.v. spectrum of $MoO_2(acac)_2$ in ethanol.

Kinetics.—Kinetic experiments were performed following the procedure previously described.[1] Carefully dried ethanol was used, and freshly prepared solutions of the catalyst were employed in each run. In most instances, as well as sulphide oxidation, the metal-catalysed decomposition of the hydroperoxide was monitored under identical conditions.

RESULTS

Similar to the vanadium catalysed reaction,[1] we find that oxidation of organic sulphides to the parent sulphoxides by Bu^tO_2H occurs readily in the presence of $MoO_2(acac)_2$. Upon reacting equimolar quantities of Bu^n_2S with Bu^tO_2H in ethanol containing molybdenum in catalytic amounts $\{$*i.e.* $[Bu^tO_2H]_0/[MoO_2(acac)_2]_0$ 20—50$\}$, the 1 : 1 stoicheiometry was established by the nearly quantitative yield of the product sulphoxide (see Experimental section).

Kinetic experiments were carried out under pseudo-first-order conditions with sulphide 10—60 times in excess over Bu^tO_2H; log$[Bu^tO_2H]$–time plots were linear to at least 80% reaction in the great majority of runs. By following the decay of Bu^tO_2H concentration in the presence of the metal-ion chelate, but in the absence of sulphide, it was verified that metal-catalysed peroxide decomposition does not compete with substrate oxidation. Preliminary kinetic data are collected in Table 1.

Apparently, neither the presence of nitrobenzene (a radical trap) nor a change of atmosphere from dry nitrogen to oxygen affect the rates significantly. This finding, coupled with the straight forward reaction stoicheiometry and reproducible kinetics observed, rules out a radical-chain path.

Data in Table 2 show that di-n-butyl sulphoxide is much less reactive than the parent sulphide. For the three substrates examined, the rate constant decreases in the order $Bu^n_2S \gg Bu^n_2S{=}O \gg$ cyclohexene. As this is also the order of decreasing substrate nucleophilicity,[5] it is apparent that oxidation involves transfer of electrophilic oxygen from the metal-activated hydroperoxide molecule.

At constant Bu^tO_2H and Bu^n_2S initial concentrations, the rates increase on increasing metal catalyst concentration (Table 3). A plot of k_{2obs} *versus* $[MoO_2(acac)_2]_0$ is linear up to *ca.* 1×10^{-5}M-catalyst: a log–log plot of data in this interval gives a slope of *ca.* 0.9, indicating that the order in catalyst is near unity.

Limited to the initial range of metal catalyst concentrations, therefore, the rate equation (4) can be assumed to

$$v = -(d[Bu^tO_2H]/dt) = (k_2^0 + k_3[Cat]_0)[S][Bu^tO_2H] \quad (4)$$

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[4] H. Gehrke and J. Veal, *Inorg. Chim. Acta*, 1969, **3**, 623.

[5] R. Curci, R. A. Di Prete, J. O. Edwards, and G. Modena, *J. Org. Chem.*, 1970, **35**, 740.

hold. In the k_{2obs} *versus* $[MoO_2(acac)_2]_0$ plot, the deviation from linearity becomes increasingly pronounced at higher concentrations, yielding a curve with rapidly diminishing slope. This indicates departure from simple first-order dependence on the metal ion and might be rationalized by invoking formation of catalyst dimers and/or special complexing.[6,7] Although this phenomenon seems worthy of further investigation, we decided to restrict our kinetic studies within the range of catalyst concentration where an uncomplicated rate law, *i.e.* equation (4), is likely to hold. Hence, on basis of the data in Table 3, a catalytic third-order rate constant (k_3) of 162 ± 1 $l^2\ mol^{-2}\ s^{-1}$ could be estimated. This is *ca.* 80 times higher than the k_3 value estimated for $VO(acac)_2$-catalysed di-n-butyl sulphide oxidation by Bu^tO_2H in the same solvent.

TABLE 1

Rates of oxidation of di-n-butyl sulphide by t-butyl hydroperoxide catalysed by added $MoO_2(acac)_2$ at 25.00 ± 0.05° in dry ethanol

Atmosphere	$[Bu^n_2S]_0$/M	$[Bu^tO_2H]_0$/M	$10^5[Mo^{VI}]_0$/M	$10^3k_{1obs}/s^{-1}$	10^3k_{2obs} [a]/ $l\ mol^{-1}\ s^{-1}$
Dry N_2	0.280	0.011	0.91	0.417	1.49 [b]
Dry O_2	0.280	0.011	0.91	0.419	1.50
Dry N_2 [c]	0.280	0.011	0.91	0.166 [c]	0.59 [c]
Dry N_2	0.500	0.044	1.49	0.933	1.99
Dry N_2	0.250	0.044	1.49	0.479	1.92
Dry N_2	0.100	0.044	1.49	0.196	1.96

[a] Estimated as $k_{1obs}/[Bu^n_2S]_0$ from experiments under pseudo-first-order conditions. [b] Unaffected by the addition of 0.01M-nitrobenzene. [c] Solvent 99% ethanol.

TABLE 2

Rates of oxidation of some organic substrates by t-butyl hydroperoxide catalysed by added $MoO_2(acac)_2$ in dry ethanol at 25.0° under N_2

Compound	[Substrate]$_0$/M	$[Bu^tO_2H]_0$/M	$10^5[Mo^{VI}]_0$/M	$10^5k_{2obs}/l\ mol^{-1}\ s^{-1}$ [a]
Bu^n_2S	0.250	0.011	1.19	197
Bu^n_2SO	0.720	0.011	1.19	0.132
Cyclohexene	0.700	0.011	1.19	0.01 [b]
Bu^n_2S	0.185	0.026	150	676
Bu^n_2SO	0.180	0.025	150	1.04
Cyclohexene	0.50	0.045	150	0.07 [c]

[a] From experiments under pseudo-first-order conditions, as k_{1obs}/[substrate]$_0$. [b] Roughly estimated from the first 10% reaction, as independent experiments revealed that, under these conditions, peroxide decomposition competes effectively with alkene oxidation. [c] Estimated at 25.0° from an Arrhenius plot by using k_{2obs} values of 6.20×10^{-5} and $1.19 \times 10^{-5}\ l\ mol^{-1}\ s^{-1}$ obtained at 60.0 and 45.0°, respectively.

TABLE 3

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

$10^5[Mo^{VI}]_0$/M	0.000	0.098	0.136	0.195	0.273	0.365	0.445
$10^3k_{2obs}/l\ mol^{-1}\ s^{-1}$	0.011	0.230	0.300	0.410	0.550	0.815	0.868
$10^5[Mo^{VI}]_0$/M	0.586	0.909	1.90	5.18	11.0	18.0	30.0
$10^3k_{2obs}/l\ mol^{-1}\ s^{-1}$	1.20	1.55	2.44 [b]	3.08 [b]	4.22 [b]	4.71 [b]	5.21 [b]
$10^5[Mo^{VI}]_0$/M	47.0	60.0	150				
$10^3k_{2obs}/l\ mol^{-1}\ s^{-1}$	5.40 [b]	5.60 [b]	6.76 [b]				

[a] In the majority of runs $[Bu^n_2S]_0$ was in the range 0.28—0.22M, with $[Bu^tO_2H]_0$ *ca.* 0.011M; k_{2obs} were estimated as $k_{1obs}/[Bu^n_2S]_0$ from experiments under pseudo-first-order conditions. [b] Data not considered in estimating the catalytic third-order rate constant k_3 from a k_{2obs} *versus* $[Mo^{VI}]_0$ plot; this gives $k_3 = 162 \pm 1\ l^2\ mol^{-2}\ s^{-1}$.

TABLE 4

Catalysis by methanesulphonic acid in the oxidation of di-n-butyl sulphide by t-butyl hydroperoxide in dry ethanol at 25.00 ± 0.05°, and effect of addition of small amounts of the same strong protic acid on rates of $MoO_2(acac)_2$ catalysed oxidation [a]

$10^5[Mo^{VI}]_0$/M	$10^5[MeSO_3H]_0$/M	10^3k_{2obs}/ $l\ mol^{-1}\ s^{-1}$ [b]
	242	0.051 [c]
	1 000	0.154 [c]
	10 000	0.902 [c]
0.586		1.20
0.586	1.32	0.75
0.586	13.2	0.25

[a] [Sulphide]$_0$ and $[Bu^tO_2H]_0$ were in each case near to 0.20 and 0.01M, respectively. [b] Estimated as $k_{1obs}/[Bu^n_2S]_0$. [c] A plot of k_{2obs} *versus* $[MeSO_3H]_0$ gives $k_3 = 8.6 \pm 0.2 \times 10^{-3}\ l^2\ mol^{-2}\ s^{-1}$.

Wishing to compare catalysis of sulphide oxidation by metal ions with the better established catalysis by strong protic acids,[8] we collected the data shown in Table 4. Application of equation (4) gives k_3 value of 0.008 6 ± 0.000 2 $l^2\ mol^{-2}\ s^{-1}$ for catalysis by methanesulphonic acid (a typical strong protic acid) for the oxidation of Bu^n_2S by Bu^tO_2H in dry ethanol. As pointed out previously,[1-3] a reaction path of the kind in the scheme implies that kinetics conform to a Michaelis–Menten type rate law (5). Here,

$$v = k_{II}[Cat]_0[S][Bu^tO_2H]/(K' + [Bu^tO_2H]) \qquad (5)$$

k_{II} is the limiting rate constant, which would be observed at very high hydroperoxide : catalyst ratios, and K' is a 'steady-state' constant related to $1/K_p$, the dissociation

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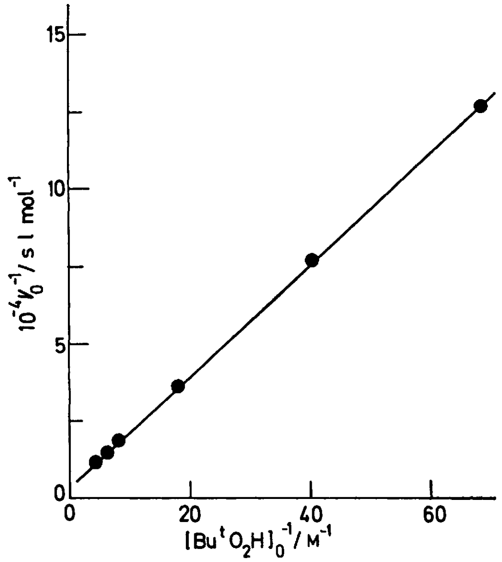
[6] P. C. H. Mitchell, *Quart. Rev.*, 1966, **20**, 103.

[7] R. A. Sheldon, *Rec. Trav. chim.*, 1973, **92**, 253, 367.

[8] M. A. P. Dankleff, R. Curci, J. O. Edwards, and H. Y. Pyun, *J. Amer. Chem. Soc.*, 1968, **90**, 3209; see also references therein.

constant of the active hydroperoxide–metal ion complex (2) [equation (1)].

It should be noted, however, that K' is also related to the equilibrium involving regeneration of the active complex [equation (3)], and may embrace all equilibria that, starting with $MoO_2(acac)_2$, yield (*via* ligand exchange) the actual active complex precursor (1). Indeed, the structure of the latter was represented as a generic hexaco-ordinate metal-ion species (Mo^{VI}, in our case) in the Scheme. For these reasons, we shall refer to K' as to the ' apparent ' Michaelis constant.



Lineweaver–Burk type plot for the molybdenum catalysed oxidation of di-n-butyl sulphide by t-butyl hydroperoxide in dry ethanol at 25.00°, showing the effect of changing [peroxide]$_0$ on rates at constant sulphide ($[Bu_2^nS]_0$ 0.5M) and metal catalyst ($[Mo^{VI}]_0$ 0.6 × 10^{-5} M)

Kinetic data in the Figure illustrate the effect of changing initial hydroperoxide concentration on initial rates. Treatment of the data according to the method of Lineweaver and Burk[9] provides, from $1/v_0$ *versus* $1/[Bu^tO_2H]_0$ plots, k_{II} and K' values; these are 103 ± 5 l mol^{-1} s^{-1} and 0.56 ± 0.03 mol l^{-1}.

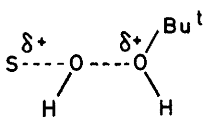
DISCUSSION

Consistent with the general mechanism summarized in the Scheme, the observed rate law (4) suggests a transition state composed by one molecule each of sulphide, hydroperoxide, and catalyst. Similar to the transition metal ion-catalysed oxidation of alkenes by hydroperoxides,[2] nucleophilic attack by the substrate at the O–O bond of a hydroperoxide–catalyst complex formed in a prior stage can be envisaged. Formation of a Bu^tO_2H–metal ion complex was also suggested by spectroscopic evidence (see Experimental section).

The kinetic data (Tables 3 and 4) clearly show that, as for vanadium(v),[1] the molybdenum(vi) species are much more effective catalysts than H^+. As already pointed out,[1] transition state (7) proposed for metal-catalysed sulphide oxidation bears much resemblance to transition state (6) advanced for catalysis by strong protic acids in the same oxidation; this involves pre-equilibrium protonation of the hydroperoxide to give $Bu^tO_2H_2^+$.[10] For the catalytic intermediate complex, of course, structure (2), related to (7), is not the only one that can be conceived, as the formation of other metal–hydroperoxide species such as, *e.g.*, (8) and (9) can also be envisaged.

Interconversion of metal–hydroperoxide complexes having different geometry might occur by fast equilibrium reactions, and indeed the steady-state concentration of catalytically active species can be quite small. Finally, the possibility exists that $MoO_2(acac)_2$ loses, at least in part, its original acetylacetonato-ligand in the solvent and conditions adopted.

Granted that further detailed studies are needed to shed light on the complexities of the catalyst system, our first attempt was to study the effect of adding a strong protic acid on the rate. The results reported in Table 4 show that addition of small amounts of CH_3SO_3H significantly *depress* the rate of the molybdenum catalysed oxidation. Seemingly opposed to this finding stands the observation that addition of acetic acid (in large excess) enhances the rates of the $VO(acac)_2$ catalysed epoxidation of cyclohexene by Bu^tO_2H in hydrocarbon solvents.[3a] Although this suggests that acid catalysis is operative,[2a] our results would indicate that more than one phenomenon should be taken into account in interpreting the effect of added protic species on rates of metal–hydroperoxide oxidations.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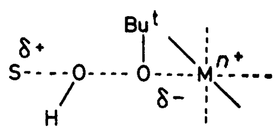
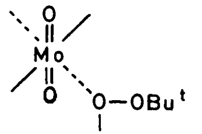

(7)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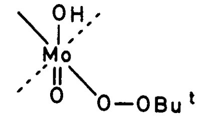
(9)

Also, as one might expect that protic acids favour formation of molybdenum peroxides such as (9),[2a,11] it is unlikely that the intervention of such reactive intermediates plays a major role.

Comparing catalysis by Mo^{VI} with V^V for our system, we find that, in the oxidation of Bu^n_2S, the former is a more efficient catalyst than the latter by a factor of *ca.* 80, based on estimated third-order rate constants. From equations (4) and (5), it is seen that $k_3 \simeq k_{II}/(K' + [Bu^tO_2H])$; therefore, differences in k_3 may arise from

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[9] K. J. Laidler, ' Chemical Kinetics,' McGraw-Hill, London–New York, 1965, 2nd edn., pp. 474*ff*.

[10] (*a*) R. Curci, R. A. Di Prete, J. O. Edwards, and G. Modena in ' Hydrogen-Bonded Solvent Systems,' eds. A. K. Covington and P. Jones, Taylor and Francis, London, 1968, pp. 303*ff*; (*b*) R. Curci and J. O. Edwards, in ref. 2*c*, vol. I, ch. 4.

[11] G. B. Payne and P. H. Williams, *J. Org. Chem.*, 1959, **24**, 54.

changes in the limiting rate constant k_{II}, in the apparent Michaelis constant K', or both. Comparison of the k_{II} and K' values estimated for Mo^{VI} (see Results section) with those obtained for V^V (*i.e.*, $k_{II} = 1.9 \pm 0.4$ l mol^{-1} s^{-1} and $K' = 0.71 \pm 0.15$ mol l^{-1}) [1,*] reveals that the higher k_3 value observed for Mo^{VI} should be ascribed mainly to its higher limiting specific rate constant k_{II} with respect to V^V.

Based on the data in Table 2, the relative rates of molybdenum-catalysed oxidation of three substrates of varying nucleophilicity are $Bu^n_2S(100) > Bu^n_2S{=}O(0.15) \gg$ cyclohexene ($\leqslant 0.01$); for V^V catalyst in the same solvent medium the relative rates are $Bu^n_2S(100) > Bu^n_2S{=}O(1.7) >$ cyclohexene(0.2).[1] Comparison of relative rates suggests that, in the given system, molybdenum–hydroperoxide complexes are more selective than the corresponding vanadium(v) species in the oxidation of nucleophilic substrates.

Although we have not studied the metal-catalysed oxidation of cyclohexene in detail, a comparison of k_{2obs} value for Mo^{VI} [$\simeq 0.07 \times 10^{-5}$ l mol^{-1} s^{-1}] at $[Cat_0] = 1.5 \times 10^{-3}$M with $k_{2obs} \simeq 0.5 \times 10^{-5}$ l mol^{-1} s^{-1} for vanadium, at comparable concentration ($[Cat_0] = 1.3 \times 10^{-3}$M), leads to the conclusion that the remarkably higher catalytic activity of Mo^{VI} with respect to V^V in the hydroperoxide oxidation of sulphides vanishes on passing to cyclohexene as substrate in the solvent medium adopted.

This seems to contrast with the observation made by Gould *et al.*[3a] that $MoO_2(acac)_2$ catalysed epoxidations proceed *ca.* 100 times faster than those catalysed by vanadium complexes in hydrocarbon solvents. These findings, while pointing out the relevance of the solvent in determining the differences in catalytic behaviour of the two metal chelates, stress the need for further investigations.

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[*] Units of K' were given incorrectly as l mol^{-1} in Part 1.[1]