Metal Catalysis in Oxidation by Peroxides. Vanadium Catalysed Oxidation of Organosulphur Compounds by t-Butyl Hydroperoxide

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The reaction of di-n-butyl sulphide with t-butyl hydroperoxide proceeds at a convenient rate in ethanol at 25° in the presence of catalytic amounts of bisacetylacetonato-oxovanadium(IV) [$VO(acac)_2$] affording di-n-butyl sulphoxide in quantitative yield. With $[Bu^tO_2H]_0/[VO(acac)_2]_0 \geqslant 8$ and $[VO(acac)_2]_0$ 0·0001—*ca.* 0·002M the reaction is first order in sulphide and first order in vanadium catalyst. With an excess of sulphide and varying the initial concentration of hydroperoxide, the kinetics conform to a Michaelis–Menten-type rate law. The relative rates of vanadium catalysed oxidation of some substrates by Bu^tO_2H were found to decrease in the order $Bu^n{}_2S$ (100) > $PhSBu^n$ (58) > $Bu^n{}_2S{=}O$ (1·7) > cyclohexene (0·2). The data suggest a mechanism involving rate-determining nucleophilic attack by the sulphur substrate on the O–O bond of a hydroperoxide–vanadium(V) complex.

It is well known that catalytic amounts of transition metal ions can strongly influence the reactivity of both organic and inorganic peroxides.[1-4] For metal ion chelates to be effective catalysts in oxygen transfer from hydroperoxides to nucleophilic substrates, the metal ion should not give rise to ready one-electron redox reactions involving the peroxide and it should possess unoccupied, low-lying *d* orbitals to yield co-ordination of peroxide molecules.[5] In fact, only a few of the transition metals in their accessible oxidation states behave as efficient catalysts in simple oxygen transfer reactions.[5-7] Indeed, Indictor and Brill showed that the acetylacetonate (acac) complexes of VO^{2+}, $MoO_2{}^{2+}$, and V^{3+} are the most efficient catalysts in the epoxidation of alkenes by t-butyl hydroperoxide.[6] The kinetics of cyclohexene epoxidation by Bu^tO_2H, catalysed by $VO(acac)_2$, have been investigated by Gould *et al.*; first-order kinetics in both catalyst and alkene were observed, whereas the rate dependence on Bu^tO_2H was found to be similar to the Michaelis–Menten equation for enzyme catalysis.[5] Inhibition by Bu^tOH, a reaction product, was observed; another noticeable feature of these systems was the rapid catalyst deactivation.[5,7] Kinetic data on the epoxidation of oct-1-ene by Bu^tO_2H in the presence of hexacarbonylmolybdenum have been reported by Zajacek *et al.*;[8] at high olefin concentrations, excellent fits of a pseudo-first-order rate equation were observed. In agreement with the general mechanism proposed by Gould *et al.*,[5,7] the observed pseudo-first-order rate constants were found to be concentration dependent.[8]

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[1] A. G. Davies, 'Organic Peroxides,' Butterworths, London, 1961, pp. 174*ff* and references therein.

[2] G. Sosnowsky and D. J. Rawlison, in 'Organic Peroxides,' ed. D. Swern, Wiley-Interscience, New York, 1970—1971, vol. I, chs. 9 and 10; vol. II, chs. 2 and 3.

[3] A. R. Gallopo and J. O. Edwards, *J. Org. Chem.*, 1971, **36**, 4089 and references therein.

[4] K. Koubek, M. L. Haggett, C. J. Battaglia, K. M. Ibne-Rasa, H.-Y. Pyun, and J. O. Edwards, *J. Amer. Chem. Soc.*, 1963, **85**, 2263 and references therein.

[5] E. S. Gould, R. R. Hiatt, and K. C. Irwin, *J. Amer. Chem. Soc.*, 1968, **90**, 4573 and references therein.

[6] N. Indictor and W. F. Brill, *J. Org. Chem.*, 1965, **24**, 54.

[7] C.-C. Su, J. W. Reed, and E. S. Gould, *Inorg. Chem.*, 1973, **12**, 337.

[8] T. N. Baker, III, G. J. Mains, M. N. Sheng, and J. G. Zajacek, *J. Org. Chem.*, 1973, **38**, 1145.

Metal ion catalysis in the oxidation of sulphides and sulphoxides by peroxides has also received attention, although most studies appear to deal with water-soluble sulphides and catalysts in aqueous solvents.[9,10]

This paper describes the results of a kinetic study of the VO(acac)$_2$ catalysed oxidation of di-n-butyl sulphide by t-butyl hydroperoxide. Ethanol was chosen as solvent since our previous studies on oxidation of sulphides by hydroperoxides indicated that uncomplicated rate-laws are observed in hydroxylic media.[11] Given the renewed technological interest in metal catalysed peroxide oxidation,[2] we took the view that organic sulphides are useful model substrates for a study of the general features of nucleophilic attack on the ' metal-ion-activated ' peroxide O–O bond.

EXPERIMENTAL

Materials.—Commercial t-butyl hydroperoxide, b.p. 40° at 21 mmHg, and di-n-butyl sulphide, b.p. 186—187°, were purified by distillation. Di-n-butyl sulphoxide, b.p. 141—142° at 20 mmHg, and n-butyl phenyl sulphide, b.p. 116—117° at 14 mmHg, were prepared and purified by known methods.[12,13] Commercial cyclohexene (Fluka), b.p. 84°, was freshly distilled over sodium and stored under dry nitrogen. Bisacetylacetonato-oxovanadium(IV) [VO(acac)$_2$] (Baker) was recrystallized from anhydrous acetone, m.p. 252—255° (decomp.). Anhydrous ethanol was obtained by standard procedures starting from high purity commercial samples.

Stoicheiometry.—In a typical experiment $Bu^n{}_2S$ (1·39 g, 9·5 mmol) and VO(acac)$_2$ (0·106 g, 0·4 mmol) were dissolved in anhydrous ethanol under dry nitrogen; to this solution, 10 ml of an ethanol solution containing Bu^tO_2H (0·9 g, 10 mmol) were added and the resulting mixture kept at 25° for 5 h. After removing most of the solvent *in vacuo*, the residue was treated with warm n-hexane (the metal catalyst being only slightly soluble in this solvent) and filtered. The filtrate was chromatographed (silica gel) eluting with n-hexane–chloroform. Thus, di-n-butyl sulphoxide (1·38 g, 8·50 mmol, *ca.* 90%), identical with an authentic sample, was isolated. In the absence of the metal catalyst the oxidation was inconveniently slow at the same temperature.

Kinetics.—All operations were performed under dry nitrogen with temperature control $> \pm 0{\cdot}05°$.* A freshly prepared solution of the catalyst was employed in each run; the reactions were started by adding an aliquot portion of a standard Bu^tO_2H solution in ethanol to the sulphide–catalyst mixture in the same solvent. At measured intervals the residual hydroperoxide was determined by titration (iodometric analysis) following known procedures.[14,15] With the sulphide in large excess over Bu^tO_2H, clean pseudo-first-order kinetics were observed, as log[Bu^tO_2H] *vs.* time plots were linear to at least 80% reaction in the great majority of cases. Addition of 0·05M-nitrobenzene, a radical trap, had no effect on rates. In some kinetic experiments, parallel to the disappearance of the hydroperoxide, the formation of product sulphoxide was also followed by g.l.c. (8 ft × 1/8 in column; 5% FFAP on 80—100 Chromosorb G AW-DMCS; 200°). Rate constants estimated from both techniques agreed satisfactorily. Preliminary kinetic experiments showed that runs carried out in flasks exposed to the atmosphere also exhibited regular pseudo-first-order behaviour, but rate constants were somewhat higher than those for experiments performed under nitrogen. This has not been further investigated. Similarly, runs performed under nitrogen but employing ethanol containing 2% water as solvent gave rate constants which were consistently 1·5—2 times higher than in anhydrous ethanol. In the absence of catalyst, oxidation of the sulphide by Bu^tO_2H was performed under pseudo-first-order conditions at 30, 40, and 50°, and second-order rate constants calculated as $k_1/[Bu^n{}_2S]_0$. From these ($k_2 = 1{\cdot}7 \times 10^{-5}$, $4{\cdot}2 \times 10^{-5}$, and $8{\cdot}9 \times 10^{-5}$ l mol^{-1} s^{-1} at 30, 40, and 50° respectively) we calculate $E_a = 16{\cdot}3 \pm 0{\cdot}3$ kcal mol^{-1} and hence $k_2 = 1{\cdot}1 \times 10^{-5}$ l mol^{-1} s^{-1} at 25° for the uncatalysed oxidation. The interpretation of some kinetic runs aimed at elucidating the main features of Bu^tO_2H decomposition in the presence of the metal catalyst (but in the absence of sulphide) was hampered by the poor reproducibility of data; analysis of initial rates indicated a fractional order (0·5—0·8) in the hydroperoxide.

RESULTS AND DISCUSSION

Although organic sulphides can be converted into sulphoxides in a number of ways, many oxidizing agents are unsuitable for this reaction for they also promote the formation of sulphones or side reactions take place.[1]

We find that the oxidation of simple dialkyl and alkyl aryl sulphides by t-butyl hydroperoxide occurs smoothly in ethanol at 25° in the presence of catalytic amounts of VO(acac)$_2$ [equation (1)]. The 1 : 1 stoicheiometry is demonstrated by the nearly quantitative isolation of sulphoxide (see Experimental section).

$$R_2S + Bu^tO_2H \xrightarrow[25^\circ]{VO(acac)_2\text{–}EtOH} R_2S{=}O + Bu^tOH \qquad (1)$$

In agreement with the observations made by Gould *et al.*,[5,7] we find that a strongly absorbing red species is rapidly formed when an excess of Bu^tO_2H is mixed with blue-green solutions of VO(acac)$_2$, both in the absence and in the presence of the sulphide.

Catalytic Species.—The formation of the active catalytic species from VO(acac)$_2$ and Bu^tO_2H in ethanol was studied in detail. The main features are as follows.

(a) The visible–u.v. spectrum of VO(acac)$_2$ consists of two bands with maxima at 775 and 580 nm.[16-18]

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* Details will be sent on request.

[9] For a recent review see: N. Connon, Eastman Kodak Co., Org. Chem. Bull., 1972, **44**, No. 1.

[10] L. Kuhnen, *Angew. Chem. Internat. Edn.*, 1966, **5**, 893.

[11] (*a*) R. Curci, R. A. DiPrete, 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 ' Organic Peroxides,' ed. D. Swern, Wiley-Interscience, New York, 1970, vol. I, ch. 4.

[12] A. Cerniani, G. Modena, and P. E. Todesco, *Gazzetta*, 1960, **90**, 3.

[13] G. Modena, *Gazzetta*, 1959, **89**, 834.

[14] (*a*) V. R. Kokatnur and M. Jelling, *J. Amer. Chem. Soc.*, 1941, **63**, 1432; (*b*) H.-Y. Pyun, M.Sc. Thesis, Brown University, 1964.

[15] M. A. P. Dankleff, R. Curci, J. O. Edwards, and H.-Y. Pyun, *J. Amer. Chem. Soc.*, 1968, **90**, 3209.

[16] C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, 1962, **1**, 111.

[17] I. Bernal and P. H. Rieger, *Inorg. Chem.*, 1963, **2**, 256.

[18] (*a*) J. Selbin, R. T. Ortolano, and F. J. Smith, *Inorg. Chem.*, 1963, **2**, 1315; (*b*) T. R. Ortolano, J. Selbin, and S. P. McGlynn, *J. Chem. Phys.*, 1964, **41**, 262.

These are attributed to *d–d* transitions of this C_{2v} symmetry complex and are expected to disappear upon removal of the lone *d* electron.[18] Figure 1 shows this to be the case when an excess of hydroperoxide is added to $VO(acac)_2$; repeated scans of the spectrum indicate that the newly formed vanadium species is stable in EtOH under nitrogen.

(b) Blue-green solutions of $VO(acac)_2$ in EtOH give e.s.r. spectra characterized by eight resonance lines[17] with *g* 1·968 and *A* 102·5 G; upon mixing with an excess of Bu^tO_2H the e.s.r. signal quickly disappears. At $[VO(acac)_2]_0$ 0·5 × 10^{-2}M and $[Bu^tO_2H]_0$ 5 × 10^{-2}M, based on peak-height measurements, we estimate a half-life of *ca.* 20 s for the vanadium(IV) species.

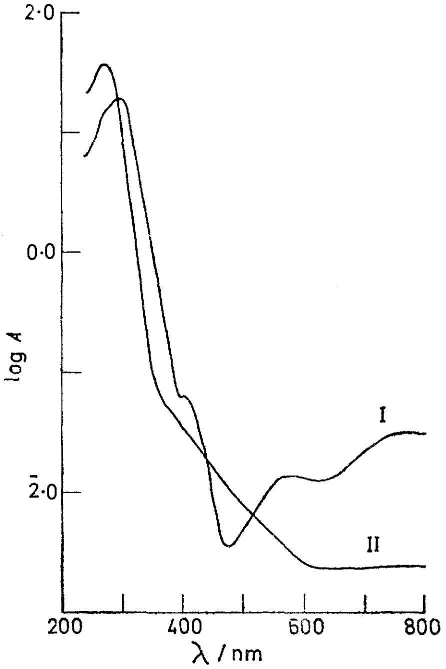

FIGURE 1 Absorption spectra of I, 0·12 × 10^{-2}M-$VO(acac)_2$ and II, upon reaction with 5 × 10^{-2}M-Bu^tO_2H. Both spectra run in anhydrous ethanol under nitrogen at 25° (absorbances are referred to cell path = 1 cm)

(c) Oscilloscope traces of stopped flow experiments clearly show that in the rapid reaction of Bu^tO_2H with $VO(acac)_2$ to produce the red vanadium species at least one transient intermediate appears. This, at 475 nm and with $[VO(acac)_2]_0$ 0·15 × 10^{-2}M and $[Bu^tO_2H]_0$ 4·6 × 10^{-2}M, reaches its maximum concentration after *ca.* 8 s from mixing and decays in *ca.* 20 s.

(d) The stoicheiometry seems to be complex. However, when the hydroperoxide is in moderate (5—20-fold) excess over initial $[VO(acac)_2]$ the formation of the red vanadium species is accompanied by a rapid reduction of initial peroxide titre which roughly corresponds to the initial concentration of $VO(acac)_2$. After this, a comparably slow decomposition of the hydroperoxide (to Bu^tOH and O_2) takes place at a rate which depends on the Bu^tO_2H–metal chelate ratio (being higher at lower ratios). Analysis of preliminary kinetic data reveals that a complex rate law is likely to be followed in the rapid formation of the red vanadium species.

On the grounds of the evidence above we conclude that the red vanadium compound, the catalytically active species in oxidation of sulphides by Bu^tO_2H, is a vanadium(V) and not a vanadium(IV) species. Consistent with the stopped-flow experiments above, its rapid formation may occur through a vanadium(IV)–hydroperoxide complex, analogous to the transient peroxyvanadium complexes observed in aqueous systems.[19-21]

Kinetics.—Runs were performed under dry nitrogen at hydroperoxide–catalyst ratios usually in the range from 5 to 200, with the sulphide always being in large excess (see Experimental section). Typical rate data are collected in Tables 1 and 2.

TABLE 1

Effect of catalyst concentration on rates of the vanadium catalysed oxidation of di-n-butyl sulphide by t-butyl hydroperoxide in ethanol at 25·0°: $[Bu^n_2S]_0$ = 0·198M, $[Bu^tO_2H]_0$ = 10·5 × 10^{-3}M

$10^3[Cat]_0$/ M	Ratios[a]	10^3k_{2obs}/ l mol^{-1} s^{-1} [b]	10^5v_0/ mol l^{-1} s^{-1}	10^5v_0 (dec)/ mol l^{-1} s^{-1}
None		0·011		
0·105	100	0·245		
0·196	53·6	0·357		
0·392	26·8	0·765		
0·967	10·9	2·07	0·43	0·01
1·20	8·75	2·50		
1·33	7·89	2·60		
1·33	7·89	2·50 [d]		
1·40	7·50	2·80	0·62	0·04
1·40	7·50	2·90 [d]		
1·57	6·70	2·88		
2·15	4·88	4·30		
2·50	4·20	4·52	1·0	0·25
3·34	3·14	4·54		
4·66	2·25	5·40	1·2	0·4

[a] Initial hydroperoxide : vanadium catalyst concentration ratios. [b] From pseudo-first-order kinetic runs, as $k_{1obs}/[Bu^n_2S]_0$. [c] In the presence of 0·05M-nitrobenzene. [d] Initial rates of peroxide decomposition in the absence of sulphide, from plots of $[Bu^tO_2H]$ *vs.* time.

TABLE 2

Vanadium catalysed oxidation of di-n-butyl sulphide by t-butyl hydroperoxide in ethanol at 25·0°: $[Cat]_0$ = 1·0 × 10^{-3}M

$10^3[Bu^tO_2H]_0$/M	$[Bu^n_2S]_0$/M	10^3k_{1obs}/s^{-1}	10^3k_{2obs}/l mol^{-1} s^{-1}
21·0	0·20	0·35	1·67
11·0	0·20	0·36	1·80
11·0	0·30	0·49	1·63
11·0	0·45	0·75	1·67
11·0	0·75	0·98	1·31

For oxidation of organic substrates by hydroperoxides catalysed by transition metal ions, a general rate law can often be written in the form (2). In this

$$v = -d[RO_2H]/dt = k_2^0[RO_2H]^m[S]^n + k_3[Cat]_0^p[RO_2H]^q[S]^r + k_{dec}[Cat]^s[RO_2H]^t \quad (2)$$

equation, the first term on the right represents the

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[19] H. B. Brooks and F. Sicilio, *Inorg. Chem.*, 1971, **10**, 2530.

[20] M. Setaka, Y. Kirino, T. Ozawa, and T. Kwan, *J. Catalysis*, 1969, **15**, 209.

[21] M. Orhanovic and R. G. Wilkins, *J. Amer. Chem. Soc.*, 1967, **89**, 278.

'uncatalysed' oxidation: when the substrate is a nucleophile, as in the case of organic sulphides, one often finds $m = n = 1$ in hydrogen-bonding solvents like water or alcohols.[1,11,13,15] This is also the case for oxidation of Bu^n_2S by Bu^tO_2H in ethanol (see Experimental section). The third term on the right of equation (2) accounts for the metal catalysed decomposition of the hydroperoxide; this side reaction often proceeds by radical-chain mechanisms[1,2] involving several intermediates and usually gives a fractional order in both metal catalyst and hydroperoxide.[3]

As judged by initial rates v_0 (Table 1) and by hydroperoxide half-lives, peroxide decomposition virtually does not compete with substrate oxidation when the sulphide is in large excess and hydroperoxide : catalyst ratios are kept $\geqslant 8$. Also, since at sizeable catalyst concentrations the 'uncatalysed' substrate oxidation is much slower than the metal ion catalysed reaction, equation (2) reduces to (3) where $k_{2\text{obs}} = k_3[\text{Cat}]_0^p$.

$$v = k_2(\text{obs})[\text{RO}_2\text{H}]^q[\text{S}]^r \qquad (3)$$

At relatively low hydroperoxide concentrations and with sulphide in large excess (Tables 1 and 2) we were able to observe very regular and reproducible pseudo-first-order kinetics. No significant inhibition by products[5,7] takes place. This is also suggested by the observation that if, under the same pseudo-first-order conditions, a fresh amount of Bu^tO_2H is added when consumption of hydroperoxide has taken place in >90%, $\log[Bu^tO_2H]$ *vs.* time plots of the newly started reaction give $k_{1\text{obs}}$ values which agree with the previous ones within ±10%. Furthermore, if excess of sulphide is added to a solution where a small fraction (10—20%) of Bu^tO_2H has decomposed in the presence of the catalyst, rate constants are obtained which are lower than those obtained with 'fresh' catalyst by only 2—20%, depending on the length of the ageing period. Therefore, oxidative 'degradation' of the catalyst[5] does not seem to be a serious problem here.

Inspection of the data in Table 1 and 2 suggests that (for excess of substrate up to 0·45M) the order in sulphide is near one, and that the reaction is also first-order in the vanadium catalyst from 0·0001 to at least 0·002M $[\text{VO(acac)}_2]_0$. In this range therefore the kinetics conform to the simple rate law (4).

$$v = k_3[\text{Cat}]_0[\text{Bu}^t\text{O}_2\text{H}][\text{Bu}^n{}_2\text{S}] \qquad (4)$$

The effect of changing $[Bu^tO_2H]_0$ over a wider range (0·02—0·31M) indicates departure from simple first-order dependence for this reagent (Table 3). This behaviour suggests the intervention of a partially dissociated intermediate complex involving the hydroperoxide and the vanadium catalyst. Therefore, analogous to the Michaelis–Menten picture of enzyme catalysis,[21] we assume, as a first approximation, the rate law (5) to hold (with $k = k_{\text{II}}\cdot[\text{Bu}^n{}_2\text{S}]_0$). Here K'

$$v_0 = k[\text{Cat}]_0[\text{Bu}^t\text{O}_2\text{H}]_0/K' + [\text{Bu}^t\text{O}_2\text{H}]_0 \qquad (5)$$

is a constant related to the apparent dissociation constant of the vanadium–hydroperoxide and vanadium–ethanol complexes; k is the limiting specific rate constant, which would be observed when the intermediate complex concentration is maximal. According to the method of Lineweaver and Burk, which involves using equation (5) in its reciprocal form,[22] both k and K' can be estimated from plots of $1/v_0$ *vs.* $1/[\text{Bu}^t\text{O}_2\text{H}]_0$ (see Figure 2); these have slope $K'/k[\text{Cat}]_0$ and intercept $1/k[\text{Cat}]_0$. Least-squares analysis of data at $[\text{Cat}]_0 = 1{\cdot}2 \times 10^{-3}$M (Table 3; line I, Figure 2) gives $k = 0{\cdot}95 \pm 0{\cdot}20$ s^{-1} and $K' = 0{\cdot}71 \pm 0{\cdot}15$ l mol^{-1}

TABLE 3

Effect of changing initial hydroperoxide concentration on the rates of the vanadium catalysed oxidation of di-n-butyl sulphide by t-butyl hydroperoxide in ethanol: $[\text{Bu}^n{}_2\text{S}]_0 = 0{\cdot}50$M, $[\text{Cat}]_0 = 1{\cdot}2 \times 10^{-3}$M

Temp. (°C)	$10^3[\text{Bu}^t\text{O}_2\text{H}]_0$/M	Ratios [a]	$10^5 v_0$/mol l^{-1} s^{-1}	$10^4 k_{1\text{obs}}$/s^{-1}
25·0	20·2	17	3·07	15·2
25·0	31·3	26	5·04	16·1
25·0	40·1	33	6·74	16·8
25·0	60·8	51	8·79	14·6
25·0	80·4	67	11·0	13·7
25·0	160·0	133	19·7	12·3
25·0	240·0	200	30·0	12·5
25·0	314·0	262	32·0	10·2
5·0	91·8	76	4·27	4·65
5·0	120·0	100	5·60	4·67
5·0	200·0	167	7·80	4·00

[a] Initial hydroperoxide : vanadium catalyst concentration ratios.

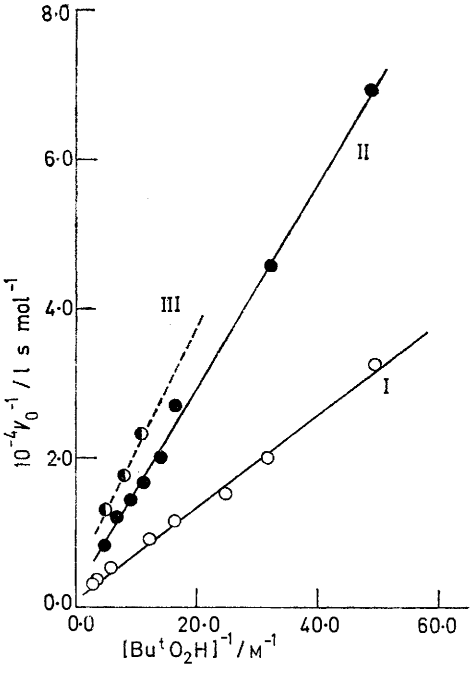


FIGURE 2 Lineweaver–Burk plots of rates for the vanadium catalysed oxidation of di-n-butyl sulphide by t-butyl hydroperoxide in ethanol: I, $[\text{VO(acac)}_2]_0 = 1{\cdot}2 \times 10^{-3}$M at 25·0°; II, $[\text{VO(acac)}_2]_0 = 0{\cdot}6 \times 10^{-3}$M at 25·0°; III, $[\text{VO(acac)}_2]_0 = 1{\cdot}2 \times 10^{-3}$M at 5·0°

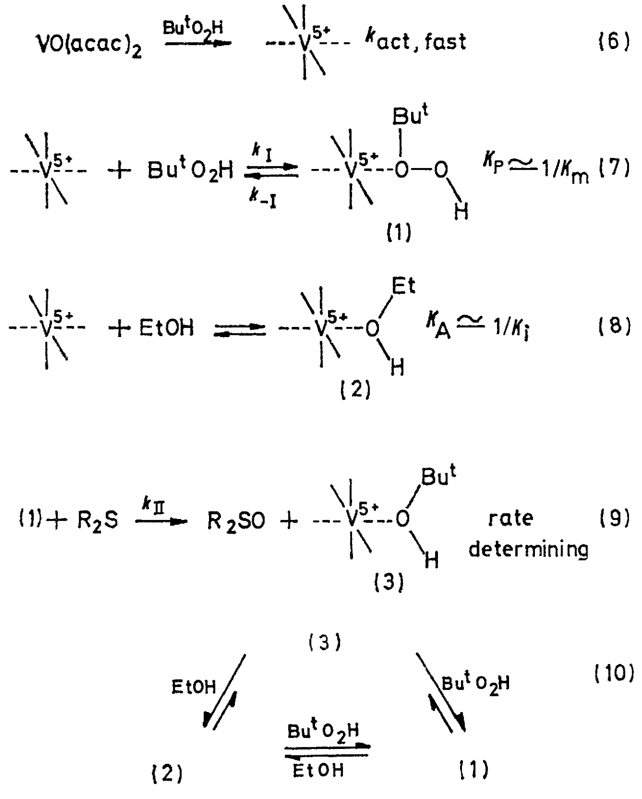
[22] K. J. Laidler, 'Chemical Kinetics,' McGraw-Hill, London–New York, 1965, 2nd edn., pp. 474*ff*.

at 25·0°. A series of kinetic runs in identical conditions but for $[Cat]_0$, which was $0·6 \times 10^{-3}$M, also gave a linear Lineweaver–Burk plot (line II, Figure 2) yielding k and K' values which agreed with those given above within error limits. A straight line drawn through three points (line III, Figure 2) corresponding to experiments performed at 5·0° gives k $0·23 \pm 0·06$ s^{-1} and K' $0·5 \pm 0·15$ l mol^{-1} at this temperature.

The relative rates of the vanadium catalysed oxidation of some nucleophilic substrates by Bu^tO_2H in ethanol at 25° were found to be $Bu^n_2S(100) > PhSBu^n(58) > Bu^n_2S{=}O(1·7) >$ cyclohexene (0·2). These leave no doubt that 'electropositive oxygen' is being transferred from the 'metal-activated' hydroperoxide to the substrate.

Reaction Mechanism.—A polar mechanism can be advanced similar to that proposed for transition metal catalysed epoxidation of olefins.[1,2,5-8,23] In fact, a radical-chain oxidation path is ruled out by the observation of reproducible kinetics, the simple rate law, the failure of radical traps to influence rates, and by the absence of products expected to arise from radical intermediate species.[1-3,24]

The simple sequence of reactions expressed in the Scheme by equations (6)—(10) is consistent with all the observations made in this study. In fact, the kinetic first-order dependence on sulphide, hydroperoxide, and vanadium catalyst observed [equation (4)] implies that one molecule of each reactant is involved in the transition state of the rate-determining step. Assuming that a termolecular collision does not occur, two of the components must have interacted at some prior stage and a hydroperoxide–catalyst complex seems the logical choice [equation (7)].



SCHEME

A reaction path including the formation of a ternary complex containing one molecule each of vanadium, hydroperoxide, and sulphide would also be consistent with our kinetic picture. However, as already pointed out by Gould *et al.*,[5,7] such a path would be more likely to apply to d^8 and d^{10} systems rather than to d^0 transition metal complexes, as in our case.

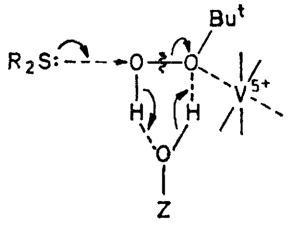
Indeed, we find that addition of sulphide in moderate excess has practically no effect on the spectra of either $VO(acac)_2$ or the red vanadium(V) species mentioned.

The solvent, of course, can compete with Bu^tO_2H in complexing the catalyst [equation (8)]. Therefore analogous to equation (5), adopting the notation of the Scheme, this produces equation (11). Assuming that

$$K' = (K_mK_i + K_m[EtOH])/K_i \qquad (11)$$

$K_mK_i \ll K_m[EtOH]$ and taking $K' = 0·71 \pm 0·15$ l mol^{-1} (at 25·0°) and EtOH = 17·1M, we can estimate K_i/K_m and hence K_P/K_A as *ca.* 25, which would correspond to the equilibrium constant for ligand exchange $(2) \rightleftharpoons (1)$. This is expected in view of the higher nucleophilicity of hydroperoxides (α-nucleophiles [11b]) compared to alcohols and suggest an efficient regeneration of the active intermediate complex (1) [equation (10)].

Nucleophilic attack by the sulphide on O–O bond of the metal-linked peroxide molecule occurs in the transition state of the rate-determining step [equation (9)]. Separation of charges need not be envisaged here[5,7,23] as there is ample evidence that this is by-passed in these systems *via* concomitant hydrogen-transfer promoted by the intervention of at least one protic solvent molecule (or, in its absence, by a second hydroperoxide) [activated complex (4)].[11,15]



(4)

According to this formulation of the transition state the role of the transition metal catalyst in promoting the heterolysis of the peroxide O–O bond would be similar to that of H^+ in the strong acid catalysis of sulphide oxidation.[10,11,14] Vanadium catalysis, however, seems to be much more effective than catalysis by H^+. The catalytic third-order constant [k_3, *cf.* equation (14)] for $HClO_4$ catalysed oxidation of 1-thia-

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[23] G. R. Howe and R. R. Hiatt, *J. Org. Chem.*, 1971, **36**, 2493.

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4-oxacyclohexane by Bu^tO_2H in water is $1{\cdot}9 \times 10^{-3}$ l^2 mol^{-2} s^{-1},[15] whereas our data yield k_3 *ca.* $2{\cdot}0 \pm 0{\cdot}2$ l^2 mol^{-2} s^{-1} for vanadium catalysed oxidation of $Bu^n{}_2S$ in ethanol. This increase of the catalytic constant by a factor of 10^3 is too large to be attributed to differences in sulphide and solvent structures. Furthermore, k_{II} values estimated from Lineweaver–Burk plots (see above) at 25·0 and 5° give E_a $11{\cdot}7 \pm 1{\cdot}5$ kcal mol^{-1}; this is *ca.* 4·5 kcal mol^{-1} lower than the activation energy estimated for the ' uncatalysed ' sulphide oxidation (see Experimental section).

Conclusions.—Although the number and detailed structures of the vanadium(V) species responsible for the activation of the hydroperoxide molecules still remain obscure, the high efficiency of this catalyst in the homogeneous oxidation of organic sulphides has been demonstrated. As could have been anticipated,[11,15] the solvent choice is quite important to allow uncomplicated kinetics to be observed. Our findings for sulphide oxidation compare reasonably well with other observations of olefin epoxidation and amine oxidation.[5-7,23,25] Thus, further extention of these studies seems warranted.

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