# Metal Catalysis in Oxidation by Peroxides. Part 3.[1] Significance of Ligand Exchange and Acid–Base Equilibria of Vanadium(v) Catalyst in Oxidation by t-Butyl Hydroperoxide in Alcohols

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Kinetic and spectroscopic evidence suggests that, in alcoholic solvents (ROH) and in the presence of t-butyl hydroperoxide, bis(acetylacetonato)oxovanadium(iv) [$VO(acac)_2$] is rapidly converted to vanadate esters $VO(OR)_3$. These vanadium(v) triesters undergo acid–base equilibria leading to anionic or cationic species depending on the acidity of the medium. Kinetic studies on the vanadium(v) catalysed oxidation of di-n-butyl sulphide by t-butyl hydroperoxide in methanol, ethanol, and propan-2-ol, respectively, at 25° indicate that the most active catalyst is the neutral species $VO(OR)_3$. The significant depression of oxidation rates observed when vanadium anion species are present, even at low concentration, suggests that vanadium(v) species might be involved in aggregation phenomena which become more significant as the acidity decreases. Thus, the seemingly large differences observed in the rates of catalysed oxidation in the three alcohols mentioned stem from changes in the position of acid–base equilibria involving the catalyst species in the three solvents. Indeed, the dependence of oxidation rates upon the medium acidity shows that rather small differences in rates are found in the range where the neutral catalyst ester $VO(OR)_3$ is the dominant species.

A DETAILED study of the mechanism of catalysis of oxygen atom transfer from hydroperoxide to alkenes in hydrocarbon solvents by transition metals (such as V, Mo, W, and Ti) in their higher oxidation states has been hampered by the complexity of the kinetics. This is probably a consequence of the formation of alcohols in the reaction resulting in modification of the medium and/or interaction with the metal catalyst.[2]

In order to overcome this difficulty we earlier carried out a thorough study of the catalysis [by bis(acetylacetonato)dioxomolybdenum(vi), $MoO_2(acac)_2$, and by bis(acetylacetonato)oxovanadium(iv), $VO(acac)_2$] of dialkyl sulphide oxidation in ethanol solvent.[1,3] These reactions were in most cases slower than those reported for oxidation in hydrocarbon solvents. The use of a more reactive substrate made possible a detailed kinetic investigation and the partial elucidation of the mechanism. These studies did not, however, provide significant information on the co-ordination shell of the metal as it is in the reaction medium. The ligand environment should depend on the composition of the medium, and definitive evidence for this conclusion was given by the significant induced optical activity obtained from prochiral sulphide oxidation carried out in chiral alcohols[4] and by several other reports in the literature.[5]

We have now approached this co-ordination shell problem by carrying out a spectroscopic and kinetic study in three alcohols (methanol, ethanol, and propan-2-ol) on the vanadium-catalysed oxidation of di-n-butyl sulphide with t-butyl hydroperoxide. The effect of added acid (methanesulphonic) and base (alkoxide ion) were also examined and were found to be of considerable importance in understanding the nature of the catalyst species.

## EXPERIMENTAL

*Materials.*—Di-n-butyl sulphide, t-butyl hydroperoxide, and bis(acetylacetonato)oxovanadium(iv) were purified as previously reported.[3] Vanadium(v) triesters, $VO(OEt)_3$, used in the majority of rate experiments, and $VO(OPr^i)_3$, used in the spectrophotometric and potentiometric experiments were prepared by known methods[6] and purified by repeated vacuum distillation before use. Anhydrous alcohols were obtained by standard procedures starting from high purity commercial samples, and kept over 4A molecular sieves.

*Spectroscopic Experiments.*—The spectroscopic measurements were made at 25 ± 1 °C with either a Perkin-Elmer 402 or a Cary 15 spectrophotometer, using matched 1.00 or 0.20 cm cells, and minimum slit widths. Solutions of the vanadate esters and of $VO(acac)_2$ were prepared just before use. When solutions of $VO(acac)_2$ and $Bu^tOOH$ were employed, the required amount of hydroperoxide and acetylacetone was added to the solvent in the reference cell.

*Potentiometric Experiments.*—A standard glass electrode on a Radiometer TIT-1 potentiometer was used for the potentiometric experiments. The glass electrode was maintained for 48 h in methanol before use. The measurements of the potential, $E$/mV, were carried out at 25 °C. The equilibrium potential was achieved in 2—5 min. Each titration was made by stepwise addition of 0.1M solutions of methanesulphonic acid (5 ml) to methanol (50 ml) and to a 0.001M solution of $VO(OPr^i)_3$ in methanol (50 ml) for comparison purposes.

*Rate Experiments.*—All operations were performed under dry nitrogen with temperature control to better than ±0.05°, following the procedure previously reported.[1,3]

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[1] Part 2, R. Curci, F. Di Furia, and G. Modena, *J.C.S. Perkin II*, 1977, 576.

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

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

[4] F. Di Furia, G. Modena, and R. Curci, *Tetrahedron Letters*, 1976, **50**, 4637.

[5] For a recent review see R. A. Sheldon and J. K. Kochi, *Adv. Catalysis*, 1976, **25**, 271.

[6] F. Cartan and C. N. Caughlan, *J. Phys. Chem.*, 1960, **64**, 1756.

## RESULTS

*Spectroscopic Experiments.*—Ethyl and isopropyl vanadate esters have similar electronic spectra in the range 220—600 nm in either methanol, ethanol, or propan-2-ol. Furthermore, $VO(acac)_2$ in the presence of an excess of t-butyl hydroperoxide also gives the same spectra as the vanadate esters when the absorbance due to the remaining hydroperoxide is corrected for.

The results confirm that vanadate esters undergo fast and complete ligand exchange with the solvent alcohol.[7] Moreover, when vanadium(IV) is oxidized to vanadium(V), the acetylacetonato ligands are totally removed from the coordination sphere of the metal. The alternative rationale based on almost complete independence of optical density from the nature of the ligands (acetylacetone compared with alcohols), even though conceivable, does not seem likely. Evidence based on kinetics, discussed below, also leads to the conclusion that acetylacetonato is removed from vanadium in the course of metal oxidation.

The electronic spectra of $VO(OPr^i)_3$ in the three alcohols are similar but not identical; they show shoulders at *ca.* 284 (log ε 3.44) in MeOH, 291 (3.52) in EtOH, and 295 nm (3.64) in $Pr^iOH$; in the last two solvents well defined maxima are found at 242 (log ε 3.89) and 244 nm (3.98) for EtOH and $Pr^iOH$ respectively. They are strongly acid dependent; addition of methanesulphonic acid causes the appearance of a new maximum at 410, 395, and 390 nm in MeOH,EtOH, and $Pr^iOH$, respectively. The increase in optical density around 400 nm with increasing acid concentration follows a sigmoid curve (Figure 1) as expected for the occurrence of protonation equilibria of the ester to form its conjugate acid. It should be noted that the protonation process occurs at significantly different acid concentrations in the three alcohols. The shape of the curves, however, does not change much. This is expected if a simple protonation occurs. The same dependence upon added $MeSO_3H$ is shown by solutions of vanadium(V) produced by reaction of $Bu^tOOH$ with $VO(acac)_2$ in EtOH;[3] addition of the acid produces a u.v. maximum at 395 nm whose absorption is enhanced by increasing concentration of the acid again giving the sigmoid curve B (Figure 1).

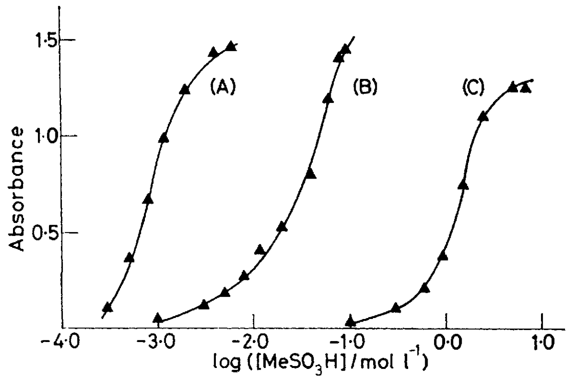

FIGURE 1 Effect of increasing concentration of added methanesulphonic acid upon the absorbance of $0.001\text{M}$-$VO(OPr^i)_3$ in MeOH (A), EtOH (B), and $Pr^iOH$ (C), at 410, 395, and 390 nm, respectively. Temperature 25.0°

For the same ester concentration, *i.e.*, $1 \times 10^{-3}\text{M}$, protonation occurs in the range of acid concentrations $1 \times 10^{-4}$—$5 \times 10^{-3}$, $1 \times 10^{-4}$—$1 \times 10^{-3}$, and $3.0 \times 10^{-2}$—$5.0\text{M}$ in methanol, ethanol, and propan-2-ol, respectively.

The effect of addition of increasing base ($MeO^-$, $EtO^-$, and $Pr^iO^-$) concentration to ester solutions has also been studied. By monitoring the decrease in optical density in the u.v. region (Figure 2) equilibrium processes may again be observed, probably leading to anionic species. The formation of these anionic species occurs, in the same range of base concentration, *i.e.*, $5.0 \times 10^{-5}$—$5.0 \times 10^{-4}\text{M}$, in the three alcohols for the same ester concentration, $0.5 \times 10^{-3}\text{M}$.

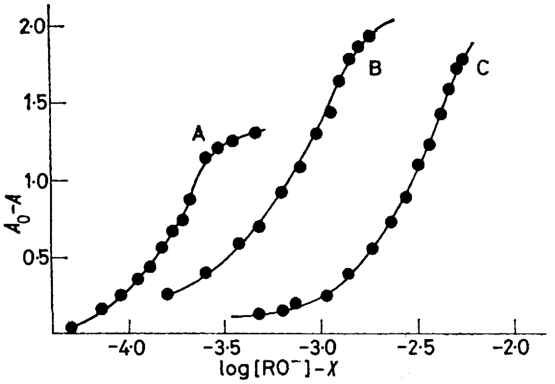

FIGURE 2 Variation of difference in absorbance caused by addition of base to solutions of $0.5 \times 10^{-3}\text{M}$-$VO(OPr^i)_3$ dissolved in alcohols, with $A_0$ being absorbance at zero added base. Curve A: solvent MeOH, $RO^- = MeO^-$, $X = 0$, λ 215 nm; curve B: solvent EtOH, $RO^- = EtO^-$, $X = 0.5$, λ 245 nm; curve C: solvent $Pr^iOH$, $RO^- = Pr^iO^-$, $X = 1.0$, λ 245 nm. Temperature 25°

In the u.v. spectra of solutions of $V^V$ produced from $VO(acac)_2$ and $Bu^tOOH$ in EtOH, the same trend of decreasing absorbance is observed upon addition of $EtO^-$; indeed, $A_0 - A$ values were found to fit well on curve B (Figure 2).

Comparison of the spectroscopic results for the acidic and alkaline solutions suggests that vanadium(V) esters behave as weak bases and as relatively strong Lewis acids.

On the other hand the absorption spectra of the isopropyl ester in neutral ethanol and at the highest studied acid and base concentrations shows that protonation of the vanadium(V) species causes a decrease in the absorbance in the u.v. region between 220 and 280 nm. These results parallel those of Figure 1. Interestingly enough, however, at very low acid concentrations which produce no variation in the visible portion of the spectrum, a measurable increase of absorbance at 230 nm was observed (log ε 3.92 in neutral alcohol and 3.98 at $[CH_3SO_3H]$ $5.0 \times 10^{-4}\text{M}$), whereas further acid addition caused the beginning of a decrease of optical density (log ε 3.88 at $[CH_3SO_3H]$ $2.5 \times 10^{-3}\text{M}$).

This is what is expected if a minor amount of an anionic species of vanadium(V) is still present in neutral ethanol. The initial increase in optical density at 230 nm should then be related to the neutralization of anions at low concentration by the small amount of added acid.

In methanol and propan-2-ol, similar behaviour is observed; the amount of acid required for neutralisation for the ester concentration employed in ethanol is *ca.* $2 \times 10^{-4}$ in methanol and *ca.* $8 \times 10^{-3}\text{M}$ in propan-2-ol. These differences are considered to be an indication of different concentration of anionic species in neutral alcohols.

*Potentiometric Experiments.*—The change in the spectral properties of vanadate esters caused by added acid might be due to some type of solvent effect and not necessarily be

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[7] P. J. White, M. J. Kans, J. O. Edwards, and P. H. Rieger, *J.C.S. Chem. Comm.*, 1976, 429.

related to ester protonation. To solve this problem, we carried out potentiometric experiments by obtaining apparent pH values, as measured by a glass electrode, for several acid concentrations both in the absence and in the presence of $VO(OPr^i)_3$ in methanol solutions. As shown in Figure 3, the curve for $\Delta E$ *versus* log $[CH_3SO_3H]_0$ matches very well the spectroscopic curve, thus confirming that protonation is in fact the process observed by both techniques.

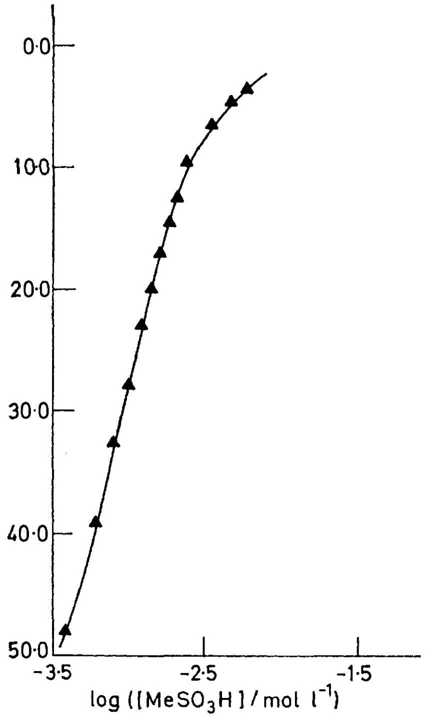

FIGURE 3 Variation of e.m.f. of $10^{-3}$M-$VO(OPr^i)_3$ in MeOH as a function of added methanesulphonic acid

*Rate Experiments*.—The variables of the system under investigation are numerous and some of them are interrelated. The spectrophotometric and potentiometric experiments indicate the presence of different species (anion, neutral molecule, and cation, presumably all monomeric) whose ranges of predominance depend on acid concentration. Furthermore a careful comparison is necessary of the behaviour of $VO(acac)_2$ and vanadate esters, since the acidity of a solution of $VO(acac)_2$ oxidized by a peroxide is not necessarily identical to the acidity of a solution made by the simple process of dissolving a triester. Careful investigation of the orders in reactant concentrations including catalyst is warranted.

An extended study was carried out in ethanol where the reaction rates were measured over a variety of acid and base concentrations in the presence of $VO(OEt)_3$ and of $VO(acac)_2$. The order in catalyst was determined at two selected acid concentrations: in one case, at $5 \times 10^{-4}$M-acid where no significant amount of ion is present, and in the other case, at 0.02M-acid which is a fairly high concentration at which the protonated fraction is still quite low. Also, the dependence of rate on $Bu^tOOH$ concentration in the presence of acid was examined. A smaller amount of data has been collected for the other alcohols for the most significant conditions suggested by the study in ethanol. For all the experiments reported here, the reductant was di-n-butyl sulphide; the order in sulphide concentration is known from previous experiments to be one. Rate data are collected in Tables 1—3; the trend of dependence of rates upon added $MeSO_3H$ is shown in Figure 4.

DISCUSSION

Spectroscopic analysis strongly suggests that the form in which vanadium(V) esters are present in neutral and weakly acid media is the uncharged ester of the solvent alcohol, irrespective of the nature of the alkoxy group present in the ester as it was originally added to the solvent. Trimethyl vanadate is immediately formed in methanol when triethyl vanadate or tri-isopropyl vanadate is put into solution.

This is also the case when the vanadium is introduced into the solvent as $VO(acac)_2$, *i.e.*, in the +4 oxidation state, provided that an excess of t-butyl hydroperoxide is present to convert the metal into the +5 oxidation state. Our results confirm our earlier suggestion and that of other authors that the hydroperoxide rapidly oxides vanadium(IV) to vanadium(V).[2]

This suggestion is further confirmed by the rate data when a misleading effect is accounted for. As shown in Figure 4, the oxidation rates with $VO(acac)_2$ and $VO(OEt)_3$ are, except for the lowest acidity in ethanol, identical within the combined experimental error. Similar results have been obtained in propan-2-ol. We think that (as discussed below in some detail) the different behaviour of the different catalysts at low acidity is related to the complicated acid–base equilibria and so, to a first approximation, can be disregarded.

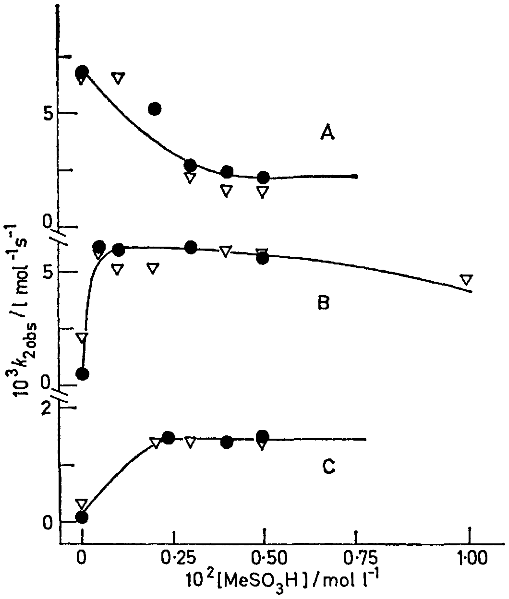

FIGURE 4 Effect of added $MeSO_3H$ upon the rates of oxidation of $Bu^n_2S$ by $Bu^tOOH$ catalysed by added $VO(OEt)_3$ (circles) or by $VO(acac)_2$ (triangles) at 25.0°. Curve A: solvent MeOH, $10^{-3}$M-vanadium species; curve B: solvent EtOH, $10^{-3}$M-vanadium species; curve C: solvent $Pr^iOH$, $2 \times 10^{-3}$M-vanadium species

The effect of catalyst concentration has been studied in detail in ethanol and found to be dependent on acid concentration. The catalyst order in ‘ neutral ’ alcohol was found to be one at low concentration, while zero order is approached at higher concentrations.[1,3] In the presence of added acid the first-order dependence in added catalyst extends over a wider range of initial

TABLE 1

Rates of oxidation of di-n-butyl sulphide by t-butyl hydroperoxide catalysed by added $\mathrm{VO(acac)_2}$ or $\mathrm{VO(OEt)_3}$ at 25.00 ± 0.05° in dry ethanol under nitrogen

| $[\mathrm{Bu^tO_2H}]_0$/ M | $10^3[\mathrm{VO(acac)_2}]_0$/ M | $10^3[\mathrm{VO(OEt)_3}]_0$/ M | $10^3[\mathrm{MeSO_3H}]_0$/ M | $10^3[\mathrm{EtONa}]_0$/ M | $10^3k_{2\mathrm{obs}}$ [a,b]/ $\mathrm{l\ mol^{-1}\ s^{-1}}$ |
|---|---|---|---|---|---|
| 0.01 | 1.00 | | | | 2.1 |
| 0.01 | 1.00 | | 0.5 | | 5.8 |
| 0.01 | 1.00 | | 1.0 | | 5.1 |
| 0.01 | 1.00 | | 2.0 | | 5.2 |
| 0.01 | 1.00 | | 4.0 | | 6.0 |
| 0.01 | 1.00 | | 5.0 | | 5.8 |
| 0.01 | 1.00 | | 10.0 | | 4.7 |
| 0.01 | 1.00 | | 20.0 | | 4.4 |
| 0.01 | 1.00 | | 160.0 | | 1.3 |
| 0.01 | 1.00 | | 200.0 | | 0.6 |
| 0.01 | | 1.00 | | | 0.5 |
| 0.01 | | 1.00 | 0.5 | | 6.1 |
| 0.01 | | 1.00 | 1.0 | | 6.0 |
| 0.01 | | 1.00 | 3.0 | | 6.1 |
| 0.01 | | 1.00 | 5.0 | | 5.7 |
| 0.01 | | 1.00 | 100.0 | | 1.4 |
| 0.01 | 0.05 | | 0.5 | | 0.35 |
| 0.01 | 0.10 | | 0.5 | | 0.64 |
| 0.01 | 0.25 | | 0.5 | | 1.5 |
| 0.01 | 0.80 | | 0.5 | | 4.0 |
| 0.01 | 3.00 | | 0.5 | | 5.9 |
| 0.01 | 5.00 | | 0.5 | | 7.4 |
| 0.01 | 7.00 | | 0.5 | | 9.0 |
| 0.01 | 0.05 | | 20.0 | | 0.37 |
| 0.01 | 0.10 | | 20.0 | | 0.62 |
| 0.01 | 0.25 | | 20.0 | | 1.6 |
| 0.01 | 0.50 | | 20.0 | | 3.1 |
| 0.01 | 1.00 | | 20.0 | | 4.4 |
| 0.01 | 2.00 | | 20.0 | | 6.5 |
| 0.01 | 3.00 | | 20.0 | | 8.2 |
| 0.01 | 5.00 | | 20.0 | | 9.7 |
| 0.01 | 7.00 | | 20.0 | | 12.2 |
| 0.01 | 12.00 | | 20.0 | | 14.1 |
| 0.01 | 1.00 | | | 0.1 | 0.67 |
| 0.01 | 1.00 | | | 0.3 | 0.51 |
| 0.01 | 1.00 | | | 0.5 | 0.36 |
| 0.01 | 1.00 | | | 1.0 | 0.09 |
| 0.005 | 1.00 | | 20.0 | | 4.3 |
| 0.010 | 1.00 | | 20.0 | | 4.5 |
| 0.021 | 1.00 | | 20.0 | | 4.7 |
| 0.057 | 1.00 | | 20.0 | | 4.7 |
| 0.076 | 1.00 | | 20.0 | | 5.2 |
| 0.108 | 1.00 | | 20.0 | | 5.4 |
| 0.147 | 1.00 | | 20.0 | | 5.1 |
| 0.195 | 1.00 | | 20.0 | | 4.8 |

[a] Estimated as $k_{1\mathrm{obs}}/[\mathrm{Bu_2^nS}]_0$ from experiments under pseudo-first-order conditions; in all experiments $[\mathrm{Bu_2^nS}]_0 = 0.2$M. [b] For experiments carried out in the presence of methanesulphonic acid, acid catalysis was taken into account and $k_{2\mathrm{obs}}$ values reported were calculated as $k_{2\mathrm{obs}} = k_2'{}_{\mathrm{obs}} - k_3^{\mathrm{H^+}}[\mathrm{CH_3SO_3H}]_0$ with $k_2'{}_{\mathrm{obs}}$ estimated as in note *a*, and $k_3^{\mathrm{H^+}}$ 0.009 $\mathrm{l^2\ mol^{-2}\ s^{-1}}$ (independently determined).

TABLE 2

Rates of oxidation of di-n-butyl sulphide by t-butyl hydroperoxide catalysed by added $\mathrm{VO(acac)_2}$ or $\mathrm{VO(OEt)_3}$ at 25.00 ± 0.05° in dry methanol under nitrogen

| $[\mathrm{Bu^tO_2H}]_0$/ M | $10^3[\mathrm{VO(acac)_2}]_0$/ M | $10^3[\mathrm{VO(OEt)_3}]_0$/ M | $10^3[\mathrm{CH_3SO_3H}]_0$/ M | $10^3[\mathrm{CH_3ONa}]_0$/ M | $10^3k_{2\mathrm{obs}}$ [a,b]/ $\mathrm{l\ mol^{-1}\ s^{-1}}$ |
|---|---|---|---|---|---|
| 0.01 | 1.0 | | | | 6.5 |
| 0.01 | 1.0 | | 1.0 | | 6.6 |
| 0.01 | 1.0 | | 3.0 | | 2.2 |
| 0.01 | 1.0 | | 4.0 | | 1.6 |
| 0.01 | 1.0 | | 5.0 | | 1.6 |
| 0.01 | | 1.0 | | | 6.8 |
| 0.01 | | 1.0 | 2.0 | | 5.2 |
| 0.01 | | 1.0 | 3.0 | | 2.7 |
| 0.01 | | 1.0 | 4.0 | | 2.4 |
| 0.01 | | 1.0 | 5.0 | | 2.2 |
| 0.01 | 1.0 | | | 0.3 | 2.9 |
| 0.01 | 1.0 | | | 1.2 | 0.32 |

[a] See note *a*, Table 1. [b] As note *b*, Table 1 with $k_3^{\mathrm{H^+}}$ 0.014 $\mathrm{l^2\ mol^{-2}\ s^{-1}}$.

concentrations (Figure 5). When no acid is added the order in catalyst rapidly drops from *ca.* 1 to almost zero with increasing $[VO(acac)_2]_0$; on the other hand in the presence of acid the order in catalyst changes from one (initial range) to a minimum of *ca.* 0.5.

Monomer–dimer equilibria of vanadium(v) species might be thought responsible for this behaviour. However it is likely that more complex aggregation phenomena of vanadium(v) species are responsible for the departure from first-order dependence in catalyst, especially in the absence of acid.[8]

The order in hydroperoxide at a fixed acid concentration has been found to be one over a wide concentration range. The deviation towards lower orders appears to be significant only at very high peroxide concentrations. A decrease in a kinetic order on increase in concentration (where no polymerization occurs) is usually assumed to be an indication of a saturation effect, such as occurs with enzymes and substrates to give the Michaelis–Menten type rate law.[1,3] In this respect, in acid media, saturation of the metal catalyst by association with hydroperoxide seems to be relatively unimportant.

TABLE 3

Rates of oxidation of di-n-butyl sulphide by t-butyl hydroperoxide catalysed by added $VO(acac)_2$ or $VO(OEt)_3$ at 25.00 ± 0.05° in dry $Pr^iOH$ under nitrogen

| $[Bu^tO_2H]_0$/ M | $10^3[VO(acac)_2]_0$/ M | $10^3[VO(OEt)_3]_0$/ M | $10^3[CH_3SO_3H]_0$/ M | $10^3k_{2obs}$/ [a] $l\ mol^{-1}\ s^{-1}$ |
|---|---|---|---|---|
| 0.01 | 2.0 | | | 0.33 |
| 0.01 | 2.0 | | 2.0 | 1.4 |
| 0.01 | 2.0 | | 3.0 | 1.4 |
| 0.01 | 2.0 | | 5.0 | 1.4 |
| 0.01 | | 2.0 | | 0.07 |
| 0.01 | | 2.0 | 2.4 | 1.5 |
| 0.01 | | 2.0 | 4.0 | 1.4 |
| 0.01 | | 2.0 | 5.0 | 1.5 |

[a] See note *a*, Table 1.

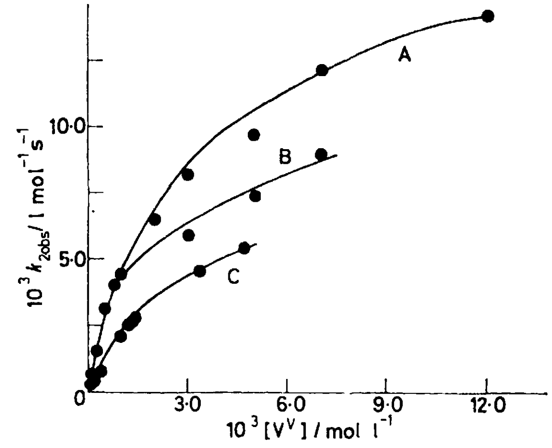

FIGURE 5 Dependence of rates upon added $VO(acac)_2$ catalyst in the oxidation of $Bu^n_2S$ by $Bu^tOOH$ in EtOH at 25.0° at different medium acidities. Curve A: 0.02M-$MeSO_3H$; curve B: 0.0005M-$MeSO_3H$; curve C: no acid added

From these considerations, we can express the general rate law at low concentrations of catalyst and peroxide as (1). When the catalyst concentration remains the

$$-d[ROOH]/dt = k_3[\text{sulphide}][Bu^tOOH][\text{catalyst}] \quad (1)$$

same and the sulphide concentration is greater than peroxide, we can define the observed first-order rate law as (2) so that equation (3) applies with an observed

$$-d[Bu^tOOH]/dt = k_1[Bu^tOOH^-] \quad (2)$$

$$k_1 = k_3[\text{sulphide}][\text{catalyst}] \quad (3)$$

$$k_{2(obs)} = k_3[\text{catalyst}] \quad (4)$$

second-order rate constant $k_{2(obs)}$ given by equation (4). The data in Tables 1—3 have been collected in terms of $k_{2(obs)}$.

*Effect of Acid and Base.*—Let us consider first the effect of acidity on the vanadate ester-catalysed oxidation in ethanol (see Table 1). Very small amounts of acid have a dramatic effect (in one instance, a 12-fold enhancement in rate); further increases in acid concentration have only a minor effect but eventually the rates significantly decrease (near $[CH_3SO_3H]$ 0.1M). When the vanadium is added as $VO(acac)_2$, the effect of acid is the same except for the higher rate in neutral ethanol. We do not attribute particular significance to this difference since in the reaction medium vanadium(v) species should be very sensitive to any acidic impurity. As the oxidation of $V^{IV}$ in fact follows stoicheiometry (5)

$$2VO(acac)_2 + 6ROH + Bu^tOOH \longrightarrow VO(OR)_3 + 2acacH + Bu^tOH + H_2O \quad (5)$$

the weakly acidic acacH formed and perhaps water might play a role in determining the difference in rate. Oxidation products of acacH should also be acidic. This point was not further investigated.

The influence of base in the $VO(acac)_2$ catalysed reaction at concentrations comparable with those of the catalyst results in a sharp decrease in the reaction rate. It is noteworthy that an amount of sodium ethoxide only 1/10 of the catalyst concentration causes an almost four-fold decrease in the rate. Thus the effect of base cannot simply be explained in terms of stoicheiometric formation of an anionic species of vanadium(v) with the latter expected to be a poor catalyst. Presumably added ethoxide causes significant polymerisation and anion formation so that the sum of these two phenomena

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[8] F. J. C. Rossotti and H. Rossotti, *Acta Chem. Scand.*, 1956, **10**, 957.

magnifies the effect of added base. Again, similar behaviour has been seen in aqueous solutions of vanadates.[9]

Turning to the acidic side, there is a close parallel of rate with the spectroscopic results. The extended plateau between $5 \times 10^{-4}$ and $5 \times 10^{-3}$M-methanesulphonic acid corresponds rather well to the delayed onset of the optical density increase at 395 nm; these results indicate that significant protonation begins only at higher acidity. The decrease in rate seen at still higher acid concentrations corresponds to the increase at 395 nm which, as shown by the potentiometric results, is linked to protonation. Why the protonated vanadate esters should be less effective as catalysts than the neutral species is not immediately clear. In fact one might have expected increasing efficiency of the catalyst with protonation as cationic species normally would be stronger electrophilic catalysts. There are, however, two relevant points. First, peroxides tend to add more strongly to basic species, as may be seen in the fact that $B(OH)_4^-$ adds peroxide strongly [reaction (6)] while its

$$B(OH)_4^- + HOOH \rightleftharpoons B(OH)_3(OOH)^- + H_2O \quad (6)$$

conjugate acid $B(OH)_3$ does not.[10] Secondly, the marked change in the u.v. spectrum in strong acid suggests that the co-ordination number of vanadium increases from four to five or six. A known case which is related is the co-ordination number change for perrhenate which is accompanied by a distinct colour change.[11] Since a feature common to all oxyanion systems is increase of replacement rate with acidity, the rate decrease cannot be ascribed to slower formation of a peroxo intermediate. In the other two alcohols studied, the same general considerations can explain the results. In the more basic propan-2-ol, the effect of acid on rates is stronger and the plateau is apparently more extended. The differences between the oxidation rates in neutral alcohol for added $VO(acac)_2$ and $VO(OEt)_3$ are also larger.

On the other hand, in methanol the influence of base is the same as in ethanol, but the effect of acid appears to be different. In particular, the rates in neutral alcohol are the same for the two catalysts and addition of acid causes, at very low concentration, a decrease in rate. The rationale for this is again found in the spectroscopic results which show that protonation in methanol begins at low acid concentrations and the resulting decrease in rate presumably depends on the same factors discussed above for the reaction in ethanol.

From our data, we conclude the following. (1) The vanadium species which acts as catalyst is related to the vanadate ester of the particular alcohol which is also the solvent. Other forms are rapidly converted by metathesis and/or oxidation into this triester. (2) The triester can exist in at least three forms (anion, neutral molecule, or cation) depending on the acidity. Of these three, the neutral species $VO(OR)_3$ is the most active catalyst. (3) Oligomerisation of the vanadium triesters can occur and it is more pronounced as the acidity decreases. (4) It is important when comparing rate data for different transition metal catalysts to make all other variables constant. For example, if one compares reaction rates in neutral alcohols, large effects are seen for different catalysts and different alcohols. These differences are not solely due to a simple solvent effect on reaction rates but rather to a solvent effect on rates plus an effect on acid–base equilibria. To obtain therefore a ' true ' solvent effect on reaction rate which, for the data reported above, is the effect of changing the nature of the solvent (other than its acid–base properties), one should compare the rates at the plateau. For methanol, ethanol, and propan-2-ol, these values are $6.8 \times 10^{-3}$, $5.4 \times 10^{-3}$, and $1.5 \times 10^{-3}$ $l^2$ $mol^{-2}$ $s^{-1}$, respectively. There is only a small difference for propan-2-ol.

This study, originally inspired by the solvent-induced asymmetric synthesis of sulphoxides, comes full circle with a more definitive explanation for this discovery since (when the alcohol present in the solvent system is chiral) a chiral vanadate ester is formed very rapidly and is the catalytic species.

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