Polymer-supported Oxobis(pentane-2,4-dionato)vanadium(IV) Catalyst for Reactions involving t-Butyl Hydroperoxide

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The polymer-supported title compound catalyses the homolytic decomposition of $\mathrm{Bu^tO_2H}$ and its reactions with $\mathrm{Me_2SO}$, $\mathrm{Bu^n{}_2S}$, and cyclohexene to give $\mathrm{Me_2SO_2}$, $\mathrm{Bu^n{}_2SO}$, and cyclohexene oxide respectively. Polymer-chain participation in the radical reactions seems to give additional catalytic pathways for the decomposition of $\mathrm{Bu^tO_2H}$. Recycling of the polymer-supported complex in the conversion of $\mathrm{Me_2SO}$ into $\mathrm{Me_2SO_2}$ results in lower product yields due to the loss of metal ions. Comparative studies between the polymer-supported and the homogeneous systems suggest extra stability for the polymer-anchored, catalytically active species. The diffusion barrier between the reactants in solution and the polymer influences the rates and may be responsible for this extra stability.

THE rate of a chemical reaction catalysed by a polymer-bound homogeneous catalyst is determined by a number of factors, none of which is fully understood at present. Two effects that seem to play important roles in these reactions are stabilisation of reactive organometallic species on the polymer and diffusion of the substrate into the polymer ' porous ' system which depends on the size of the substrate.[1] Examples are known where immobilisation has led to the stabilisation of co-ordinative unsaturation or of unusual oxidation states.[2,3] Similarly, the kinetic effect of diffusion or the size effect, leading to steric restrictions around the catalytic centre, has been clearly demonstrated.[4,5]

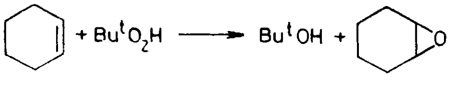
We wanted to find out the relevance of these two effects to some oxidation reactions involving t-butyl hydroperoxide $\mathrm{Bu^tO_2H}$ and polymer-supported $[\mathrm{VO(pd)_2}]$ (Hpd = pentane-2,4-dione). Vanadium(IV) and molybdenum(VI) complexes are known to act as efficient oxygen-transfer catalysts for reactions involving organic hydroperoxides and sulphides, sulphoxides, amines, olefins, *etc.*[6,7] Linden and Farona[8a] recently reported the epoxidation of cyclohexene with $\mathrm{Bu^tO_2H}$ and a number of polymer-supported vanadium catalysts. Although these authors have given details of the catalyst preparation, very few comparative studies with the corresponding homogeneous reactions are mentioned.

In this paper we report studies on reactions (i)—(iv) with polymer-supported $[\mathrm{VO(pd)_2}]$ as the catalyst. A comparison has been made between kinetic data obtained from these reactions in the homogeneous and polymer-bound systems. The results indicate extra stability for the polymer-bound catalytically active species, and the importance of the diffusion factor, in all the reactions.

$$\mathrm{Bu^tO_2H \longrightarrow Bu^tOH + \tfrac{1}{2}O_2} \qquad \text{(i)}$$

$$\mathrm{Me_2SO + Bu^tO_2H \longrightarrow Me_2SO_2 + Bu^tOH} \qquad \text{(ii)}$$

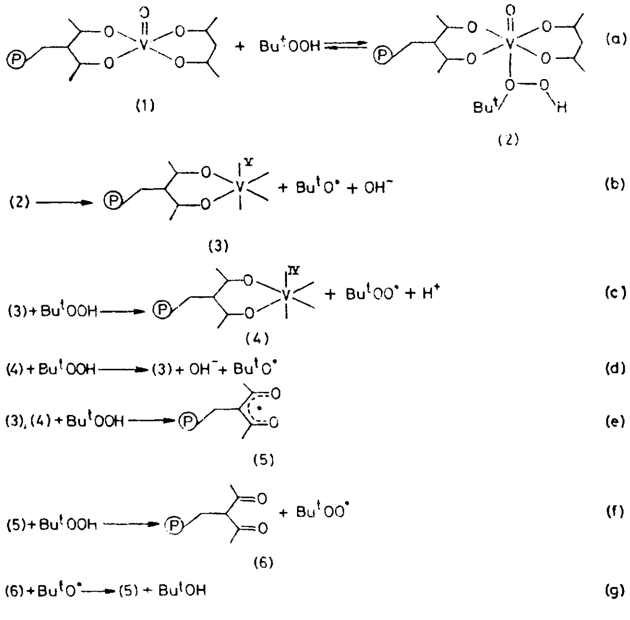
$$\mathrm{Bu^n{}_2S + Bu^tO_2H \longrightarrow Bu^n{}_2SO + Bu^tOH} \qquad \text{(iii)}$$



(iv)

RESULTS

The polymer-supported catalyst was prepared by a procedure somewhat different from the one reported by Linden and Farona.[8b] Divinylbenzene cross-linked polystyrene beads (8%) were first chloromethylated and then treated for 24 h at 65 °C with pentane-2,4-dione and a catalytic amount of sodium ethoxide in tetrahydrofuran. After separation, the brownish yellow beads were heated with $[\mathrm{VO(pd)_2}]$ in toluene, at 109 °C, for another 24 h, to give greenish blue polymer-supported $[\mathrm{VO(pd)_2}]$. Estimation of vanadium by atomic absorption spectroscopy showed 0.003 g of vanadium to be present per gram of beads. The functionalised and the vanadium-containing polymers showed strong, broad, i.r. bands at 1 700 and 1 580 $\mathrm{cm^{-1}}$ attributable to free and chelated carbonyl groups respectively. In accordance with Linden and Farona's formulations, the functionalised and the vanadium-containing polymers are essentially represented as (6) and (1) in Scheme 1. The problem of multiple co-ordination by the functionalised polymer will be discussed elsewhere.



Ⓟ = Polymer backbone

SCHEME 1

A known quantity of Bu^tO_2H was diluted with an inert solvent such as ethanol or benzene and maintained at a constant temperature. For reactions (ii)—(iv) the organic reactant was added to this mixture and allowed to reach thermal equilibrium. After withdrawing a small quantity of the reaction mixture for analysis, the polymer beads containing a known amount of vanadium ions were added, and the mixture was stirred magnetically. Samples were withdrawn periodically for iodometric and gas chromatographic (g.c.) analyses. All the reactions were allowed to continue for various lengths of time after which the polymer beads were filtered off, dried, and analysed by i.r. spectroscopy.

For reactions (i)—(iii) the rates of hydroperoxide consumption were monitored iodometrically, while for (iv) the rate of formation of cyclohexene oxide was measured by gas chromatography. The initial rates of the corresponding homogeneous reactions were obtained under identical conditions. Values of the ' relative rate ', defined as the ratio between the initial rate of the polymer-supported reaction and that of the homogeneous reaction, are given in the Table.

Reaction	Relative rate [a]
Catalytic decomposition of Bu^tO_2H	1.4
Dimethyl sulphoxide to dimethyl sulphone	0.45 [b]
Di-n-butyl sulphide to di-n-butyl sulphoxide	0.1
Cyclohexene to cyclohexene oxide	0.3 [c]

[a] Initial rate with (1) as the catalyst: initial rate with [VO(pd)$_2$] as the catalyst. [b] For the first run. [c] Mol ratio of cyclohexene to Bu^tO_2H was 50 : 1.

In all these reactions, on addition of hydroperoxide, compound (1) underwent a colour change from greenish blue to brownish red. The metal contents of the polymer beads, after being exposed to Bu^tO_2H for various lengths of time, were measured by atomic absorption spectroscopy. It was found that exposure for *ca.* 5 h, under the conditions employed in most of the reactions, caused *ca.* 30% loss of the metal ions. Due to the reversible reaction with the hydroperoxide, these beads, after drying, were still greenish blue in colour, although the intensity was somewhat less than that of the original beads (see below). The i.r. spectra recorded periodically showed a gradual change: the broad band for the metal-bound ligand at *ca.* 1 580 cm^{-1} slowly disappeared while the band for the free ligand at 1 700 cm^{-1} became stronger. No distinguishable new bands were observed in between.

For reaction (i) at 40 °C the relative rate was found to be 1.4. The reactions were continued for 24 h throughout which a higher rate was maintained with the polymer-supported catalyst. At the end of this period the amount of unreacted Bu^tO_2H in the polymer-supported reaction was about half that in the homogeneous reaction. Identical results were obtained by carrying out the reaction with a mixture of the support material, *i.e.* functionalised resin, and free [VO(pd)$_2$]. The concentrations of metal ions and polymer beads were of course the same for both the reactions.

Reaction (ii), carried out at 56 °C with freshly prepared (1) for 5 h, gave a nearly quantitative yield of dimethyl sulphone. The polymer beads were filtered off, dried, and re-used for the next run under identical conditions. This process was repeated until the yield of sulphone was reduced to a low level. The amount of unreacted Bu^tO_2H was estimated at the end of each run. Figure 1 shows the variation in the yield of dimethyl sulphone with the number of runs. For the first run the rate of disappearance of Bu^tO_2H was monitored iodometrically and the value for the relative rate was 0.45. Reaction (iii) was performed in a similar fashion at 25 °C. In this case, however, successive runs were not carried out. The relative rate was found to be 0.1.

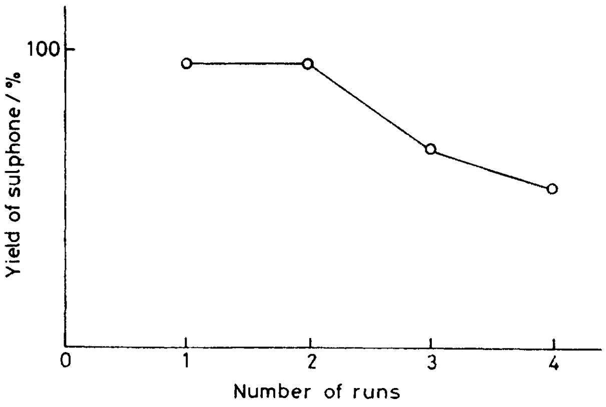


FIGURE 1 Variation in the percentage of dimethyl sulphone with successive runs

Linden and Farona [8] reported that the overall yield of cyclohexene oxide after 6 h of reaction at 80 °C with polymer-supported [VO(pd)$_2$] was about double that with the free complex. Since no explanation was offered for the increased yield we decided to study reaction (iv) in more detail. The reaction was carried out at 40 °C with two different (1 : 2 and 50 : 1) cyclohexene : Bu^tO_2H mol ratios. At the 1 : 2 ratio the relative rate could not be measured accurately. After 10 min with (1) or free [VO(pd)$_2$] the concentration of cyclohexene oxide was virtually the same. However, for the homogeneous reaction the concentration of cyclohexene oxide in solution gradually decreased. After 2 h the yield was about 20 times larger for the polymer-supported catalyst. Although the relative rate at the 50 : 1 ratio was only 0.3, the rate of the homogeneous reaction rapidly decreased with time. The rate for the polymer-supported system, however, was fairly constant. After 1.5 h the yield of cyclohexene oxide with (1) was about 1.5 times greater than in the homogeneous reaction. The

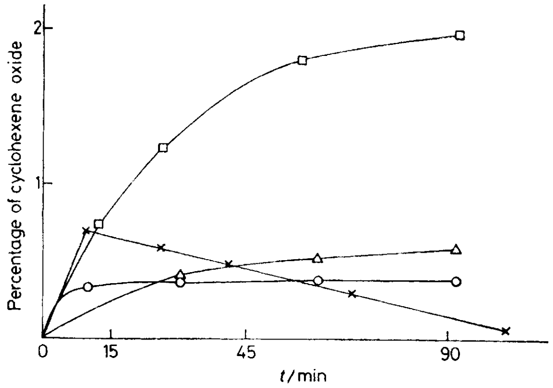


FIGURE 2 Rate of cyclohexene oxide formation. Catalysis with (1) and [VO(pd)$_2$] respectively with cyclohexene to Bu^tO_2H mol ratios of 1 : 2 (□, ×) and 50 : 1 (△, ○)

concentration of cyclohexene oxide plotted against time for these reactions is shown in Figure 2.

DISCUSSION

Extensive kinetic and physicochemical studies on catalytic oxidations of organic substrates with hydroperoxides, in the presence of $[VO(pd)_2]$ as a catalyst, have been reported by various workers.[9-12] The interaction of $[VO(pd)_2]$ with hydroperoxides only has also been investigated.[13,14] Based on these results, this class of reactions can be best described by the following sequence of events.

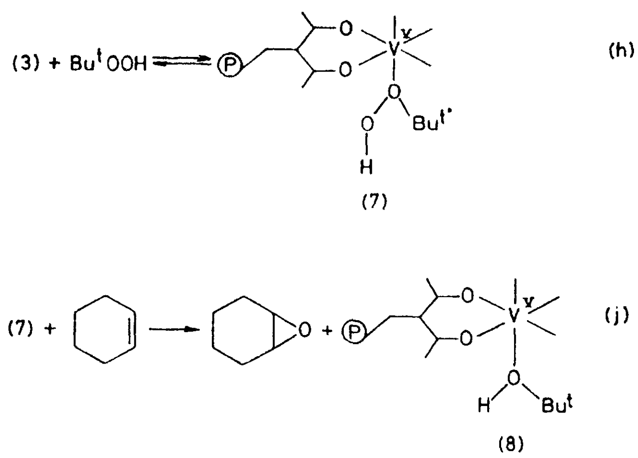
The catalyst is first activated in a rapid irreversible manner, *via* a red intermediate taken as a vanadium(IV)–hydroperoxide complex, to a vanadium(V) species of unknown composition. This reaction produces alkoxy- or hydroxy-radicals which can initiate a competing radical-chain decomposition process. Reversible formation of a complex between the vanadium(V) species and Bu^tO_2H then takes place. The subsequent rate-determining oxygen-atom transfer from this complex to the organic reactant gives the final oxidised product and alcohol. The vanadium(V) species can also oxidise the hydroperoxide to generate peroxy-radicals. In some cases, the organic reactant and the oxidised product, *e.g.* cyclohexene and cyclohexene oxide, react with these radicals, lowering the selectivity of the reaction.[15]

A ligand effect is observed in the initial stages of the epoxidation reaction, indicating that the catalysts retain, at least in part, their ligand environments when converted into catalytically active vanadium(V) species.[10] It is also found that, superimposed on the inhibitory effect of Bu^tOH, a further mode of inhibition arises from oxidative degradation of the catalyst. Similar observations have been made with $[MoO_2(pd)_2]$ as the catalyst, which gives a higher rate of epoxidation initially, but the rate then decreases with time due to the formation of a less active 1,2-diol complex.[16]

It is reasonable to assume that when polymer-supported $[VO(pd)_2]$, *i.e.* (1), is treated with Bu^tO_2H, with or without an organic reactant, reactions similar to the ones observed in the homogeneous system will take place. However, the compositions of various intermediates, their stabilities, and the rates of the competing steps might be altered markedly due to polymer attachment. Based on the results obtained from the homogeneous systems, Schemes 1 and 2 are proposed for the polymer-supported reactions.

Activation of the catalyst takes place through a red vanadium(IV) intermediate (2) as shown by reaction (a). This species is then converted into the active vanadium(V) complex (3), and radicals are generated. In (3) the metal ion is still polymer-bound although part of its ligand environment has been destroyed. In the absence of an organic reactant, only the reactions shown in Scheme 1 can then proceed. Reactions (c) and (d) are similar to the well known transition-metal-catalysed redox pathways for the breakdown of Bu^tO_2H. Reaction (e) is of importance since this leads to the complete removal of the metal from the polymer backbone. Radical species (5), produced in this step, can then give additional catalytic pathways for the breakdown of the hydroperoxide, as shown by reactions (f) and (g).

Thus the relative rate of reaction (i) can be explained in terms of steps (f) and (g). For the homogeneous system, the comparable reactions would be less effective for two reasons. First, due to polymer anchoring, a diffusion barrier exists between Bu^tO_2H in solution and (5) and (6). As a consequence, oxidative degradation of the ligand groups does not take place to the same extent as in the homogeneous reaction. This is evident from the i.r. spectrum of the beads isolated after 24 h of reaction. As mentioned earlier, the overall spectrum and the intensity of the band at 1 700 cm^{-1}, attributable to the carbonyl stretching of the free ligand, are comparable with those of a freshly prepared sample of (6). Secondly, for (f) and (g), tertiary carbon atoms are involved, rather than secondary ones as would have been the case for the homogeneous reaction.



$(7) + Me_2SO \longrightarrow Me_2SO_2 + (8)$ (k)

$(7) + Bu^n{}_2S \longrightarrow Bu^n{}_2SO + (8)$ (l)

$(8) + Bu^tOOH \longrightarrow (7) + Bu^tOH$ (m)

$(3),(7),(8) + Bu^tOOH \longrightarrow (6) +$ inactive vanadium species in solution (n)

SCHEME 2

An alternative explanation, based on the argument that attachment of $[VO(pd)_2]$ to the polymer increases the intrinsic rates of (b)—(d), can be ruled out as follows. The relative rates for (1) and (6) with free $[VO(pd)_2]$ are the same. This is so because $[VO(pd)_2]$ in this experiment can generate sufficient radicals, making (f) and (g) feasible and giving a relative rate which is almost equal to 1.4. Under the conditions employed, *in situ* formation of (1) from (6) and the free complex does not take place. This has been confirmed by separate experiments.

The increased rate for reaction (i), with (1) as the catalyst, can therefore be reasonably attributed to the participation of the polymer-anchored ligand groups in the reaction.

The observations made for the selective oxidation of dimethyl sulphoxide, di-n-butyl sulphide, and cyclohexene can similarly be explained by referring to Scheme 2. A reversible complex formation between (3) and Bu^tO_2H [step (h)] leads to polarisation of the peroxy-bond. In the presence of a suitable substrate, transfer of an oxygen atom from (7) can then give selective oxidation products and (8) [steps (j)—(l)]. Step (n) is the oxidative degradation of (3), (7), and (8) and, as will be seen, is an important aspect of the epoxidation reaction. Since, in the homogeneous medium, oxidation of di-n-butyl sulphide is considerably faster than epoxidation of cyclohexene, this step is somewhat less important for reaction (iii).

As mentioned earlier, estimation of vanadium clearly indicates that *ca.* 30% of the metal is lost after 5 h of reaction (ii). This is reflected in the lower yields of dimethyl sulphone, and in the higher concentration of unreacted hydroperoxide, for the third and fourth runs. However, Figure 1 shows that equal amounts of dimethyl sulphone are obtained for the first two runs and the concentration of unreacted hydroperoxide, left at the end, is slightly more for the second run. This apparent discrepancy could easily be explained since a certain amount of Bu^tO_2H will be initially required for converting (1) into (3), the catalytically active, polymer-bound, vanadium(V) species. Polymer beads isolated at the end of the first run can be considered as a mixture of 70% of (1) and (3) and 30% of (6). No distinguishable change in the i.r. spectrum of these beads would be expected, as the characteristic bands are broad enough to mask any fine change due to the formation of (3). Thus, for the second run, more hydroperoxide is effectively used for the conversion of Me_2SO into Me_2SO_2.

Both reactions (ii) and (iii) have relative rates considerably less than 1. For the rate-determining reactions (k) and (l) to take place, it is necessary that Me_2SO and $Bu^n{}_2S$ diffuse into the polymer chain and come into the vicinity of the metal centres in (7). Since for the homogeneous reactions there are no such restrictions, the low values of relative rates could be taken as a manifestation of this diffusion barrier. The fact that for the bulkier $Bu^n{}_2S$ the relative rate is only 0.1, while for Me_2SO it is 0.45, tends to support the above explanation.

Epoxidation with (1) as the catalyst takes place according to reaction (j) shown in Scheme 2. For both the homogeneous and the polymer-supported reactions, oxidative degradation of the catalyst and radical degradation of cyclohexene oxide compete with selective epoxidation. It is proposed that the stabilities of the catalytically active vanadium(V) species in (3), (7), and (8) towards oxidative degradation are greater compared to their homogeneous counterparts. This is primarily due to polymer anchoring, which results in a diffusion barrier between Bu^tO_2H in solution and the metal centres in (3), (7), and (8). As a result, the ligand environments around the metal ions are maintained for a longer time.

Thus, although the initial rate of epoxidation in the homogeneous reaction at a high olefin to hydroperoxide mol ratio is high, it soon falls off to zero due to rapid degradation of the catalyst. The same diffusion barrier, which gives extra stability to the active vanadium(V) centres in (3) and (7), is responsible for the low relative rate. However, due to slower degradation, the polymer-supported catalyst remains active for more than 4 h and gives a higher yield of cyclohexene oxide at the end of the reaction.

With a high hydroperoxide to olefin mol ratio in the homogeneous reaction the radical degradation of cyclohexene oxide is noticeable. Three competing reactions, *i.e.* selective epoxidation, oxidative degradation of the catalyst, and radical degradation of cyclohexene oxide, determine the overall rate of epoxide formation. Since the catalyst is deactivated very rapidly, initial rate measurements with sufficient accuracy are difficult to carry out. Presumably the epoxidation reaction comes to a stop as soon as catalyst degradation is complete. Consumption of cyclohexene oxide through a number of radical pathways then causes a gradual decrease in its concentration with respect to time. On the other hand, the polymer-supported catalyst, even under these conditions, remains active for more than 2 h and maintains a positive rate for formation of cyclohexene oxide. This further illustrates the extra stability of the polymer-bound catalytically active species.

EXPERIMENTAL

Iodometric titrations for the estimation of Bu^tO_2H were carried out according to the literature procedure.[17] G.l.c. analyses were performed with a H.P. 5830A instrument according to the procedure described by Gould *et al.*[9] The reproducibility of each rate was within ±2%. Rate data obtained from three separate experiments was averaged to obtain the relative rate values. Infrared spectra were recorded on a Perkin-Elmer 377 grating spectrophotometer. Metal contents were determined by treating metal-containing polymer beads with aqua regia for 6 h at 100 °C and then estimating the metal-ion concentration in the diluted filtered solution using an IL 751 atomic absorption spectrophotometer. t-Butyl hydroperoxide solution (70%) was purchased from Aldrich Chemical Co. (U.K.) Ltd. and used without further purification. Divinylbenzene cross-linked polystyrene beads (8%) of fine mesh were kindly supplied by Industrial and Agricultural Engineering Co. (Bombay) Ltd. Chloromethylation of the polymer beads was carried out according to the reported method.[18]

Preparation of Polymer-supported [VO(pd)$_2$].—Chloromethylated polystyrene beads (40 g) were heated for 24 h at 65 °C with pentane-2,4-dione (20 g) and sodium ethoxide (1 g) in tetrahydrofuran (250 cm^3). The beads were then filtered off, washed with tetrahydrofuran, and dried under vacuum. These functionalised beads (20 g) were heated at 109 °C for 24 h with [VO(pd)$_2$] (5 g) in toluene (250 cm^3). The filtered, toluene-washed, dried beads (1) are greenish blue and exhibit a new, strong, broad band at 1 580 cm^{-1}; they contain 0.06 mmol of vanadium per gram.

Decomposition of Bu^tO_2H.—(*a*) *With* (1). t-Butyl hydroperoxide (2.5 cm^3, 19.3 mmol) was added to a mixture of ethanol (47.5 cm^3) and polymer-supported [VO(pd)$_2$] (2 g, 0.12 mmol vanadium). The mixture was stirred magnetically while maintaining the temperature at 40 °C. Small portions (1 cm^3) of the solution were withdrawn periodically and titrated iodometrically. The homogeneous reaction was similarly carried out with [VO(pd)$_2$] (0.032 g, 0.12 mmol).

(*b*) *With free* [VO(pd)$_2$] *and* (6). t-Butyl hydroperoxide (2.5 cm^3, 19.3 mmol) was added to a mixture of ethanol (47.5 cm^3), functionalised polymer beads (6) (1.97 g), and [VO(pd)$_2$] (0.032 g, 0.12 mmol). The mixture was maintained at 40 °C and stirred magnetically. Small portions of the solution were withdrawn periodically and titrated iodometrically. In a separate experiment the same reaction was carried out without the addition of the hydroperoxide. The beads isolated at the end were not coloured at all and had an i.r. spectrum identical with that of (6).

Conversions.—(*a*) *Dimethyl sulphoxide into dimethyl sulphone*. Polymer-supported [VO(pd)$_2$] (3 g, 0.18 mmol vanadium) was placed in ethanol (40 cm^3) and dimethyl sulphoxide (5 cm^3, 70 mmol). t-Butyl hydroperoxide (9.1 cm^3, 70 mmol) was added and the mixture stirred magnetically for 5 h while the temperature was maintained at 56 °C. The solution was filtered, reduced in volume, and cooled at 0 °C for 6 h to obtain crystals of dimethyl sulphone (6.1 g, 65 mmol). The beads were filtered off, washed, dried, and re-used for the second run. Vanadium estimation by atomic absorption spectroscopy of these beads gave a value of 0.042 mmol vanadium per gram of beads. The homogeneous reaction was carried out under identical conditions with [VO(pd)$_2$] (0.048 g, 0.18 mmol). In a separate experiment, the reaction was carried out in a similar fashion while the rate was monitored iodometrically.

(*b*) *Di-n-butyl sulphide into di-n-butyl sulphoxide*. Compound (1) (3 g, 0.18 mmol vanadium) was placed in ethanol (40 cm^3) and di-n-butyl sulphide (1.7 cm^3, 9.5 mmol). t-Butyl hydroperoxide (1.7 cm^3, 10 mmol) was added and the mixture stirred magnetically at 25 °C for 5 h. After filtering off the beads and removing most of the solvent under reduced pressure, the residue was treated with warm n-hexane, filtered, and chromatographed over silica gel with n-hexane–chloroform (1 : 1) as eluant. Di-n-butyl sulphoxide (1.3 g, 8.5 mmol), identical with an authentic sample, was isolated. In a separate experiment small portions (1 cm^3) of the solution were periodically withdrawn and titrated iodometrically to give the rate of hydroperoxide consumption. The homogeneous reaction was similarly carried out with [VO(pd)$_2$] (0.048 g, 0.18 mmol).

(*c*) *Cyclohexene into cyclohexene oxide*. Polymer-supported [VO(pd)$_2$] (1 g, 0.06 mmol of vanadium) was placed in benzene (20 cm^3) and cyclohexane (1 cm^3, 10 mmol) at 40 °C. t-Butyl hydroperoxide (2.57 cm^3, 20 mmol) was added and the solution stirred magnetically. Small portions (0.1 cm^3) of the solution were periodically removed by syringe and analysed by g.c. with chlorobenzene as the internal standard. In a separate experiment, cyclohexene (5 cm^3, 50 mmol) and Bu^{t}O$_2$H (0.13 cm, 1 mmol) were treated with (1) (1 g, 0.06 mmol of vanadium) in benzene (20 cm^3) at 40 °C and the rate monitored in a similar fashion.

The corresponding homogeneous reactions were carried out with [VO(pd)$_2$] (0.016 g, 0.06 mmol) under identical conditions.

[0/321 *Received*, 26*th February*, 1980]

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