Polymer-supported Complexes. Part 3.† Synthesis of a Polystyrene-anchored Molybdenum(v) Dithiocarbamato-derivative and its Applications in Reactions involving t-Butyl Hydroperoxide

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A dithiocarbamato-complex of Mo^V has been anchored on functionalised cross-linked polystyrene and characterised. Polymer-supported $[Mo_2O_3(S_2CNEt_2)_4]$ has been used as the catalyst in the conversion of Me_2SO to Me_2SO_2 and cyclohexene to cyclohexene oxide with Bu^tO_2H. Although loss of metal ions from the polymer backbone is observed in both cases, prior activation of the polymer-supported species with Bu^tO_2H results in improved yields. Under identical conditions the polymer-supported system gave better yields of cyclohexene oxide than the homogeneous counterpart. These results are discussed in the light of reported mechanisms.

The attachment of organic groups capable of acting as ligands for transition-metal ions onto cross-linked polystyrene is important since the functionalised resin can be used as a support material for homogeneous catalysts.

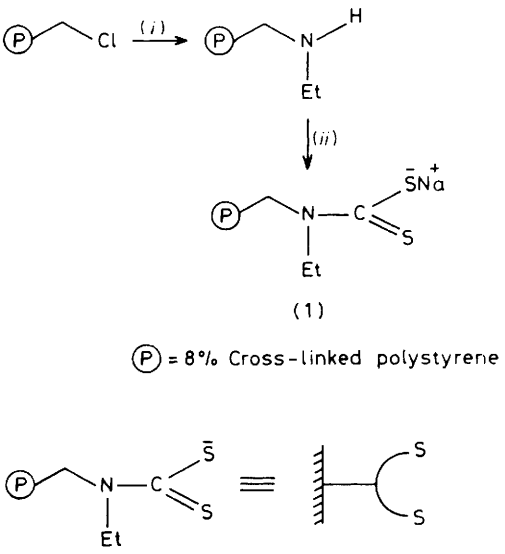
In previous papers we reported the syntheses, reactions, and catalytic applications of some polymer-anchored pentane-2,4-dionato-complexes.[1,2] Use of polymer-supported [VO-(pd)$_2$] (Hpd = pentane-2,4-dione) in oxygen-transfer reactions involving Bu^tO_2H have been described and comparative studies with the corresponding homogeneous reactions were made.

We have now extended our studies to a polystyrene supported dithiocarbamato-complex of molybdenum. The synthesis, characterisation, and application of the supported Mo^V dithiocarbamato-complex as a catalyst in the conversion of Me_2SO to Me_2SO_2 and cyclohexene to cyclohexene oxide by Bu^tO_2H are described.

Results and Discussion

(*a*) *Syntheses and Characterisation.*—As shown in Scheme 1, treatment of chloromethylated, 8% cross-linked polystyrene beads with base and ethylamine, followed by its reaction with CS_2 in the presence of a base produces complex (1) the functionalised resin. The sulphur analysis of (1) suggests the degree of functionalisation to be 12%. As calculated from the nitrogen and chlorine percentages of the aminated and chloromethylated beads respectively, the degrees of functionalisation with ^-NHEt and $^-CH_2Cl$ groups are *ca.* 36% and 68% respectively. This progressive drop in degree of functionalisation is presumably a result of the non-accessibility of some of the functional groups, *i.e.* only about one third of the total ^-NHEt groups are accessible to CS_2 and NaOH for reaction leading to the formation of dithiocarbamato-functionality.

Dithiocarbamato-complexes of molybdenum in the oxidation states of +4, +5, and +6 have been extensively studied by several workers.[3,4] When complex (1) is heated with yellow $[MoO_2(S_2CNEt_2)_2]$ in tetrahydrofuran (thf) at 65 °C for 12 h it undergoes a colour change from orange to purple-pink. After washing the resultant beads with a variety of solvents to remove all the surface adsorbed material, the presence of molybdenum is established by direct quantitative estimation. In a separate experiment, free $[MoO_2(S_2CNEt_2)_2]$ in refluxing thf undergoes disproportionation to give the known purple Mo^V species $[Mo_2O_3(S_2CNEt_2)_4]$. The complex $[MoO_2(S_2CNEt_2)_2]$ is known to react with PPh_3 to give quantitative yields of $[Mo_2O_3(S_2CNEt_2)_4]$ and $PPh_3(O)$.[4b] The disproportionation reaction probably follows a similar pathway, the dissociated thiocarbamato-ligand itself acting as the reducing agent.



Scheme 1. (*i*) NH_2Et, NaOH; (*ii*) CS_2, NaOH

Infrared spectra of the purple-pink beads provided little information about the identity of the anchored species since the characteristic stretches of $[MoO_2(S_2CNEt_2)_2]$ or $[Mo_2O_3(S_2CNEt_2)_4]$ appear in regions which are obscured by the absorptions of the polymer backbone. However, polymer beads having virtually the same analytical data and physical appearance (*i.e.* purple-pink) could also be obtained by treating (1) with $[Mo_2O_3(S_2CNEt_2)_4]$ in thf at 65 °C. This observation along with the fact that the resultant polymer has an e.s.r. spectrum identical in essential details to that of $[Mo_2O_3(S_2CNEt_2)_4]$ (see Figure 1) suggests its formulation as complex (2) in Scheme 2. The support material (1) has a very weak e.s.r. signal due to the presence of some paramagnetic impurity. However, the signal for Mo^V is much more intense and has observable fine structures. The signal for (2) is weak compared to that of free $[Mo_2O_3(S_2CNEt_2)_4]$ due to the dilution of paramagnetic Mo^V centres with the polymer matrix. Oxidation of (2) with Bu^tO_2H involves conversion of

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† Part 2 is ref. 2.

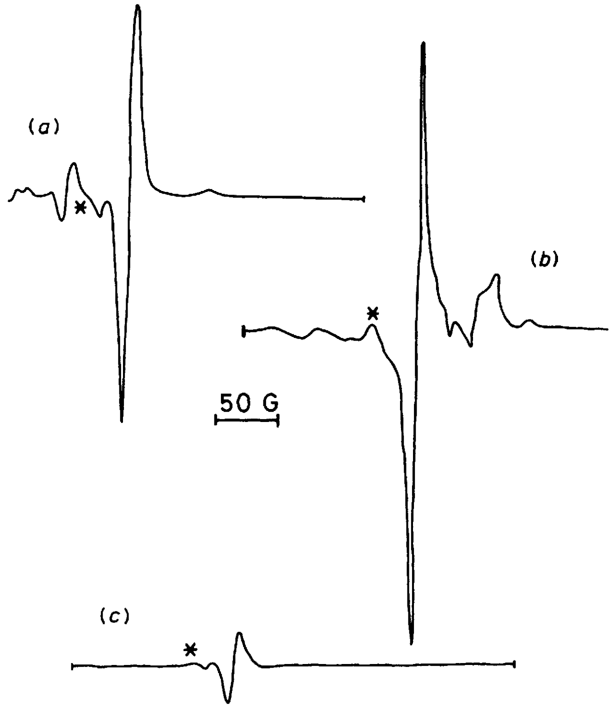
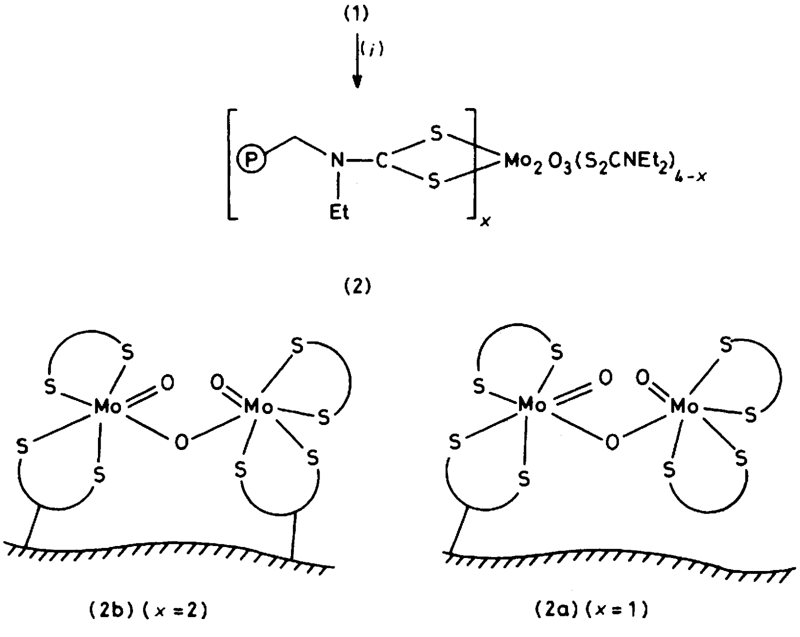


Figure 1. E.s.r. spectra of (*a*) powdered, polymer-anchored Mo^V complex (2), (*b*) free $[Mo_2O_3(S_2CNEt_4)_4]$, and (*c*) complex (1). The e.s.r. signal for the marker, tetracyanoethylene, is shown by an asterisk



Scheme 2. (*i*) $[MoO_2(S_2CNEt_2)_2]$ or $[Mo_2O_3(S_2CNEt_2)_4]$

Mo^V to Mo^{VI} and results in the disappearance of the characteristic molybdenum signal; the very weak background signal remains, however.

As pointed out by other workers, microanalytical data for polymeric samples are best taken as a qualitative rather than a quantitative guide.[5] On the basis of such data the distinction between formulations (2a) and (2b) cannot be made. In the case of polymer-supported pd complexes it was found that under certain conditions mobility of the polymer chain makes it behave as a polydentate ligand.[2] A ligand environment as shown in (2b) is therefore quite likely. However, keeping in mind the limited mobility of the cross-linked polymer chain, formulations with $x = 3$ or 4 seem unlikely.

(*b*) *Complex* (2) *as a Catalyst in Reactions involving* Bu^tO_2H.—Use of Mo^{VI} complexes as homogeneous catalysts in oxygen-transfer reactions involving Bu^tO_2H has been extensively studied.[6] The basic mechanism appears to be co-ordination of the hydroperoxide to Mo^{VI} causing weakening of the peroxo-bond. This is followed by transfer of the oxygen atom of the ^-OH group, *i.e.* heterolytic cleavage of the peroxo-bond, to organic substrates such as olefins, sulphides, sulphoxides, or tertiary amines. Vanadium(IV) complexes also act as effective catalysts in these reactions through a similar mechanism and mechanistic studies on homogeneous and polymer-supported reactions involving $[VO(pd)_2]$ as the catalyst have been reported.[1,7,8]

Treatment of (2) with Bu^tO_2H for 12 h causes a colour change from purple-pink to yellow and the e.s.r. signal attributable to Mo^V disappears. This prior activation of (2) with Bu^tO_2H, which presumably involves oxidation of Mo^V to Mo^{VI}, is important for the catalytic oxidation of cyclohexene and Me_2SO (see later). In homogeneous reactions when a low-valent molybdenum complex such as $[Mo(CO)_6]$ is used as the catalyst precursor, Bu^tO_2H is consumed by two different reactions. Part of it is used in oxidising the original ligand environment, *i.e.* the CO groups, the remainder is utilised in converting Mo^0 to Mo^{VI}.[6] Similar observations have been made for $[VO(pd)_2]$ where Bu^tO_2H oxidises the metal ion as well as the pd groups.[1,7]

Rates of consumption of Bu^tO_2H by (2) and the free complex $[Mo_2O_3(S_2CNEt_2)_4]$ with equivalent amounts of metal ions have been monitored by iodometry, and the results for the first 5 h are shown in Figure 2. It is obvious that the free complex undergoes oxidation at a much faster rate than the corresponding polymer-supported derivative. The rapid

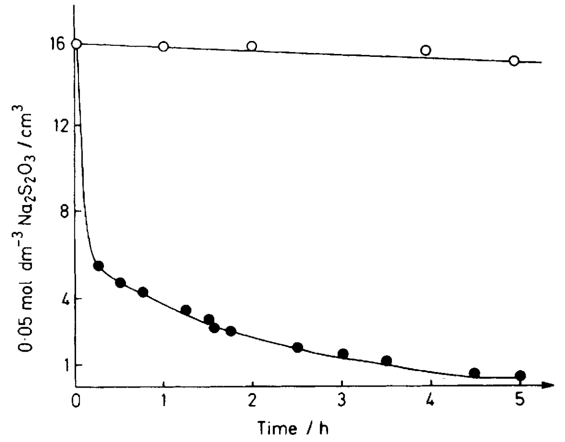


Figure 2. Decomposition of Bu^tO_2H by the polymer-supported Mo^V complex (2) (○) and free $[Mo_2O_3(S_2CNEt_4)_4]$ (●) monitored by iodometry

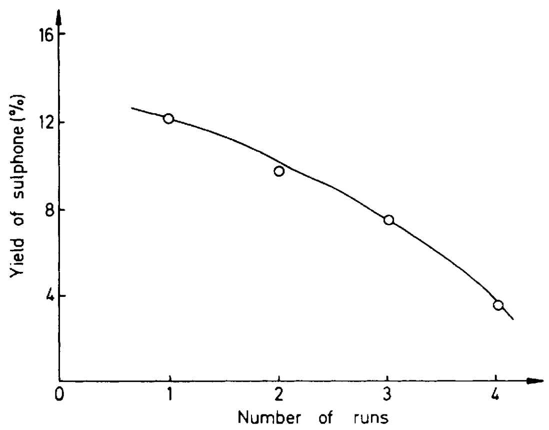


Figure 3. Recycling of the polymer-supported Mo^V complex (2) in the conversion of Me_2SO to Me_2SO_2. Each run was carried out for 5 h at 56 °C

consumption of Bu^tO_2H by the free complex could therefore be attributed to the fast and extensive oxidation of the ligand while the diffusion barrier that exists between Bu^tO_2H in solution and the polymer-anchored Mo^V complex prevents rapid oxidation of the ligand environment in the case of the polymer-supported system. With $[VO(pd)_2]$ however the rate of decomposition of Bu^tO_2H is higher with the polymer-supported rather than the free complex.[1] This is explained in terms of participation of the polymer chain in the radical decomposition of Bu^tO_2H. In the present system, involvement of radicals is of secondary importance since Mo^{VI} is known not to take part in the Haber–Weiss mechanism of radical decomposition of hydroperoxides.

Yields of Me_2SO_2 from the oxidation of Me_2SO with Bu^tO_2H and (2) as the catalyst were found to be crucially dependent on the reaction times. Thus while a run of 5 h with freshly prepared (2) gave 12% (based on Me_2SO) of Me_2SO_2, a run of 16 h with all other conditions remaining equal gave yields of *ca.* 70%. As has already been mentioned the oxygen-transfer reaction requires the creation of Mo^{VI}, which because of the diffusion barrier between the polymer and the bulk solution is not rapid. Complex (2) was recycled four times in the oxidation of Me_2SO and, as can be seen from Figure 3, the yield of Me_2SO_2 progressively reduces. This is caused by the partial loss of metal ions from the polymer backbone, as established by separate experiments. Thus treatment of (2) with an excess of Bu^tO_2H for 5 h led to a loss of molybdenum of *ca.* 10%. Loss of metal due to oxidative cleavage of the polymer–metal bond has also been observed with polymer-anchored $[VO(pd)_2]$.[1]

The reaction between Bu^tO_2H and cyclohexene with (2) as the catalyst has a variable induction time, the length of which primarily depends on the relative amounts of Bu^tO_2H, cyclohexene, and the catalyst. The reaction is further complicated by the fact that the product, cyclohexene oxide, is easily degraded in the presence of Bu^tO_2H. As already mentioned, the induction time is necessary for the oxidation of Mo^V to Mo^{VI} by Bu^tO_2H. Since excess Bu^tO_2H causes a substantial amount of metal leaching, (2) is best activated by treating it with a little more than the stoicheiometric amount of Bu^tO_2H in a medium of benzene and cyclohexene. Although the e.s.r. signal due to Mo^V disappears after *ca.* 12 h, as expected little or no cyclohexene oxide is formed under these conditions over a period of 24 h due to the shortage of Bu^tO_2H. The polymer beads are then filtered off and used as the catalyst in benzene, containing a known amount of cyclohexene and Bu^tO_2H. Under these conditions provided the cyclohexene to Bu^tO_2H molar ratio is $\geqslant 25:1$, more than 70% cyclohexene oxide (based on Bu^tO_2H) is obtained after 18 h. Yields of cyclohexene oxide are much lower ($\leqslant 20\%$) under identical conditions when $[Mo_2O_3(S_2CNEt_2)_4]$ is used as the homogeneous catalyst. This presumably is a result of consumption of Bu^tO_2H through the oxidation of the S_2CNEt_2 ligands which in a homogeneous medium could compete with cyclohexene oxide formation. However, in the polymer-supported system, because of the diffusion barrier, oxidation of the ligand environment is restricted. The Bu^tO_2H is therefore mainly used for the formation of cyclohexene oxide. This explanation is in agreement with the observations made on Bu^tO_2H consumption by the homogeneous and polymer-supported systems.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 377 grating spectrophotometer. Metal contents were usually determined by treating metal-containing polymer beads with aqua regia for 24 h at 100 °C and then estimating the metal concentration in the diluted filtered solution, using an IL 751 atomic absorption spectrophotometer. Gas chromatographic (g.c.) analyses were performed with a Pye-Unicam 204 instrument. A Carlo-Erba 1106 instrument was used for the microanalyses. Electron spin resonance spectra were recorded on a Varian E-112 instrument.

Divinylbenzene cross-linked polystyrene beads (8%) of fine mesh were kindly supplied by Industrial and Agricultural Engineering Co. (Bombay) Ltd. t-Butyl hydroperoxide solution (70%) was purchased from Aldrich Chemical Co. (U.K.) Ltd. and used without further purification. Unless otherwise specified all reactions were carried out under nitrogen in dry distilled solvents. Chloromethylation of the polymer beads and preparations of $[MoO_2(S_2CNEt_2)_2]$ and $[Mo_2O_3(S_2CNEt_2)_4]$ were carried out according to literature procedures.[5a,9]

Preparation of Cross-linked Polystyrene functionalised with Dithiocarbamato-groups (1).—Chloromethylated 8% cross-linked polystyrene beads (15.0 g) were refluxed with ethylamine (70% solution, 150 cm^3) in thf (100 cm^3) and sodium hydroxide (20% solution, 60 cm^3) for 24 h. The aminated beads (10.0 g) were added with thf (100 cm^3) to an ice-cold solution of carbon disulphide (68.5 g, 0.9 mol), sodium hydroxide (36.0 g, 0.9 mol) in water (80 cm^3), and ethanol (150 cm^3). The bright red solution was heated at 60 °C for 24 h after which the bright orange beads were filtered off, washed with water, thf, ethanol, and dried at 40 °C under vacuum (Found: N, 3.0; S, 4.8%. Degree of functionalisation on the basis of sulphur is 12%).

Preparation of Cross-linked Polystyrene-supported $[Mo_2O_3(S_2CNEt_2)_4]$ (2).—Beads of (1) (8.0 g) were refluxed with $[MoO_2(S_2CNEt_2)_2]$ (2.0 g, 4.8 mmol) in thf (250 cm^3) for 24 h with stirring. The purple-pink beads of (2) were filtered off, washed with thf-ethanol, $CHCl_3$, CH_2Cl_2, and dried under vacuum. The same polymer-supported material can also be obtained by heating beads of (1) (2.0 g) with $[Mo_2O_3(S_2CNEt_2)_4]$ (0.5 g, 0.6 mmol) in thf at 65 °C for 24 h [Found: N, 3.3; S, 8.2; Mo, 7.0%. Degree of functionalisation on the basis of molybdenum and formulation (2a) is 7.8%].

Rate of Consumption of Bu^tO_2H *with* (2).—t-Butyl hydroperoxide (2.5 cm^3, 19.3 mmol) was added to a mixture of thf (47.5 cm^3) and (2) (2.0 g, 1.45 mmol molybdenum). The mixture was stirred magnetically while maintaining the temperature at 40 °C. Small portions (1 cm^3) of the solution were withdrawn and titrated iodometrically. The homogeneous reaction was similarly carried out with $[Mo_2O_3(S_2CNEt_2)_4]$ (0.6 g, 0.72 mmol).

Conversions.—(*a*) *Dimethyl sulphoxide into dimethyl sulphone.* Beads of (2) (3 g, 2.18 mmol molybdenum) were 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 give crystals of dimethyl sulphone (0.8 g, 8.5 mmol). The beads were filtered off, washed, dried, and reused for the second run. Molybdenum estimation by atomic absorption spectroscopy of these beads gave a value of 0.58 mmol of molybdenum per gram of beads. In a separate experiment, fresh beads of (2) were used under identical conditions with the reaction time extended to 16 h to give dimethyl sulphone (4.6 g, 48.9 mmol).

(*b*) *Cyclohexene into cyclohexene oxide.* Beads of (2) (1.0 g, 0.72 mmol of molybdenum), cyclohexene (5 cm^3, 50 mmol), benzene (20 cm^3), and t-butyl hydroperoxide (0.13 cm^3, 1 mmol) were stirred together for 24 h at room temperature. The e.s.r. spectrum of a portion of the beads (0.2 g) isolated after 12 h showed only a very weak signal identical to that of (1). G.c. analyses after 12 and 24 h showed a total absence of cyclohexene oxide. The beads were filtered off after 24 h, washed with benzene, and treated with cyclohexene (2.5 cm^3, 25 mmol) and t-butyl hydroperoxide (0.13 cm^3, 1 mmol) in benzene (20 cm^3) at 60 °C for 18 h. G.c. analysis at the end of this period showed the presence of cyclohexene oxide (0.073 g, 0.75 mmol). The homogeneous reaction was similarly carried out with $[Mo_2O_3(S_2CNEt_2)_4]$ (0.300 g, 0.36 mmol of molybdenum) and t-butyl hydroperoxide (0.3 cm^3, 2.3 mmol) in benzene (20 cm^3) at 60 °C for 42 h. Samples analysed at various time intervals only showed the presence of small quantities of cyclohexene oxide, the maximum yield never exceeding more than 0.020 g, 0.20 mmol.

Disproportionation of $[MoO_2(S_2CNEt_2)_2]$ *to* $[Mo_2O_3(S_2CNEt_2)_4]$.—The complex $[MoO_2(S_2CNEt_2)_2]$ (1.0 g, 2.4 mmol) was heated at 65 °C in thf (50 cm^3) for 3 h. The colour of the solution changed from yellow to purple, and was then filtered and reduced in volume. Addition of n-hexane gave a purple precipitate of $[Mo_2O_3(S_2CNEt_2)_4]$ (0.4 g, 0.48 mmol) which was characterised by comparing its i.r. spectrum with that of the authentic material.

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Received 2*nd April* 1982; *Paper* 2/561