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Polymer-Supported Mo and V Cyclohexene Epoxidation Catalysts: Activation, Activity, and Stability

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The immobilisation of MoO_2acac_2 and $VOacac_2$ on a polystyrene support carrying a hydroxypropylated aminomethylpyridine ligand occurs via a ligand exchange reaction involving displacement of the acetylacetonate (acac) groups. In the case of the molybdenum species, the resulting blue polymer complex contains both Mo=O and Mo–O–Mo groups and immobilised ligand–metal bonds. Activation of the resulting complexes to form bright yellow species by pretreatment with excess *t*-butyl hydroperoxide is required before the supported complexes can become active catalysts for the epoxidation of cyclohexene by *t*-butyl hydroperoxide. *In situ* activation does not occur. It is believed that in the case of molybdenum activation involves oxidation of Mo(V) to new supported Mo(VI) species and that this is inhibited in the presence of alkene. Both polymer-immobilised Mo and V systems are catalysts of the epoxidation reaction, but the Mo-based system is considerably more active. Epoxidation reactions are characterised by an induction period followed by a relatively long linear conversion/time relationship. The induction period is probably associated with formation of the reactive intermediate which constitutes the true catalytic species, and this probably involves the reaction of the immobilised Mo(VI) complex with cyclohexene or traces of its epoxide. Polymer complexes subjected to more severe activation conditions display shorter induction periods and faster rates of epoxidation as a result of formation of more Mo(VI) centres. Additional Mo(VI) centres do not appear to be generated during epoxidation reactions. Mo and V are leached from their supports during activation. More severe activation conditions cause more metal leaching but the amounts lost are small (always <1.6%). The supported Mo complex remains an active catalyst when recycled up to nine times. Apart from an initial small drop, the activity remains essentially constant on reuse. Mo is also leached during epoxidations but the leached species make no significant contribution as catalyst-immobilised complexes are the active catalysts. The amounts of Mo leached are small (<0.4% per cycle) and fall progressively to essentially zero after nine cycles. The immobilised Mo complex offers the prospect of a technologically useful alkene epoxidation catalyst for continuous liquid phase oxidations using *t*-butyl hydroperoxide.

INTRODUCTION

Currently propylene is converted to its epoxide in a liquid phase process using an alkyl hydroperoxide as the oxidant in the presence of a molybdenum or titanium catalyst. In the Halcon process a soluble Mo complex is used with *t*-butyl hydroperoxide (tBHP) (*1*) while Shell has patented a heterogeneous catalyst involving Ti on silica and favours ethylbenzene hydroperoxide (EBHP) as the oxidant (*2*). Typically, reactions are run at ~100°C in a suitable solvent. The most versatile catalysts appear to be those based on Mo(VI), and the development of a viable polymer-supported alkene Mo(VI) epoxidation catalyst and a corresponding heterogeneous liquid (or gas) phase process is therefore an important objective.

The attempts to immobilise Mo and V complexes on polymers have included the use of sulphonic acid type cation exchange resins (*3*), anion exchange resins (*4*), and, more recently, a number of chelating ion exchange resins (*5, 6*). The use of these

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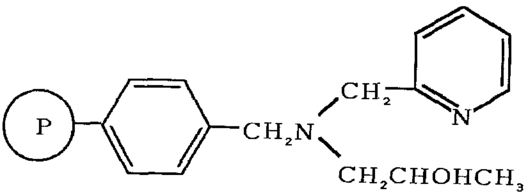
species has been reviewed (*7*). Most recently of all a bimetallic B(III)–Mo(VI) catalyst has been heterogenized on polyacrylamide and polystyrene-based supports (*8*) and used with tBHP or EBHP to epoxidize cyclohexene. Mainly these reports have focussed on demonstrating that the catalytic species are active and have paid relatively little attention to stability, whether in terms of polymer degradation, catalyst deactivation, or metal leaching. Where reference is made to stability, the results are generally poor, with systems displaying significant deactivation in use and/or catalyst leaching.

We now report on our own efforts in this area in which we have used a powerful chelating ligand bound to a polymer resin to complex both Mo and V. When appropriately activated these quickly proved to be potent catalysts for the liquid phase epoxidation of cyclohexene using tBHP as the oxidant, allowing our attention to be focussed on the stability and recycling of these systems.

EXPERIMENTAL

Materials

The poly(styrene–divinylbenzene)-based chelating resin (**1**) was obtained as a gift from the Dow Chemical Company (XFS 43084) and although the full comonomer composition has not been disclosed it is known to be derivatised with a *N*-hydroxypropylated 2-aminomethyl pyridine residue (*9*). The particle diameter was ~300–1100 μm, the surface area (N_2, BET) 34 m^2g^{-1}, and the pore volume (dry, Hg intrusion) 0.14 cm^3g^{-1}. The resin was stirred overnight in pyridine, washed well with distilled water, exhaustively extracted with acetone in a Soxhlet (24 h), and finally dried under vacuum; elemental microanalysis was C, 66.2%, H, 6.78%; N, 6.29%, corresponding to a ligand loading of 2.24 mmol g^{-1} resin.



(1)

"Anhydrous" *t*-butyl hydroperoxide (tBHP) was prepared from 70% aqueous tBHP (Aldrich Chemical Co) using the method described in the literature (*10*). 1,2-Dichloroethane was used to azeotrope out the water and the precise molarity of each batch of tBHP was estimated by iodimetry. In practice small traces of water remain in the tBHP/1,2-dichloroethane and this is believed to considerably improve its stability (*10*).

Molybdenyl acetylacetonate, $MoO_2(acac)_2$, and vanadyl acetylacetonate, $VO(acac)_2$, (Aldrich Chemical Co) were recrystallised from ethanol. Cyclohexene (Aldrich Chemical Co), cyclohexene oxide (Aldrich Chemical Co), 1,2-dichloroethane (Fisons Laboratories), cyclohexane (Aldrich Chemical Co), toluene (May and Baker), and bromobenzene (Fisons Laboratories) were fractionally distilled before use.

Preparation of Polymer-Supported Mo and V Complexes (PsMo and PsV)

Supported metal complexes were prepared by a ligand exchange reaction using a two molar excess of each metal acetylacetonate. The preparation of PsMo was as follows, and that of PsV was similar.

Resin **1** (5.3 g, 11.9 mmol ligand) and molybdenyl acetylacetonate (7.8 g, 24 mmol) were heated under reflux in toluene (200 ml) for 4 days. During this period the resin changed colour from greyish-tan to blue. The beads were separated by filtration, washed with acetone, then extracted in a Soxhlet for 72 h with acetone before being dried *in vacuo* (40°C). During extraction the solvent became deep blue despite being replaced several times. Eventually, however, no more blue colour was detected in fresh extractant.

Metal Analysis of Supported Metal Complexes

The supported complex (~0.1 g) was ground to a fine powder and then digested for 48 h in aqua regia (15 ml). After dilution to 100 ml with distilled water the metal content was assayed using normal atomic absorption spectrophotometric methods. The results agreed well with a colorimetric method for Mo (*11*). PsMo was found to have a metal content of 1.20 mmol Mo g^{-1} resin, and PsV 0.73 mmol V g^{-1} resin. Taking account of the mass of metal on each resin, this yields superficial ligand : metal ratios of 1.65 : 1 and 2.95 : 1, respectively.

Catalyst Activation

As we show later, supported complexes prepared as described above required to be activated before displaying significant catalytic activity. A typical procedure was as follows.

PsMo (0.05 g, 0.06 mmol Mo), anhydrous tBHP (60–1400 μl, 0.21–5.00 mmol) and dichloroethane (10 ml) were heated under reflux for a predetermined period ranging from 1 to 72 h. During this time the beads turned from a blue to a bright yellow colour which became more intense as the activation procedures became more severe. The beads were filtered off, washed with dichloroethane, and then sucked dry on a water pump before being introduced into a reaction mixture. The initial filtrate was assayed for metal to determine the loss of Mo during the activation process.

Catalytic Epoxidations

Typically the activated polymer-supported metal complex, PsMo or PsV, (0.06 mmol metal) cyclohexene (8.4 ml, 0.083 mol), an internal gas–liquid chromatographic standard (bromobenzene, 0.5 ml) and 1,2-dichloroethane (0.2 ml) were placed in a two-necked round-bottomed flask fitted with a reflux condenser and a septum cap. This was left to equilibrate at ~80°C for 15 min. "Anhydrous" tBHP (1.4 ml, 5 mmol tBHP) was added accurately by syringe to bring the total volume to 10.5 ml and the reaction at ~80°C was monitored by gas–liquid chromatography (GLC), attention being focussed on the appearance of cyclohexene oxide.

Homogeneous reactions using molybdenyl and vanadyl acetylacetonates were carried out in an identical batch procedure, omitting the activation process.

Typically reactions were allowed to proceed for 1–2 h and conversion/time curves were generated from the GLC data.

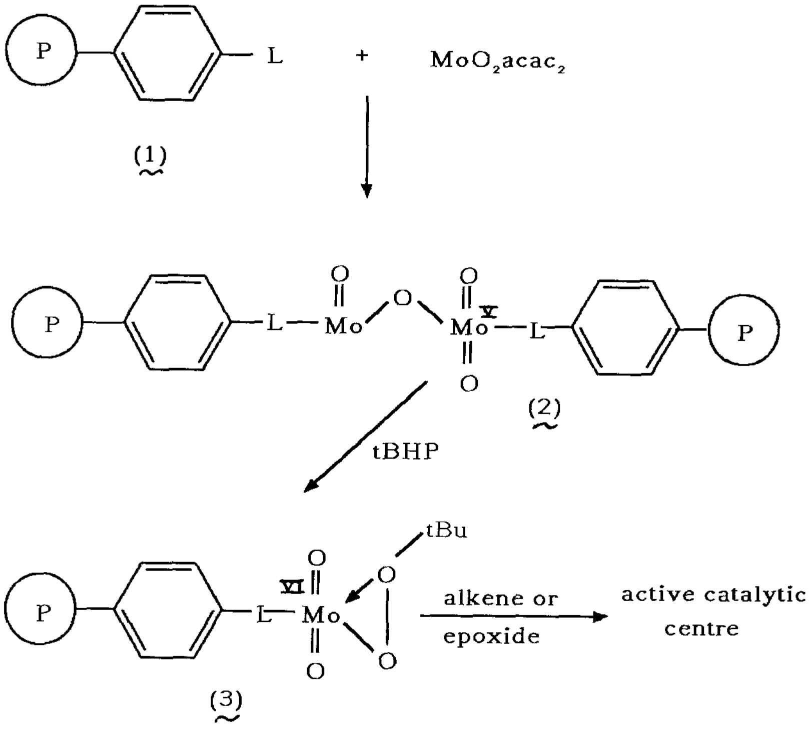
Catalyst Recycling and Metal Leaching

After a reaction was complete (1–2 h) the catalyst beads were filtered from the reaction solution and 5 ml of the latter retained for metal analysis. The beads were washed with 1,2-dichloroethane and then stored (generally overnight) in 1,2-dichloroethane (10 ml) and "anhydrous" tBHP (0.06 mmol). The latter solution was removed by filtration before the beads were used in a second reaction, as described above. A given sample of polymer-supported catalyst was used up to 10 times in this way.

The liquid from a reaction solution (and solutions recovered from each activation process) was removed on a rotary evaporator and the containing flask left overnight *in vacuo* (40°C). Dilute hydrochloric acid (0.1 *M*, 20 ml) and then concentrated hydrochloric acid (4 ml) were added to the yellow residue (from PSMo) and this was left on a shaker for 48 h. The resultant isotropic solution was then assayed for Mo.

Instrumentation

Infrared spectra were recorded on a Nicolet 20 SXB spectrometer. Liquid samples were recorded as films, whereas metal com-



SCHEME 1. Formation of active polymer-supported Mo^{VI} alkene epoxidation catalytic centre.

plexes and polymer-supported metal complexes were recorded in KBr discs. Ultraviolet/visible absorption spectra of Mo complexes were recorded on a Perkin–Elmer 124 double beam spectrophotometer. Mo and V metal analyses were made on an IL 251 atomic absorption spectrometer. Gas–liquid chromatographic analyses were performed on a Perkin–Elmer F 11 instrument equipped with a 10% carbowax on firebrick column. The oven temperature was 110°C and nitrogen (20 psi, 45 ml min^{-1}) was the carrier gas.

RESULTS AND DISCUSSION

Synthesis and Characterisation of Polymer-Supported Complexes

In general polymer-supported metal complexes tend to become more stable as the dentate number of the immobilising ligand increases (*5*, *12*). Also, it has been reported recently that complexes anchored on a macroporous polymer support display superior kinetic properties to those supported on gel-type resins (*5*). With this background, therefore, chelating resin **1** was identified as a potentially highly useful support for the immobilisation of Mo and V complexes. Furthermore, this resin contains both N and O donor atoms in its ligand and several Mo complexes with structurally related ligands have been reported to survive in the presence of hydroperoxides (*13*).

Direct ligand exchange of **1** with Mo and V acetylacetonates yielded the supported complexes PsMo and PsV. No attempt was made to optimise the immobilisation procedure and from our previous experience it is likely that the 4-day treatment is far longer than necessary to achieve full ligand exchange. PsMo contained 1.20 mmol Mo g^{-1} resin and PsV 0.73 mmol V g^{-1} resin. The superficial ligand : metal ratios were 1.65 : 1 and 2.95 : 1, respectively. The IR spectrum of PsMo showed two strong bands at 916 and 933 cm^{-1} which can be assigned to the asymmetric and symmetric stretches of terminal MoO_2, and a band at 726 cm^{-1} characteristic of a bridged Mo–O–Mo species (*14–20*). Information on the extent of coordination of the metal by N and O donor atoms was not clear from the spectrum; however, bands attributable to the bonding of the acetylacetonate ligand in, e.g., MoO_2acac_2, were not present (*21*).

A plausible structural picture of the initial polymer complex therefore involves complete ligand exchange of the acetylacetonate groups of the homogeneous complex, with simultaneous reduction of Mo(VI) to an oxo-bridged species (**2**) (Scheme 1). This probably contains some Mo(V) simply as a consequence of replacing the anionic acac ligand with a neutral one. However, the oxidation state of all the Mo centres and the number of linking oxo-bridges per complex are not clear and further experimental work is required to clarify this. Nevertheless, this picture is consistent with the known occurrence of blue mixed oxides of Mo containing at least some Mo(V), with the present microanalytical data, and with the calculated immobilised ligand: metal ion ratio of <2 : 1 in the case of PsMo.

A less detailed investigation of the V system was carried out because this proved to be a less useful catalyst in these reactions. However, we believe that an analogous structure occurs in the V system. (See later for a discussion of the structure of the active catalyst).

CATALYST EVALUATION

Initial Investigation

(*i*) *Homogeneous catalysts.* Table 1 summarises the results obtained using the homogeneous complexes MoO_2acac_2 and $VOacac_2$. Control experiments (rows 1–4 of Table 1) showed no reaction in the absence of catalyst; however, in the presence of either molybdenyl or vanadyl acetylacetonate epoxide product was obtained rapidly and in good yield. This is particularly true for the Mo complex and the results are comparable to those already reported for simple olefins (*22*). In fact, MoO_2acac_2 as the catalyst gave high epoxide yields (>90%) almost instantaneously (within our experimental procedure) at high temperature (83°C) and with high alkene concentration. Yields of epoxide and reaction rates were both reduced at lower temperature (30°C) and also when the alkene concentration is reduced. $VOacac_2$ proved to be a less effective catalyst as was expected. V(V) catalysed reactions in particular are known to be retarded by the coproduct *t*-butyl alcohol (*22*), and also V(V) catalyses the unimolecular decomposition of hydroperoxides more effectively than Mo(VI). The trends with the V catalyst were, however, the same as those observed with MoO_2acac_2.

(*ii*) *Polymer-supported catalysts.*Table 1 summarises the results of the preliminary reactions with the polymer-supported catalysts. Using PsMo in its blue form as prepared showed this to be essentially inactive as a catalyst. This came as a surprise, since although the complex was believed to contain some Mo(V), and Mo(VI) is generally regarded as the active catalyst in homogeneous reactions (*23*), it was anticipated that oxidation would occur *in situ,* as it does when required in homogeneous reactions (*24*), by the action of the more than adequate amount of tBHP present. Indeed, the blue colour of the polymer was retained throughout the period of monitoring (240 min) although at high temperature (83°C) and high alkene content (84 mmol) ~10% yield of epoxide was achieved, implying some minor generation of Mo(VI) species *in situ*.

Since all the liquid components were shown (separately) to imbibe significantly (0.25–0.5 g liquid g^{-1} polymer complex) and rapidly into the polymer catalyst beads, slow diffusion of tBHP to the vicinity of the metal centres cannot be invoked as an explanation for the lack of metal ion oxidation and catalytic activity. The only ratio-

TABLE 1

Epoxidation of Cyclohexene using *t*-Butyl Hydroperoxide Catalysed by Homogeneous Mo and V Acetylacetonate Complexes and Polymer-Supported Mo and V Complexes[a]

Catalyst	Temp (°C)	Cyclohexene (mmol)	% Yield cyclohexene oxide[b]		
			10 min	60 min	240 min
—	30	84	4	4	5
	30	5	0	0	0
	83	84	6	7	8
	83	5	0	0	0
MoO_2acac_2	30	84	40	57	70
	30	5	11	18	23
	83	84	95	94	92
	83	5	48	59	55
PsMo	30	5	1	1	1
	83	84	5	6	10
PsMo[c]	30	84	3	3	6
	30	5	1	1	1
	83	84	35	99	~100
	83	5	1	21	50
$VOacac_2$	30	84	6	18	32
	30	5	1	1	4
	83	84	21	50	57
	83	5	2	7	7
PsV[c]	30	84	1	2	4
	30	5	0	0	0
	83	84	8	26	34
	83	5	1	2	4

[a] 0.06 mmol metal; tBHP = 5 mmol; total volume adjusted to 10.5 ml with 1,2-dichloroethane.

[b] Yield based on consumption of tBHP, i.e., 100% yield = 5 mmol cyclohexene oxide.

[c] Polymer complex activated before use by treatment with tBHP (tBHP/Mo = 3.5) for 18 h at room temperature.

nalisation available at the moment therefore is that cyclohexene becomes coordinated rapidly and preferentially at the metal centres, and that the resultant complex formed is oxidized more slowly by tBHP than the noncomplexed species (see following). Presumably alkene is not, however, a retarder of the active catalyst because the latter is a different metal centre, and not least is of different oxidation state. It must be conceded that this is not very satisfactory since it is known that analogous oxidations to homogeneous complexes do occur even in the presence of alkenes (*5, 24, 25*); nevertheless, for the time being, no better explanation is available.

When the initially formed complexes PsMo and PsV are subjected to an activation/oxidation process with tBHP prior to contact with alkene in a reaction, the data in Table 1 show that potent catalysts are formed. Visually the blue PsMo species is converted to a bright yellow complex during activation, confirming, at least superficially, the oxidation of Mo(V) to Mo(VI). Generally reactions are slower than the corresponding homogeneous ones, but direct comparison is not possible since the metal complexes involved in each system are not equivalent. Nevertheless, the reactions using activated PsMo are very fast, with quantitative conversion of cyclohexene to its epoxide at 83°C in the presence of a high level of cyclohexene (84 mmol) (row 13, Table 1). In addition, in contrast to the homogeneous reaction using MoO_2acac_2, where there is evidence for secondary reactions causing a slow decay in the yield of cyclohexene oxide (row 7, Table 1), no side reactions involving the product are observed with PsMo as catalyst.

Variations in catalytic activity between Mo and V species, with temperature and with alkene content of reactions, parallel those observed with the homogeneous catalysts. Indeed, the yields observed with activated PsV are higher than those reported in the literature (*26*).

Other workers have reported the use of a stirring technique during supported metal complex catalysed epoxidations (*27*). Stirring was found to have no influence on rates of reaction nor on product yields in this work, and likewise use of a N_2 atmosphere had no effect.

Catalyst Activation

(*i*) *Effect of activation conditions.* Since the initially formed complexes PsMo and PsV proved to be inactive catalyst without prior activation and, indeed, precedent for this does exist in the literature (*28*), it was decided to examine the influence of the activation conditions in more detail and also to determine what levels of metal (if any) were leached during this procedure. More careful monitoring of epoxidation reactions showed that the conversion curves were characterised by a steady rate acceleration followed by a substantial period when the rate of reaction was essentially constant (Fig. 1). To allow convenient comparison of the effect of different activation conditions and, indeed, the effect of other reaction parameters, the "induction period" of the reaction and the "rate of reaction" were defined as shown in Fig. 1. The rate is essentially the gradient (in appropriate units) of the steady part of the conversion curve and the induction period is the intercept on the time axis of this line extrapolated to cross the tangent to the initial slope of the conversion curve.

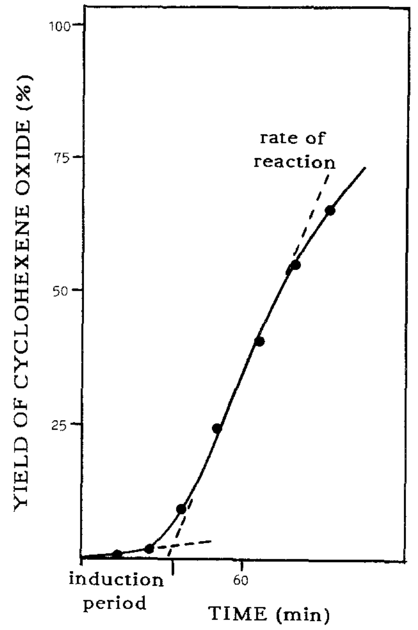


FIG. 1. Typical conversion curve showing induction period and steady rate. PsMo = 0.06 mmol; tBHP = 5 mmol; cyclohexene = 83 mmol; 10.5 ml total volume with 1,2-dichloroethane; temp. 80°C. Activation conditions: tBHP/Mo 3.5/liter; 83°C; 1 h.

Table 2 summarises the results of the activation experiments using PsMo. The data show that more severe activation conditions (i.e., longer reflux times) generally yield catalysts that display much shorter induction periods and higher reaction rates, the effect on the induction period being more pronounced than the final steady rate achieved. Metal analysis of some of the supernatant liquids from activation reactions showed that although more metal was leached from beads with the more severe treatment, the maximum loss was rather small, <1.6%. Previously large losses of metal have been reported on treatment with hydroperoxide (*28*), but in this work ligand (**1**) is a powerful chelator.

The final entries in Table 2 show that the activation process can be taken too far and that prolonged and severe oxidation conditions can yield sluggish catalysis. Unfortunately no leaching data are available here and so it is not clear whether this arises from loss of the metal, or/and from damage to the polymer and the ligand.

TABLE 2

Influence of the Catalyst Activation Conditions[a] on the Epoxidation of Cyclohexene[b] by *t*-butyl Hydroperoxide Catalysed by Polymer-Supported Molybdenum Complex, PsMo

Activation conditions			Reaction induction period (min)	Turnover frequency[c] (mol epoxide min^{-1} mol Mo^{-1})
Molar ratio tBHP/Mo	Reflux period (h)	% Mo leached		
3.5/1	1	0.10	29	0.93
	4	—	28	1.04
	12	—	5	1.67
	20	—	15	1.27
	42	1.46	9	1.25
	72	—	7	1.33
35/1	1	—	15	0.93
	20	0.22	5	1.30[d]
	42	1.59	5	1.25[e]
	72	—	7	1.33
82/1	1	—	6	1.11
	20[f]	—	10	0.68

[a] Refluxing 1,2-dichloroethane solution.

[b] Mo = 0.06 mmol; tBHP = 5 mmol; cyclohexene = 83 mmol; 10.5 ml total volume made up with 1,2-dichloroethane; temp. 80°C.

[c] The gradients of conversion curves (e.g., Fig. 1) were converted to these turnover frequencies. It can be shown that the conversion factor is 0.834.

[d] 0.19% Mo leached during reaction.

[e] 0.11% Mo leached during reaction.

[f] Reflux period repeated twice.

Overall the time period of the activation process was more important than the excess level of tBHP used (3.5/1 versus 35/1). Nevertheless, the full conversion curves (not reproduced here) showed that reaction rates fell away more significantly (~75% conversion with catalysts activated with a large excess of tBHP) than with those catalysts activated with a modest excess of oxidant. This effect is not understood but does emphasise the importance of the changes that do occur during catalyst activation.

(*ii*) *Induction period and active catalyst.* Little experimental evidence is presented here regarding the structure of the complex formed on the polymer during activation and unfortunately no data were recorded of the "active oxygen" content. Such data would be extremely valuable and our on-going work will address this issue. However, infrared absorption spectra of PsMo recovered after recycling in many separate epoxidations (see below) did show bands characteristic of the symmetrical and antisymmetrical MoO_2 stretches, and that the band characteristic of the oxo bridge, Mo–O–Mo, had disappeared. Additional bands in the region expected for a metal coordinated diol group were also present, but these could not be unambiguously assigned to such a species.

It seems reasonable to suggest therefore that activation with tBHP involves rupture of the Mo–O–Mo bridge in structure (**2**) (Scheme 1) to generate the Mo(VI) peroxometal complex (**3**), whilst the coordinating ligand-metal ion bonds remain intact. Such strong chelating species are known to be stable under these conditions (*13, 29, 30*), and the relatively small level of metal leaching observed during activation tends to confirm this. Closely related peroxo-species (**4**) from reactions of Mo and W complexes with H_2O_2 and species (**5**) from

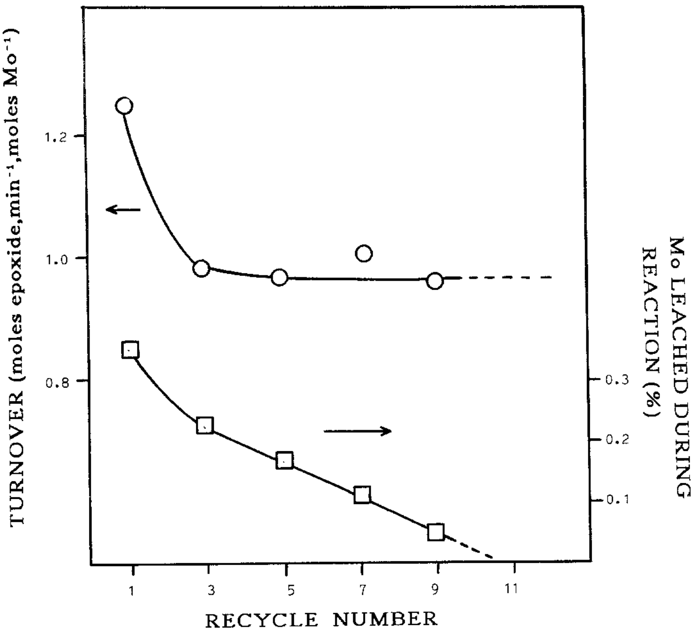
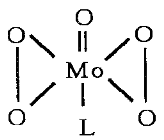


FIG 2. Recycling of PsMo catalyst. For reaction conditions see Fig. 1 caption. Activation conditions: tBHP/Mo, 3.5/liter; 83°C; 42 h.

treatment of V complexes with tBHP have been reported by Mimoun *et al.* (*31, 32*).



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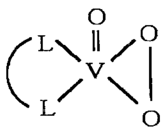

(5)

Induction periods previously reported with related homogeneous (*24, 33*) and polymer-supported (*28*) catalysts have been loosely attributed to the oxidation of the original Mo complex (sometimes Mo(O)) to a Mo(VI) species via oxidative destruction of the ligands surrounding the original complex. Interaction of tBHP with the new Mo(VI) centre then provides the species poised for catalysis via the mechanisms proposed by Brechot *et al.* (*32*) or Chong and Sharpless (*34*). The induction period observed in this work occurs *after* activation to the Mo(VI) state, and suggests that the latter undergoes at least one further slow step before the real active complex is formed. This reaction may involve an alkene molecule or its epoxide (formed slowly in traces by other inefficient processes) (Scheme 1). The reason why polymer-supported complexes subjected to more severe activation conditions subsequently show shorter induction periods may simply reflect generation of larger levels of species (**3**).

CATALYST RECYCLING AND Mo LEACHING

In the present work two separate samples of PsMo, which had been activated under different conditions, were subjected to repeated use in epoxidation reactions. Table 3 shows the results obtained. Clearly both forms of PsMo remain highly active over many catalytic cycles and offer a real prospect for continuous use, e.g., in a column reactor. For the catalysts formed with the more severe activation conditions (B) the induction period as expected was shorter. However, somewhat surprisingly the re-

TABLE 3

Repeated Use of PsMo as a Catalyst in the Epoxidation of Cyclohexene using *t*-Butyl Hydroperoxide[a]

Catalytic run	Activation conditions A		Activation conditions B	
	Turnover (mol epoxide min^{-1} mol Mo^{-1})	Mo leached[b,c] (%)	Turnover (moles epoxide min^{-1} mole Mo^{-1}	Mo Leached[b,d] (%)
1	0.92	0.36	1.25	0.35
2	0.73	0.21	—	—[e]
3	0.82	—	0.98	0.22
4	0.86	0.21	—	—[e]
5	0.70	0.16	0.97	0.17
6	0.73	0.16	—	—[e]
7	—	—	1.08	0.11
8	—	—	—	—[e]
9	—	—	0.96	0.05

Note. (A) Molar ratio tBHP/Mo = 3.5; 18 h, room temp; (B) molar ratio tBHP/Mo = 3.5; 42 h, 83°C.

[a] See Footnote *b*, Table 2.

[b] Relative to total metal originally on the resin.

[c] Mo leached during activation = 0.02%.

[d] Mo leached during activation = 0.93%.

[e] These reactions were run but not monitored.

spective induction periods were observed with repeated use of each catalyst and, indeed, the times stayed more or less constant. It had been anticipated that once the complex was rendered catalytically active, i.e., after its first use in epoxidation, it would remain in this active state ready for a fast "take-off" in subsequent epoxidation cycles. Clearly this is not the case and it seems that the storage period between catalytic runs constitutes a "down period" during which the active catalytic complex returns to its former preactive state, possibly species (**3**). In subsequent catalytic runs an induction period arises each time and as before possibly associated with the reaction of alkene (or trace epoxide) with the preactive complex, (**3**).

In each case the data in Table 3 show that the rate of first reaction using the catalyst is a little faster than subsequent rates, which remain essentially constant within experimental error. Figure 2 emphasises this point. Additionally rates using the catalyst activated by the less severe treatment, A, are consistently lower than those arising with the catalyst activated by treatment B (see Table 3). Again this is consistent with earlier results and probably reflects that a somewhat higher level of (**3**) formed. It also implies that under the conditions of the epoxidation reaction no additional catalytically active Mo sites are generated.

The data in Table 3 also indicate the level of Mo leached from both catalysts and interestingly this is always <0.4% per cycle. However, it does suggest that some inhomogeneity exists in the structure of PsMo. Perhaps the most important conclusions from the metal leaching data, however, concern the reaction mechanism and the potential long-term use of these catalysts. In both cases the reaction rate quickly assumes a steady (different) value in each catalytic run *irrespective of the amount of metal leached.* In one case the level of metal leached per cycle falls by a factor of 2 over six cycles and in the second by a factor of ~7 over nine cycles. It is extremely unlikely therefore that the homogeneous Mo species generated by leaching contribute significantly to the catalysis observed. Indeed, the lack

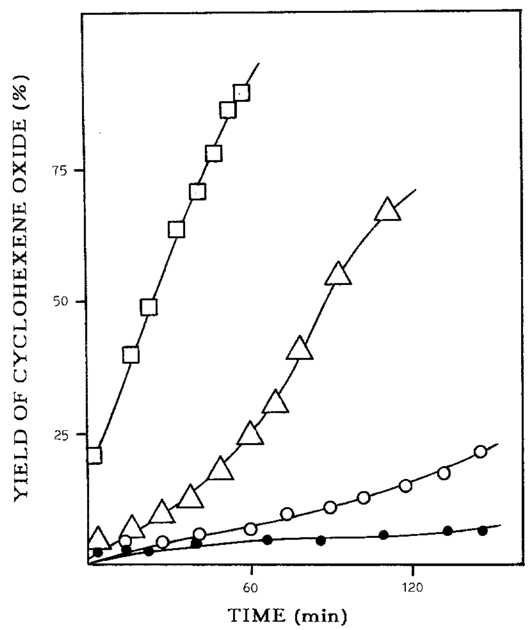

FIG. 3. Temperature dependence of PsMo-catalysed cyclohexene epoxidations. For reaction and activation conditions see Fig. 2 caption. ●, 30°C; ○, 70°C; △, 75°C; □, 80°C.

of correlation of the rate with the level of homogeneous Mo species is powerful evidence that the catalytic species is the polymer-supported one. Figure 2 emphasises that in the case of the more severe activation, the amount of Mo leached per cycle falls progressively with each reuse of the catalyst and *after nine cycles has become almost negligible* while the turnover remains essentially constant. This is an even more impressive result than that using an MoO_3-based catalyst coordinated to triethylene–tetramine immobilised on polychloromethylstyrene (*6*). In the latter case activity could be maintained over four cycles by treatment of the polymer catalyst with 30% H_2O_2; however, epoxide yields gradually fell. The difference may be due to the different ligand employed, but certainly the present catalyst system could form the basis of a technologically useful heterogenised alkene epoxidation catalyst for prolonged use in a column reactor.

TEMPERATURE AND SOLVENT EFFECTS

Figure 3 shows the effect of temperature on the epoxidation reaction using fresh samples of PsMo, each one being activated for 42 h at 83°C using a molar ratio of tBHP : Mo of 3.5. As expected, the rate of reaction falls with decreasing temperature, but the fall is much more dramatic than that predicted by a simple Arrhenius dependence. Such abrupt dependences are known in metal complex catalyses and in this instance it is difficult to explain. Almost certainly, however, it reflects the number of complex steps involved.

Figure 4 shows the influence of solvent on the epoxidation reaction. In each case PsMo was activated as described above and 6.3 ml of a given solvent was employed in an overall volume of 10.5 ml. Since the level of imbibition into the resin for all the liquids involved was very similar (tBHP, cyclohex-

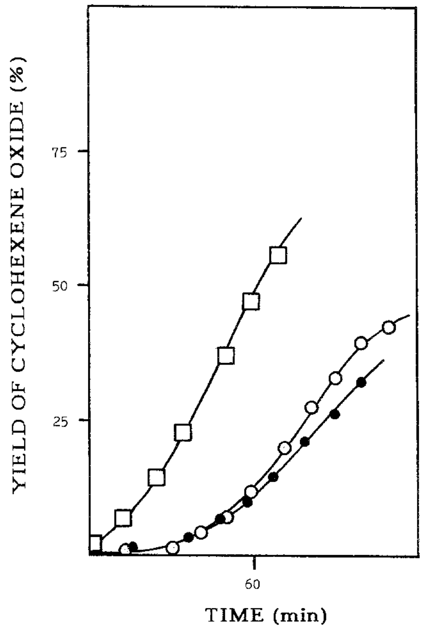

FIG. 4. Effect of solvent on PsMo-catalysed cyclohexene epoxidations. Activation conditions as in Fig. 2 caption. Reaction conditions: tBHP = 5 mmol; PsMo = 0.06 mmol; cyclohexene = 20 mmol; solvent = 6.3 ml. ● toluene; ○ cyclohexane; □ 1,2-dichloroethane.

ene, toluene, cyclohexane, 1,2-dichloroethane; 0.43, 0.23, 0.28, 0.25, and 0.30 g solvent g^{-1} supported complex, respectively) the observed effects are unlikely to be associated with differences in the swelling characteristics of the polymer matrix in each reaction mixture. Rather they are more likely to be associated with the polarity of the solvent and its influence on the slow reaction step(s). The rate of epoxidation decreased in the order 1,2-dichloroethane, cyclohexane, and toluene, with the latter two solvents behaving rather similarly. Such a reduction in rate with less polar solvents has been reported before with homogeneous and polymer-supported complex catalysts (*27, 32, 35*). It has been suggested that this is an indication that the reaction intermediate in the rate controlling process is polarised, and that nondonor polar solvents enhance the charge separation of the dipole, or that such solvents help stabilise a given charge separation (*32, 35*). The results in this study are simply consistent with this rather general view.

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