The Effect of Added Molecular Sieves on Alkene Epoxidation Reactions catalysed by [MoO_2Cl_2L], where L is a 3-(Diethoxyphosphoryl) derivative of Camphor

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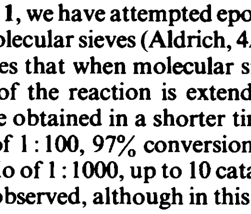
Addition of molecular sieves to the alkene epoxidation system consisting of Bu^tOOH and [MoO_2Cl_2L], where L is a 3-(diethoxyphosphoryl) derivative of camphor increases both the rate and yield of the epoxidation reactions; for styrene maximum conversions of 25% which are subsequently degraded are converted to stable conversions of 96% with 94% selectivity to styrene oxide by adding 4A molecular sieves.

We have reported[1] that the complex [$MoO_2Cl_2\{OC_{10}H_{15}PO(OEt)_2\}$] **1** containing a β-ketophosphonate derived from camphor {(*R*)-(+)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one} is a highly active and regioselective[1,2] catalyst for the epoxidation of certain alkenes using *tert*-butyl hydroperoxide (Bu^tOO*H*) as oxidant. However, analysis of rate profiles for reactions of 1-methylcyclohexene catalysed by this and a range of other catalysts indicate biphasic kinetics.[1,2] The second phase of the reaction has a similar rate profile for all of the catalysts examined, suggesting that the initial highly active catalyst is replaced by a less active form. This phenomenon has been observed[3] before and attributed[4,5] to the formation of a complex of the form [$MoO_2(OC_7H_{14}OH)$], the bidentate diolato ligand being derived from the product cyclohexene oxide, perhaps by reaction with water in the system. Molecular sieves have been used to scavenge adventitious water in epoxidation[6] or other oxidation[7] systems and it has been reported that stoichiometric reactions can be rendered catalytic[6] or improvements can be obtained in enantioselectivities.[7]



[MoO_2Cl_2L] **1**

In order to try to improve still further the very active catalytic system derived from **1**, we have attempted epoxidation reactions in the presence of molecular sieves (Aldrich, 4A, particle size 2–3 µm).[†] Fig. 1 indicates that when molecular sieves are used, the initial rapid phase of the reaction is extended so that higher yields of product are obtained in a shorter time. Using catalyst to substrate ratios of 1 : 100, 97% conversion is observed in 20 min, and using a ratio of 1 : 1000, up to 10 catalyst turnovers per second are initially observed, although in this case, deactivation of the catalyst again occurs. The initial catalyst is active for ≈650 cycles, *cf.* 480 in the absence of molecular sieves.

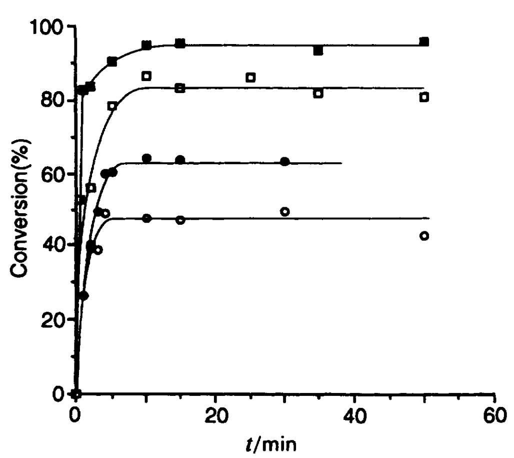


Fig. 1 Epoxidation of 1-methylcyclohexene catalysed by **1** at 0 °C at various substrate:catalyst ratios with and without molecular sieves. (○) 1000:1, no molecular sieves; (●) 1000:1, with molecular sieves; (□) 100:1, no molecular sieves; (■) 100:1, with molecular sieves

Much more dramatic, however, is the effect of molecular sieves on the epoxidation of phenyl-substituted alkenes, especially styrene, catalysed by **1**. In our previous paper,[1] we reported that **1** was inactive for the epoxidation of styrene. This result was obtained by sampling the reaction after 24 h. Closer examination of this reaction shows (see Fig. 2 and entry 1, Table 1) that styrene can be epoxidised by Bu^tOOH in the presence of **1** (25% conversion being observed in 1 min), but that the epoxide formed is subsequently degraded, largely to benzaldehyde, and after 60 min no epoxidised styrene is present (consistent with our earlier report). In the presence of molecular sieves, however, the reaction follows a totally different course and 96% conversion with 94% selectivity to styrene oxide occurs in 24 h (see Fig. 2 and entry 2, Table 1). No degradation of the epoxide appears to occur and benzaldehyde is only observed as a minor product.

A number of observations suggest that the role of the molecular sieves in these reactions is not simply to scavenge water but rather that both the catalyst and the Bu^tOOH bind to the molecular sieves. Thus, if the catalyst solution is first stirred with molecular sieves then filtered, the filtrate shows no activity for alkene epoxidation when added to a mixture of Bu^tOOH and styrene in CH_2Cl_2 (entry 3, Table 1), whilst additions of the solid fraction to a similar solution does give some styrene

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[†] Experimentally, the substrates (16 mmol) and oxidant [23.4 mmol in 2,2,4-trimethylpentane (3 mol dm^{-3})] were mixed in CH_2Cl_2 (15 cm^3) and added to preactivated molecular sieves (5 g) before stirring the mixture at room temperature for 0.5 h. Catalyst (0.16 mmol) was then added and samples were taken from the mixture at regular intervals. The samples were added to solid PPh_3 to stop the reaction and then analysed by GLC.

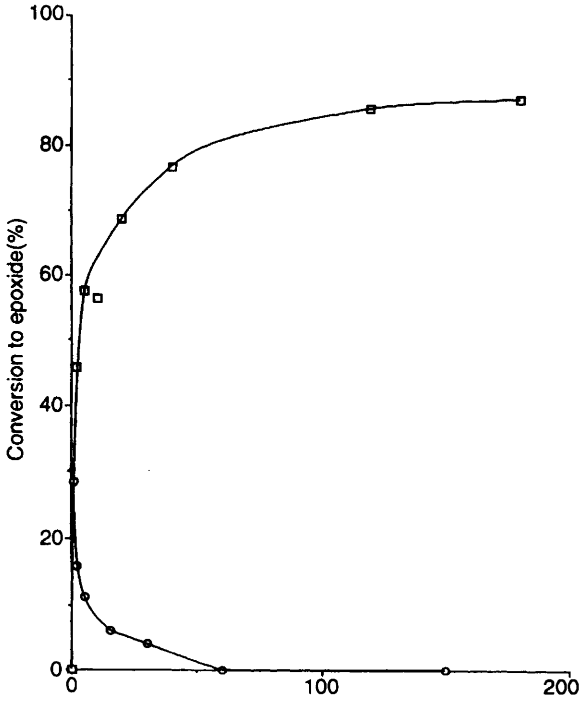

Fig. 2 Epoxidation of styrene catalysed by **1** at room temperature. (○) Without seives; (□) with molecular sieves

Table 1 Effect of different reaction protocols on the epoxidation of styrene catalysed by $[MoO_2Cl_2L]$

Protocol*	Time/h	Conversion to epoxide (%)
1 S + St + O + C	0.02	25
	1.0	0
2 Sv + S + St + O + C	0.02	45
	24	90
3 Sv + S + St + O + [C + S + Sv]F	18	0
4 S + St + O + CSv	18	20
5 Sv + S + St + [Sv + S + O]F + C	1.0	22
	48	44
6 Sv + S + St + O + CSv	18	0
7 Sv + S + C + St + O	24	43.4
	144	69.5
8 Sv + S + O + St + C	24	54.5
	144	81.3
9 Sv + S + O + [Sv + S + St]F + C	0.02	45
	24.0	90
10 Si + S + St + O + C	0.02	0
	1.0	0

* S = CH_2Cl_2, St = styrene, O = ^{t}BuOOH, C = catalyst, Si = silica, Sv = molecular sieves; [ ]F = the filtrate from stirring together the components shown in brackets; CSv means the solid obtained from filtering a solution of sieves, solvent and catalyst. The reagents were added in the order shown in each case.

Table 2 Alkene epoxidation in the presence and absence of molecular sieves[a]

	Conversion to epoxide (%)	
Alkene	Without molecular sieves	With molecular sieves
1-Methylcyclohexene[b]	74.7	95.7
Styrene	0	80[c]
α-Methylstyrene	12.5	55.5
trans-Stilbene[d]	56.3	85[e]
(*R*)-(+)-Limonene[f]	68.8	87

[a] Alkene : Bu^{t}OOH : catalyst = 100 : 150 : 1, in CH_2Cl_2, 1 h, at ambient temperature. [b] At 0 °C. [c] 97.7% after 24 h. [d] *trans*-1,2-Diphenylethene. [e] 100% after 2 h. [f] (*R*)-(+)-1-Methyl-4-(1-methylethenyl)cyclohex-1-ene; only the endocyclic double bond is epoxidized.

epoxidation activity (entry 4, Table 1). Similarly, if the Bu^{t}OOH is first stirred with sieves, filtered into CH_2Cl_2 containing styrene and molecular sieves then the catalyst added (entry 5, Table 1), the activity is significantly lower than simply adding the Bu^{t}OOH. Furthermore, almost no activity is observed if the catalyst adsorbed onto molecular sieves is added to a solution containing styrene, Bu^{t}OOH and molecular sieves (entry 6, Table 1), suggesting that both the Bu^{t}OOH and the catalyst must be adsorbed onto the sieve particles, although whether the catalyst or the peroxide is added first does not appear to matter very much (entries 7 and 8, Table 2). There is no evidence for styrene being affected by stirring with molecular sieves (entry 9, Table 1) and no reaction is observed in the absence of catalyst.

The most logical explanation is that the catalyst binds to the sieves *via* metathesis of the Mo–Cl bonds with surface-bound hydroxyl groups (the catalyst is too large to enter the pores of the 4A molecular sieves). The acidity of the support appears to be important since no activity is observed if the sieves are replaced with silica.

Styrene is generally rather a difficult alkene to epoxidise and high yields with high selectivities are unusual. The best results using molybdenum catalysts (93% selectivity at 98% conversion) have been obtained using molybdenum octanoate in the presence of $B(OPr^i)_3$ and using α,α-dimethylbenzyl hydroperoxide as oxidant, but forcing conditions (100–125 °C) are required.[8] The results we have obtained with styrene are almost as good as these but are obtained at room temperature.

Molecular sieves also greatly increase the rate and yield for production of epoxides from a variety of other alkenes (see Table 2).

Acknowledgements

We thank Rhône-Poulenc and the SERC for a studentship (to R. C.) and Dr. D. S. Barratt for helpful discussions.

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Received 15*th April* 1993; *Communication* 3/02160B