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Catalytic asymmetric heterogeneous aziridination of styrene derivatives using bis(oxazoline)-modified Cu^{2+}-exchanged zeolite Y†

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The copper-catalysed aziridination of styrene derivatives using either $Cu(OTf)_2$ as a homogeneous catalyst or copper-exchanged zeolite Y modified as a heterogeneous catalyst with bis(oxazoline) using [*N*-(*p*-nitrophenylsulfonyl)imino]phenyliodinane (PhI=NNs) as nitrene donor is described and discussed. For the homogeneously catalysed reaction virtually all the substituted derivatives gave lower yields of the aziridine with lower ee when compared with styrene, although 4-chlorostyrene did give enhanced ee. For the heterogeneous catalysed reaction the styrene derivatives often gave enhanced yield, particularly when the substituent was in the 4-position. Particularly high ee was observed for 2-chlorostyrene (95%) and 4-chlorostyrene (94%) and in general the ee observed for the heterogeneously catalysed reaction with the 2- and 4-substituted derivates was significantly higher than that for the equivalent homogeneously catalysed reaction. With copper-exchanged zeolite Y the leaching of Cu^{2+} into solution during reaction was much lower for the substituted styrene derivatives (0.4–7% of total Cu) than with styrene itself (10.3% of the total Cu). The effect of reaction time on aziridine yield reveals an S-shaped profile that is accentuated by the position of the substituent and this effect is observed for both the homogeneously catalysed pathway and the heterogeneously catalysed reaction. A series of competitive experiments in which styrene was co-reacted with equivalent quantities of 2-, 3- and 4-chlorostyrene revealed that the reaction of styrene enhanced by the other substrate, but the rate of reaction of the substituted styrene was decreased. Co-reaction of 2- and 4-chlorostyrene reveals interesting competitive effects, which are discussed in terms of the nature of the active site.

Introduction

The design and reactivity of asymmetric catalysts continues to provide a fruitful field of research given the importance of the availability of homochiral molecules for the production of pharmaceuticals and agrochemicals. Recently, attention has started to be focussed on the immobilisation of homogeneous catalysts,[1] particularly using bis(oxazoline)‡ ligands,[2] which are known to be versatile chiral ligands,[3] as this will improve the potential for the application of asymmetric catalysts in commercial processes.

We have previously shown that Cu^{2+} immobilised within microporous and mesoporous materials prepared using ion-exchange and modified by chiral bis(oxazoline) is effective for the asymmetric aziridination of alkenes.[4–7] In particular, higher enantioselection can be observed with these immobilised catalysts when compared with the non-immobilised catalysts investigated under identical conditions.[6] More recently, we have extended the use of these immobilised catalysts to asymmetric Diels–Alder reactions[8] and carbonyl- and imino-ene reactions.[9] To date, we have concentrated on the reaction of styrene as a model reactant; in an earlier paper we did explore some alternative substrates[5], but in general these were less reactive than styrene. In this paper we extend the range of substrates and we investigate the reactivity of substituted styrene derivatives in both the homogeneously and heterogeneously catalysed reactions using [*N*-(*p*-nitrophenylsulfonyl)imino]phenyliodinane§ (PhI=NNs) as nitrene donor. Previous studies by Nishikori and Katsuki,[10] using homogeneous manganese salen catalysts with PhI=NTs as nitrene donor, showed that 4-methylstyrene and 4-chlorostyrene gave lower yields compared with styrene. Diaz Requejo *et al.*[11] studied a range of styrene derivatives using a homogeneous bis(oxazoline) modified copper catalyst and showed that the reaction intermediate is a paramagnetic copper nitrene species. Recently Jain and Sain[12] have shown that a new nitrene donor, *N*-iodo-*N*-potassio-*p*-toluenesulfonamide, is effective with CuCl as homogeneous catalyst in the absence of bis(oxazoline) for the azridination of styrene derivatives. With this catalyst system 2-chlorostyrene, 3- and 4-methylstyrene all gave higher yields than styrene. However, to date there have been no reported studies of the reactions of such styrene derivatives with heterogeneous catalysts. Recently, we have shown that the ee increases with conversion for the aziridination reaction for both the heterogeneously and homogeneously catalysed reaction using copper-bis(oxazoline) catalysts,[13] and this study extends our investigation to the reactivity and reaction profiles of the aziridination of substituted styrenes.

Results and discussion

Reaction of styrene derivatives

The aziridination of styrene and styrene derivatives was investigated using PhI=NNs as nitrene donor with Cu-exchanged zeolite Y or copper(II) triflate modified by (*S*,*S*)-2,2′-isopropylidene-bis(4-phenyl-2-oxazoline) **1** and the results are shown in Table 1 following reaction for 12 h. In these reactions a 50% molar excess of the nitrene donor relative to styrene or the styrene derivative was used. For the homogeneously catalysed reaction all the styrene derivatives investigated gave lower yields of the aziridine products and substituted benzaldehydes were observed as the by-product. The by-products are considered to result from the formation of PhIO, enhanced at these nitrene : substrate mol ratios; this subsequently reacts with the substrates to form the substituted benzaldehyde and other oxygenated products, thereby decreasing the aziridine yield.[14] The ee for reaction of 4-chlorostyrene (93%) was significantly higher than that observed with styrene (81%). However, this was the only enhancement in ee observed with the homogeneously catalysed

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† Electronic supplementary information (ESI) available: Preparation of aziridines. See http://www.rsc.org/suppdata/ob/b4/b411040b/

‡ The IUPAC name for 1,3-oxazoline is 4,5-dihydro-1,3-oxazole.

§ The IUPAC name for iodinane is λ^3-iodane.

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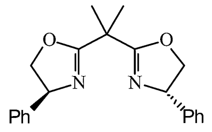
Table 1 Aziridination of styrene derivatives[a]

Substituent[b]	Cu–HY			$Cu(OTf)_2$		
	Yield (%)	Ee (%)	Substituted benzaldehydes (%)	Yield (%)	Ee (%)	Substituted benzaldehydes (%)
None	78	85	16	96	81	18
2-Cl	83	88	22	90	83	24
3-Cl	82	95	19	89	72	24
4-Cl	85	94	19	90	93	22
2-F	82	72	13	85	71	17
3-F	75	58	16	80	83	17
4-F	83	53	18	85	41	21
2-Br	60	85	15	90	68	15
3-Br	59	64	13	79	83	16
4-Br	90	74	17	90	59	17
2-CH_3	60	79	3	80	68	9
3-CH_3	75	48	3	78	80	3
4-CH_3	83	67	15	85	66	3
α-CH_3	57	34	12	61	15	13
trans-β-CH_3	42	24	10	63	23	25
4-OCH_3	71	64	20	76	76	19
3-NO_2	63	65	18	48	68	20

[a] Reaction conditions: bis(oxazoline) **1** (7 mol%), CH_3CN, 25 °C, PhI=NNs : styrene = 1.5 mol ratio, 12 h reaction time, catalyst: CuHY (300 mg $mmol^{-1}$, 3.7 wt% Cu); $Cu(OTf)_2$ (15 mol%). Absolute configuration for each substituent: S, Optical rotation: – for each substituent. [b] Styrene substituent.

reactions investigated, and was achieved at the expense of the overall yield of the aziridine. However, compared with CuHY-catalysis, the ee is notably lower in the homogeneously catalysed reaction where no diffusion limitations are expected to be apparent for access of the substrate to the active site. Interestingly, the 3 substituted F-, Br-, CH_3- derivatives gave higher ee than the corresponding 2- and 4- derivatives, and these values were similar to the ee observed with styrene. Moreover the aziridine yield was somewhat lower for the 3-substituted styrenes. Since the effect appears to be similar for substituents of quite different electronic character, the decreased yield can probably be attributed to steric factors.



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The heterogeneously catalysed reactions show significant differences for the same substrate when compared to the homogeneously catalysed counterparts. In particular, the yield of aziridine is markedly enhanced compared with styrene. This is most marked with the 4-substituted F-, Cl-, Br- and CH_3-derivatives and is probably due to the reaction proceeding in a more controlled environment within the pores of the zeolite. It is also feasible that the zeolite effectively captures water from the solvent and this decreases the formation of PhIO, leading to an enhancement in yield. However, this effect would be expected to be present to a similar extent for all the substrates and, since it is variable, we do not consider this to be significant. One could in principle have a substituent-dependent enhancement in yield if the rate of PhI=NNs hydrolysis were comparable to the rate of aziridination; the enhancement would be greatest then for the more reactive styrenes, but this does not seem to be the case in our study. Rather, since the 4-substituted styrenes and the derived aziridines have smaller molecular cross-sections than the corresponding 2- and 3-substituted analogues and consequently will diffuse more rapidly through the zeolite pore system, the reduced steric effects that can be expected for the 4-substituted styrenes over the 2- and 3-derivatives are considered to be crucial.

The ee observed with the heterogeneously catalysed reactions is in general higher than that observed with the homogeneously catalysed reaction (Table 1), except for the 3-substituted derivatives discussed previously. 3-Chlorostyrene reacts with very high ee in the heterogeneous system (95%); this is one of the highest ee's reported to date for a heterogeneously catalysed asymmetric reaction, and is to be compared with the homogeneous system for which a poor ee is recorded (72%). The experiments were repeated in triplicate to ensure reproducibility of this high yield of the *S* enantiomer. The higher ee is considered to be due to a confinement effect within the pores of the zeolite catalyst, on which we have commented previously,[6] and is also consistent with the observations of Raynor *et al.*[15] The additional steric bulk of the substrate significantly affects its interaction with the catalytically active site, which is inherently more constrained within the zeolite, and this leads to improved enantioselection. However, steric factors alone cannot explain this effect since high enantioselection would be expected for all 2- and 3-substituted substrates and this is not observed. Consequently, it must be a combination of electronic and steric factors that combine to induce high enantioselection for 3-chlorostyrene in the heterogeneously catalysed reaction. In the heterogeneous system the ee observed for the reaction of 4-chlorostyrene, is particularly high (94%) at a high yield. This substrate was also effective with the homogeneous catalyst; hence the specific steric and electronic factors must combine to achieve the enhanced enantioselection with this substrate.

For the heterogeneously catalysed reaction introduction of a methyl group on the alkene group suppresses the ee but the effect is less marked with α-methyl styrene than with β-methylstyrene. Hence, as with the homogeneously catalysed reactions, α-methylstyrene and *trans*-β-methylstyrene are aziridinated but the process is predominantly racemic. For both catalysts, 4-amino- and 4-^{t}butyl-styrene do not form aziridines; instead a very broad range of products is observed mainly the result of amination rather than aziridination. In the case of 4-^{t}butyl-styrene the reaction most likely occurs on the exterior surface of the zeolite due to steric hindrance, whereas with the 4-amino-styrene it is probable that this substrate interacts with the Brønsted acid sites of the zeolite. These sites are present as only *ca.* 50% of the protons are exchanged for Cu^{2+} in the preparation procedure.[5] As the Brønsted acid sites are not modified by the bis(oxazoline), only achiral, non aziridination reactions will be catalysed there.

Copper-exchanged zeolite catalyst stability

The effect of the different substrates on the stability of the copper-exchanged zeolite catalyst during the reaction was also

Table 2 Effect of substrate on catalyst stability[a]

Substituent[a]	Cu leached during reaction (%)
None	10.3
2-Cl	6.9
3-Cl	5.2
4-Cl	3.6
2-F	3.6
3-F	4.2
4-F	1.8
2-Br	1.6
3-Br	0.8
4-Br	2.3
2-CH_3	2.5
3-CH_3	0.4
4-CH_3	0.8
α-CH_3	3.9
trans-β-CH_3	2.3
4-OCH_3	3.0
3-NO_2	4.6

[a] Reaction conditions: bis(oxazoline) **1**, CH_3CN, 25 °C, PhI=NNs : styrene = 1.5 mol ratio using Cu-exchanged zeolite Y containing 3.7 wt% Cu, 12 h reaction time. [b] Styrene substituent.

investigated and the Cu^{2+} leaching observed was determined (Table 2). We have previously made a detailed study of Cu^{2+}-leaching in this reaction system using styrene as substrate.[7] In this previous study we have found that *ca.* 10.3% of the Cu^{2+} initially present in the Cu–H/Y catalyst leaches under standard reaction conditions (PhI=NNs : styrene = 1 : 5 : 1 molar ratio, **1**, 25 °C, CH_3CN). However, we have previously concluded that the aziridination reaction observed was due to the heterogeneously catalysed process. In particular, the leached Cu^{2+} was ineffective as a catalyst since the homogeneously catalysed aziridination reaction is poisoned preferentially by the presence of PhI, a by-product of the decomposition of the nitrene donor. Interestingly, in the present study, the leaching of Cu^{2+} was decreased for the reaction of the substituted styrenes. In some cases the leaching was almost eliminated, as observed for the reaction of 3- and 4-methyl and 3-bromo-styrenes. It is possible that the increased steric effects due to these relatively larger substrates contribute to improving the stability of the catalyst. Cu^{2+} leaching is probably caused by either the bis(oxazoline), the solvent, the nitrene donor and the aziridine all competing as nitrogen ligands for the Cu^{2+}. It is also possible that the substrate competes for the liganded Cu^{2+} and that the relative solubility of the complexes so formed could also play a role in the eventual leaching of Cu^{2+}. Steric effects alone cannot explain these effects since the least sterically hindered substrate, the 4-substituted styrene, would be expected to give higher Cu^{2+} leaching and this is not generally observed. Confinement effects have, however, been observed to play a significant role with microporous and mesoporous heterogeneous asymmetric catalysts. Fig. 1 shows a comparison between the yield of aziridine and the amount of Cu^{2+} leached during the reaction. It is clear that there is no relationship between these factors and this confirms further that the leached Cu^{2+} does not play an important role in these asymmetric aziridination reactions.

Effect of reaction time on aziridine yield

The effect of the reaction time on the conversion of styrene and the yield of aziridine was investigated for all the substrates for both the homogeneously and heterogeneously catalysed reaction and representative data are given in Figs. 2–6. It is clear that the different substrates exhibit different reaction rates, but more important is the observation that the reaction profile for aziridine yield that is observed for styrene is also present for the 2- and 3-substituted styrene derivatives. In particular the effect of reaction time on aziridine yield reveals a reaction profile in which the reaction initially proceeds rapidly then slows prior to accelerating in the latter part of the reaction. In the heterogeneously catalysed reaction, the active site within the supercage of the zeolite is highly confined. As noted previously,[6] this leads to an enhancement in the ee observed with these catalysts. It is also apparent that the active site can also interact with reaction by-products, *e.g.* PhI, $NsNH_2$, as well as the aziridine product and the nitrene donor. In our preceding communication,[9] we showed that the aziridine could interact with $NsNH_2$ and the nitrene donor and these interactions played a role in the observed enhancement in ee with styrene conversion. This observation shows that the coordination sphere of the Cu^{2+}, although highly confined within the zeolite, changes its nature during the reaction. Although the size of substrate could, therefore, play a significant role by enhancing steric confinement of the active centre we do not consider it to influence the nature of the reaction profile curves observed in this study, since the effect is observed in the homogeneously catalysed reactions when confinement effects cannot occur. The origin of this effect is still a matter of investigation and is commented on elsewhere.[16] It is interesting to note that the reaction of 4-chlorostyrene for both catalysts is very rapid when compared with the 2- and 3-chlorostyrenes. This may be the underlying effect that leads to this substrate giving such an high ee (≥93%).

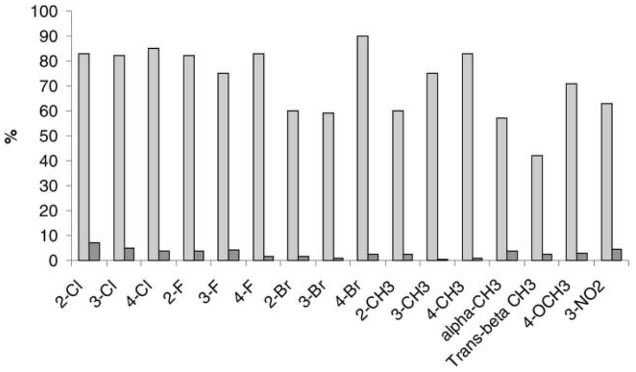

Fig. 1 Comparison of aziridine yield (light grey) and amount of Cu leached (dark grey) for different substrates reacted under standard reaction conditions with bis(oxazoline) **1**, CH_3CN, 25 °C, PhI=NNs : styrene = 1.5 mol ratio.

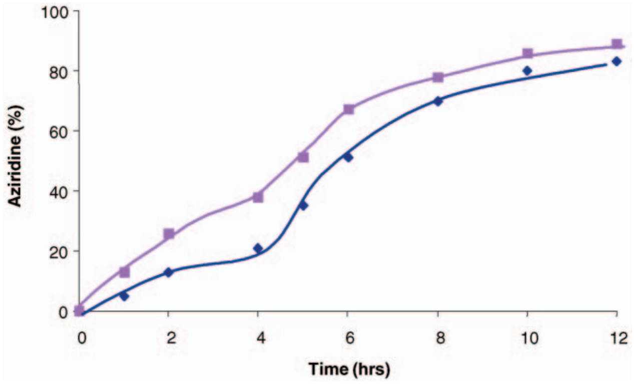

Fig. 2 Effect of reaction time on the aziridination of styrene with bis(oxazoline) **1**, CH_3CN, 25 °C, PhI=NNs : styrene = 1.5 mol ratio. Key: ◆ aziridine yield Cu–HY; ■ aziridine yield $Cu(OTf)_2$.

Competitive reaction of styrene and chlorostyrene derivatives

A series of experiments were conducted to evaluate the reaction of styrene in competition with a styrene derivative. In these experiments equimolar starting concentrations of the two substrates were used, but each being one half of that used in the earlier experiment. In this way all the other reaction parameters remained unchanged. The effect of reaction time on the yields of the aziridine products are shown in Figs. 7–9 for the competition reaction of styrene with 2-, 3- and 4-chlorostyrene

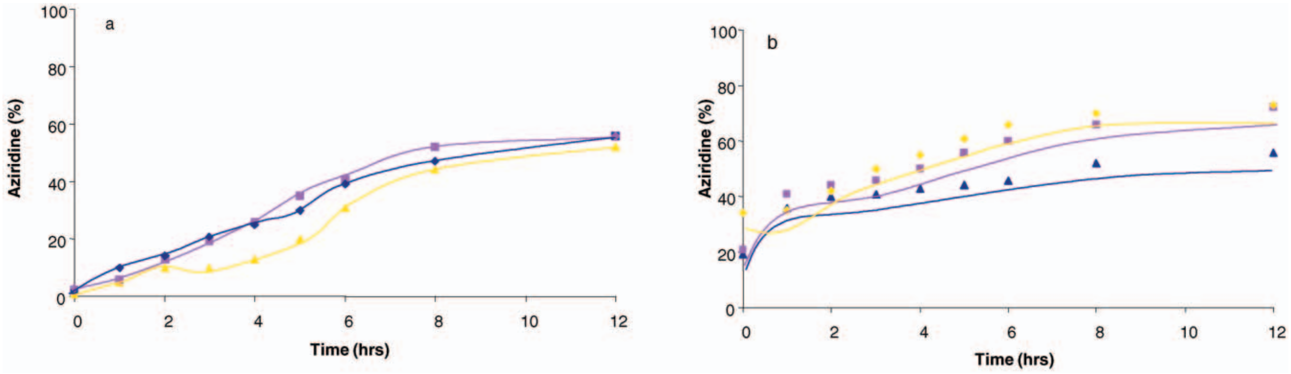

Fig. 3 Effect of reaction time on the aziridination of fluorostyrene with bis(oxazoline) **1**, CH$_3$CN, 25 °C, PhI=NNs : styrene = 1.5 mol ratio using (a) Cu-exchanged zeolite Y, and (b) Cu(OTf)$_2$. Key aziridine yield: ◆ 4-fluorostyrene; ■ 3-fluorostyrene; ▲ 2-fluorostyrene.

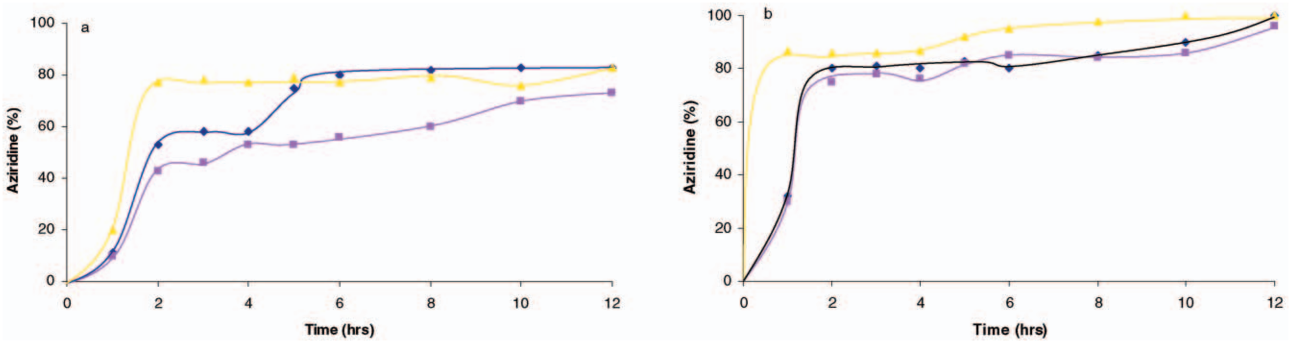

Fig. 4 Effect of reaction time on the aziridination of chlorostyrene with bis(oxazoline) **1**, CH$_3$CN, 25 °C, PhI=NNs : styrene = 1.5 mol ratio using (a) Cu-exchanged zeolite Y, and (b) Cu(OTf)$_2$. Key aziridine yield: ◆ 4-chlorostyrene; ■ 3-chlorostyrene; ▲ 2-chlorostyrene.

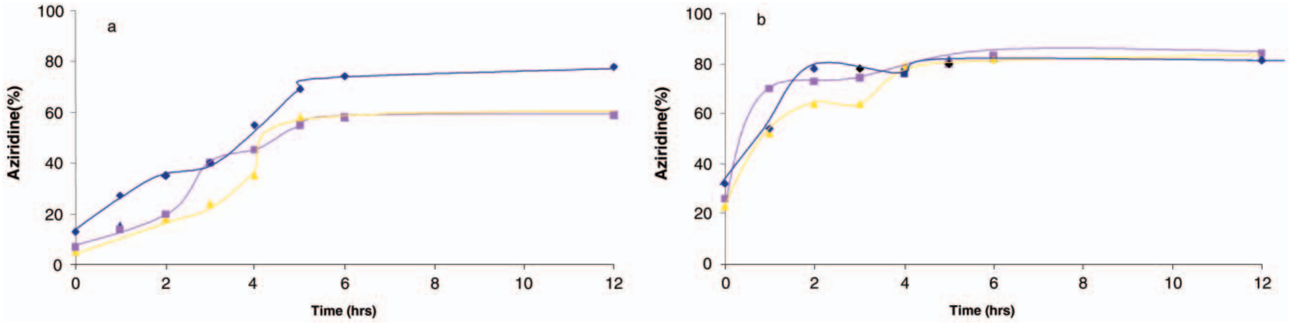

Fig. 5 Effect of reaction time on the aziridination of bromostyrene with bis(oxazoline) **1**, CH$_3$CN, 25 °C, PhI=NNs : styrene = 1.5 mol ratio using (a) Cu-exchanged zeolite Y, and (b) Cu(OTf)$_2$. Key aziridine yield: ◆ 4-bromostyrene; ■ 3-bromostyrene; ▲ 2-bromostyrene.

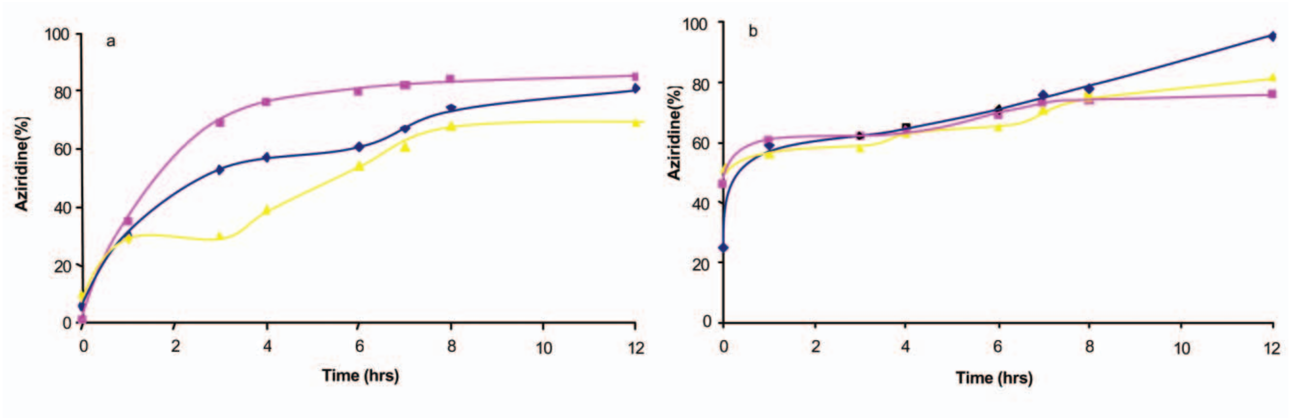

Fig. 6 Effect of reaction time on the aziridination of methylstyrene with bis(oxazoline) **1**, CH$_3$CN, 25 °C, PhI=NNs : styrene = 1.5 mol ratio using (a) Cu-exchanged zeolite Y, and (b) Cu(OTf)$_2$. Key aziridine yield: ◆ 4-methylstyrene; ■ 3-methylstyrene; ▲ 2-methylstyrene.

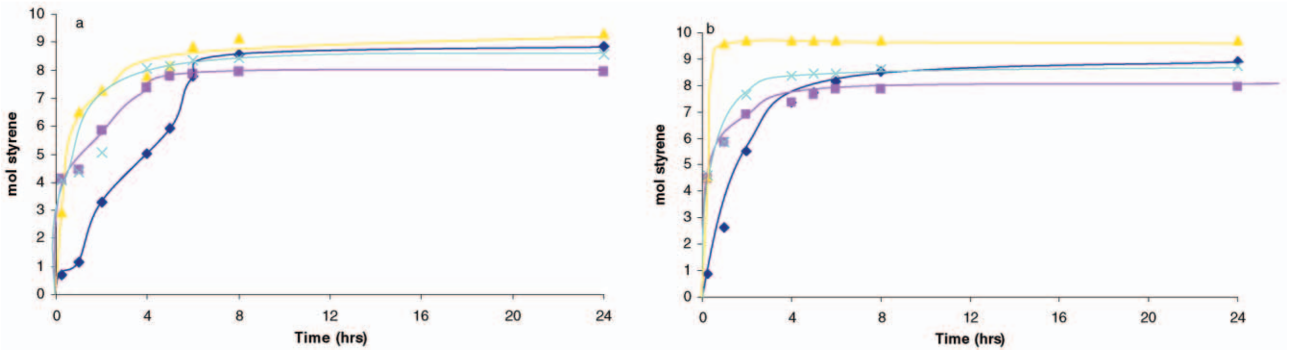

Fig. 7 Effect of reaction time on the competitive aziridination of styrene and 2-chlorostyrene with bis(oxazoline) **1**, CH_3CN, 25 °C, PhI=NNs : total substrate = 1.5 mol ratio using (a) Cu-exchanged zeolite Y, and (b) $Cu(OTf)_2$. Key aziridine yield: ◆ styrene only, ■ styrene reacted with 2-chlorostyrene; ▲ 2-chlorostyrene only; × 2-chlorostyrene reacted with styrene. (data for competitive reactions are double observed concentrations to permit direct comparison with single substrate reactions.)

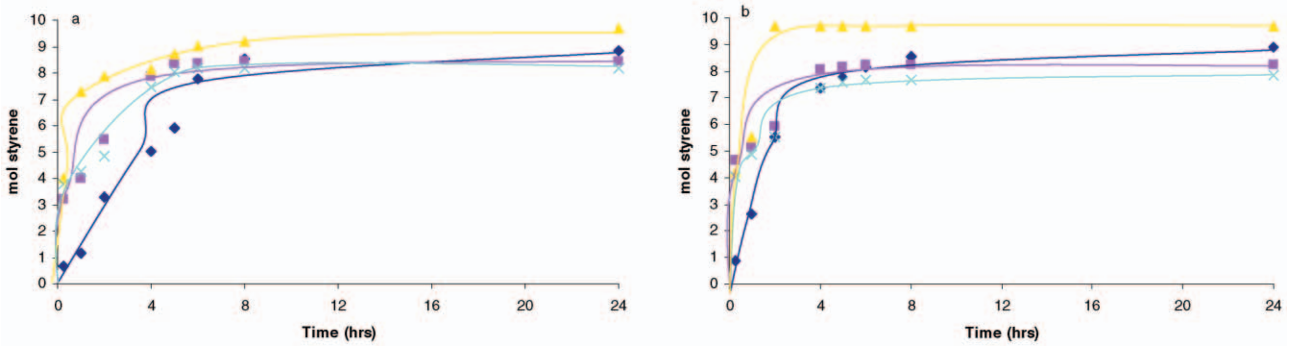

Fig. 8 Effect of reaction time on the competitive aziridination of styrene and 3-chlorostyrene with bis(oxazoline) **1**, CH_3CN, 25 °C, PhI=NNs : total substrate = 1.5 mol ratio using (a) Cu-exchanged zeolite Y, and (b) $Cu(OTf)_2$. Key aziridine yield: ◆ styrene only; ■ styrene reacted with 3-chlorostyrene; ▲ 3-chlorostyrene only; × 3-chlorostyrene reacted with styrene. (data for competitive reactions are double observed concentrations to permit direct comparison with single substrate reactions.)

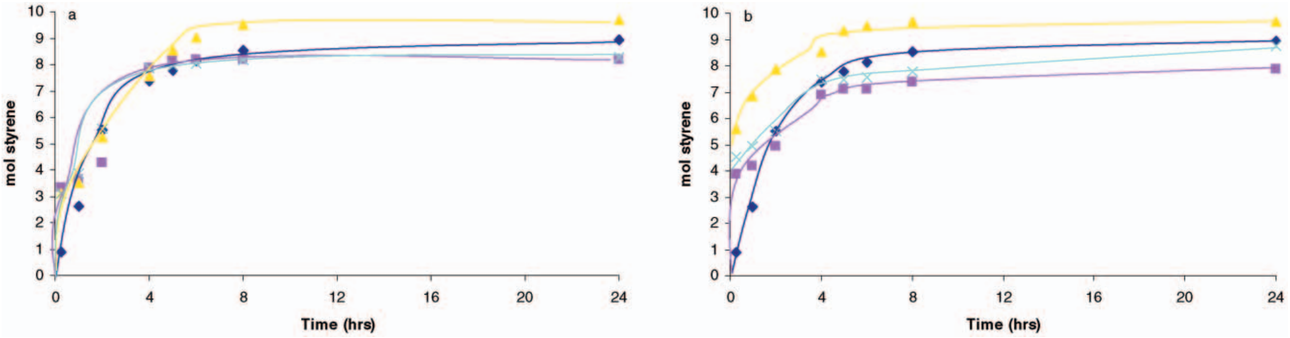

Fig. 9 Effect of reaction time on the competitive aziridination of styrene and 4-chlorostyrene with bis(oxazoline) **1**, CH_3CN, 25 °C, PhI=NNs : total substrate = 1.5 mol ratio using (a) Cu-exchanged zeolite Y, and (b) $Cu(OTf)_2$. Key aziridine yield: ◆ styrene only; ■ styrene reacted with 4-chlorostyrene; ▲ 4-chlorostyrene only; × 4-chlorostyrene reacted with styrene. (data for competitive reactions are double observed concentrations to permit direct comparison with single substrate reactions.)

respectively. These experiments have been conducted with the same conditions used for the reaction of the individual substrates (*i.e.* total substrate : nitrene donor = 1 : 1.5 mol ratio) except that half of the styrene has been replaced by the 2-, 3- and 4-chlorostyrene. However, for the data reported in Figs. 7–9 the concentration of the substrate reacted has been doubled to permit a direct comparison with the individual substrate. Normally, in competitive experiments of this type to assess relative reactivities, the competing molecules (styrenes) are allowed to react with a deficiency of the reagent (PhI=NNs) and the amount of reaction of each of the two styrenes is measured after all the reagent has been consumed. However, in the present case the nitrene donor is only partially soluble in the reaction mixture and attempts to use molar ratios substantially lower (*i.e.* styrenes : nitrene donor = 1 : 0.5 mol ratio) resulted in low yields of aziridine (*ca.* 15%) in all cases. Hence we have conducted these experiments with higher amounts of the PhI=NNs reagent.

The results (Figs. 7–9) are very interesting since the two substrates react at similar rates when both are present, *i.e.* the rate of reaction of styrene is enhanced in the presence of the substituted styrene whereas the rate of reaction of the substituted styrene is suppressed by the presence of styrene. In a further experiment, the competitive reaction of 2- and 4- chlorostyrene was carried out (Fig. 10), and again the data are presented in a similar manner to that in Figs. 7–9. In the homogeneously catalysed reaction, the rate of 2-chlorostyrene was significantly enhanced by the presence of 4-chlorostyrene and the rate of reaction of 4-chlorostyrene was suppressed, suggesting that 2-chlorostyrene preferentially interacts with the copper active site. The situation is more complex for the heterogeneously catalysed reaction where the reaction of both is enhanced, suggesting the

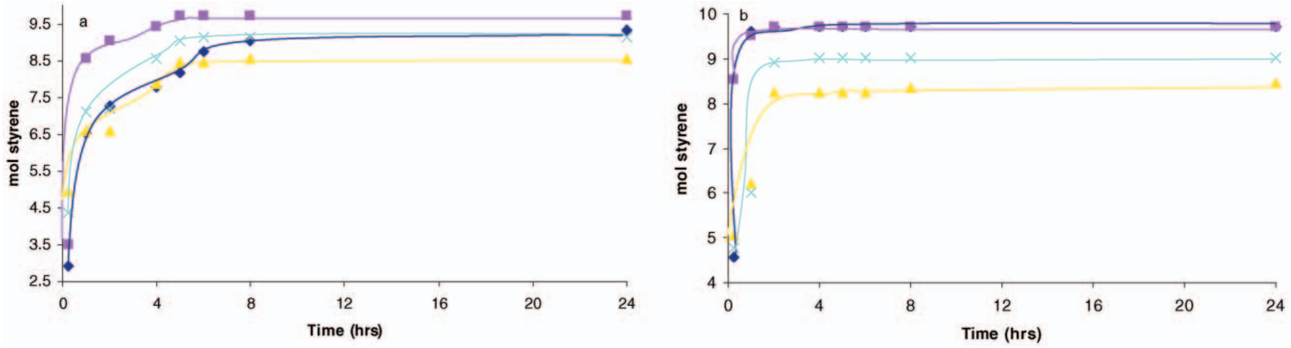

Fig. 10 Effect of reaction time on the competitive aziridination of 2-chlorostyrene and 4-chlorostyrene with bis(oxazoline) **1**, CH_3CN, 25 °C, PhI=NNs : total substrate = 1.5 mol ratio using (a) Cu-exchanged zeolite Y, and (b) $Cu(OTf)_2$. Key aziridine yield: ◆ 2-chlorostyrene only; ■ 4-chlorostyrene only; ▲ 2-chlorostyrene reacted with 4-chlorostyrene; × 4-chlorostyrene reacted with 2-chlorostyrene. (data for competitive reactions are double observed concentrations to permit direct comparison with single substrate reactions.)

involvement of an additional confinement effect. As we have noted previously[13,16] the copper active centre for the formation of aziridines changes during the course of the reaction due to the complex interaction of aziridines and by-product sulfonamides with the active nitrene intermediate. During the conversion of the substrate the ee is observed to increase substantially[13] which we consider to be due to interaction of the aziridine with the active copper nitrene intermediate. It is interesting to note, however, that compared with Fig. 2, the reaction profile (*i.e.* fast initial rate to a slower reaction) character of the plots for substituted styrenes is less pronounced, especially for the 2- and 3-substituents. We consider that, this could indicate that the binding of the aziridine to the catalytic centre, which we consider gives rise to the initial levelling off of the conversion–time curves,[16] is weaker so that the catalyst is able to turn over more times on average before inhibition occurs. Such an interpretation seems not unreasonable on steric grounds; the substituent in the phenyl group is fairly well insulated from the nitrogen and should exert little polar effect on the Lewis basicity. Hence the data for the competitive experiments show that the interaction of the substrates with the active centre, as well as the products, have to be considered in any model for the mechanism of this reaction.

Conclusions

In the catalysed aziridination of styrene derivatives using copper-bis(oxazoline) complexes with PhI=NNs, higher enantioselection can be achieved with the heterogeneously catalysed reaction when compared with the homogeneously catalysed reaction. The effect is considered to be due mainly to the enhanced confinement of the substrate within the pores of the zeolite. This confinement effect also contributes to the increased stability of the heterogeneous catalyst for the reaction of styrene derivatives when compared with the reaction of styrene. The structure of the styrene derivative has a marked effect on the rate of aziridination and by-product formation. With 4-chlorostyrene particularly high yields and ee are observed with both catalyst systems. Competitive reactions in which styrene and a styrene derivative are reacted together reveal that the rate of styrene aziridination is enhanced by the presence of substituted styrenes; whereas, the rate of aziridination of the substituted styrene is suppressed by the presence of styrene.

Experimental

Apparatus

a) ^1H NMR spectra were obtained using a Bruker 'Avance' 400 MHz DPX spectrometer, equipped with Silicon Graphics workstation. The chemical shifts of ^1H NMR spectra are recorded in deuteriated chloroform ($CDCl_3$) and deuteriated dimethyl sulfoxide (d_6-DMSO). Spectra were recorded on the δ scale and signals quoted in the form: chemical shift measured in ppm (No. of protons, multiplicity, assignment).

b) Flash column chromatography was performed on Merck Kieselgel 60 (230–400 mesh) and analytical TLC on silica gel 60 F-254 plates.

c) Atomic absorption spectroscopy was performed using a Perkin-Elmer 373 Atomic Absorption spectrometer using an air–acetylene flame.

d) HPLC analysis was recorded using a Dynamax SD200 pump equipped with Dynamax Al-3 autosampler, Dynamax injector and UV absorbance detector. An Apex ODS 5μ column was used for analytical work. The eluent system was acetonitrile–water (85 : 15). Baseline separation was achieved for all reagents and products. For chiral HPLC analysis, a 25 cm Chiralcel OJ column was used. The eluent system was hexane–propan-2-ol (82 : 18). Baseline separation was achieved for both enantiomers. Absolute configuration was confirmed by optical polarimetry and comparison with the literature.[6]

Materials

Styrene, the styrene derivatives, copper(II) triflate and the bis(oxazoline) were obtained from Aldrich. The copper-exchanged zeolite Y was prepared according to the following procedure. Ultrastabilised NH_4^+Y zeolite (Union Carbide, LZY84, 5.0 g) was calcined (550 °C) for 5 h, then stirred in 0.5 mol solution of copper(II) acetate solution (100 ml) for 24 h at room temperature. The mixture was then centrifuged and washed with distilled water. This was repeated a further two times. The CuHY zeolite was then dried at 100 °C for 24 h, then recalcined (550 °C) for 5 h. Cu content 3.7% by weight.

Preparation of PhI=NNs

Iodobenzene diacetate (3.22 g; 1.0 mmol) was added to a stirred mixture of potassium hydroxide (1.4 g; 0.025 mmol) and *p*-nitrobenzenesulfonamide (2.02 g; 1.0 mmol) in HPLC grade methanol (40 mL), keeping the temperature at 0 °C during the addition. The solution was stirred at room temperature and over a 4 hour period a cream precipitate formed. The precipitate was then filtered, washed with distilled water and dried at room temperature in a vacuum desiccator (3.23 g, 80.6%). δ_H (d_6-DMSO, 400 MHz) 8.2 (doublet, 2H), 7.95 (multiplet, 4H), 7.56 (multiplet, 1H), 7.4 (multiplet, 2H). Anal. cald. C 35.69, H 2.27, N 6.93; Found C 35.56, H 2.29, N 6.62%.

Homogeneous aziridination reactions catalysed by $Cu(OTf)_2$

Copper(II) triflate (0.15 mmol) was added together with chiral bis(oxazoline) (0.07 mmol, Aldrich, 98%) in dry acetonitrile (2.5 cm^3) at 25 °C and the reaction stirred for 15 minutes to preform the catalyst prior to the addition of the styrene and nitrene donor. Styrene or styrene derivative (1.0 mmol) and the PHI=NNs nitrene donor (1.5 mmol) were added and the mixture was stirred. The reaction was stirred in air at 25 °C until complete dissolution of the nitrene donor. The reaction mixture was then filtered through a plug of silica with ethyl acetate (50 cm^3) as eluent. Flash chromatography gave the aziridine as a white solid. Experiments were carried out in triplicate and reproducible results are reported. The aziridines were identified using NMR spectroscopy and isolated yields are reported.

Heterogeneous aziridine reaction catalysed by Cu-exchanged zeolite Y

CuHY (0.3 g) was added together with the chiral bis(oxazoline) (0.07 mmol, Aldrich, 98%) in dry acetonitrile (2.5 cm^3) at 25 °C and the reaction stirred for 15 minutes to preform the catalyst prior to the addition of the styrene and nitrene donor. Styrene or styrene derivative (1.0 mmol), and the PhI=NNs nitrene donor (1.5 mmol), were then added and the mixture was stirred. The reaction mixture was stirred in air at 25 °C until complete dissolution of the nitrene donor. The reaction mixture was then filtered through a plug of silica with ethyl acetate (50 cm^3) as eluent. Flash chromatography gave the aziridine as a white solid. Experiments were carried out in triplicate and reproducible results are reported.

Determination of leached Cu^{2+} for the heterogeneously catalysed reaction

Following reaction, as described above, the reaction mixture was filtered through a Celite plug to remove the zeolite catalyst. The filtrate was then analysed for Cu^{2+} using atomic absorption spectroscopy.

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