

## Epoxidation of Alkenes with Iodosylbenzene catalysed by a Water-soluble Chromium(III) *N,N'*-Ethylene bis(salicylideneaminato) (salen) Complex using $\beta$ -Cyclodextrin as a Phase Transfer Agent

P. A. Ganeshpure and S. Satish

Research Centre, Indian Petrochemicals Corporation Limited, PO: Petrochemicals Vadodara 391 346, India

Addition of  $\beta$ -cyclodextrin as a phase-transfer agent resulted in an increase in yields and rates of epoxidation of alkenes with iodosylbenzene, catalysed by the water soluble complex  $[\text{Cr}(\text{salen})(\text{H}_2\text{O})_2]\text{Cl}$  in water – methylene chloride.

Catalytic epoxidation of alkenes using mono-oxygenase models involving oxometal intermediates is of current interest.<sup>1–3</sup> Recently, several systems have been studied as models for the enzyme cytochrome P-450. In such systems, a metalloporphyrin catalyses the transfer of an oxygen atom to an alkene, either from a single oxygen donor (*e.g.*  $\text{PhIO}^{2,4}$   $\text{NaOCl}$ ,<sup>3</sup>  $\text{KHSO}_5$ <sup>3</sup>) or from combination of molecular oxygen

and a reducing agent (*e.g.* ascorbic acid<sup>5</sup>). Recently, metal complexes other than metalloporphyrins have been used as catalysts for epoxidation of alkenes with iodosylbenzene or alkyl hydroperoxide as an oxygen source.<sup>6–10</sup> However all these systems are limited to metal complexes that are soluble in organic solvents like methylene chloride, benzene, or acetonitrile. The use of ionic complexes which have poor solubility in these solvents, but are soluble in water, has not been reported.

We now report a system for catalytic epoxidation of alkenes, in which an aqueous solution of the cationic complex  $[\text{Cr}(\text{salen})(\text{H}_2\text{O})_2]\text{Cl}$ <sup>11</sup> was treated with an alkene dissolved in  $\text{CH}_2\text{Cl}_2$  using iodosylbenzene as an oxidant and  $\beta$ -cyclodextrin as a phase-transfer agent, to solubilize the alkene in water.  $\beta$ -Cyclodextrin binds alkene molecule in its hydrophobic cavity and is transferred to the aqueous phase<sup>12</sup> where it reacts with the oxo-metal complex. The intermediacy of the reactive oxo-metal species is well established in the case of a similar complex in acetonitrile solution.<sup>10</sup>

The results of the epoxidation of various alkenes with and without  $\beta$ -cyclodextrin are shown in Table 1.† Norbornene gave norbornene oxide as the only product whereas styrene

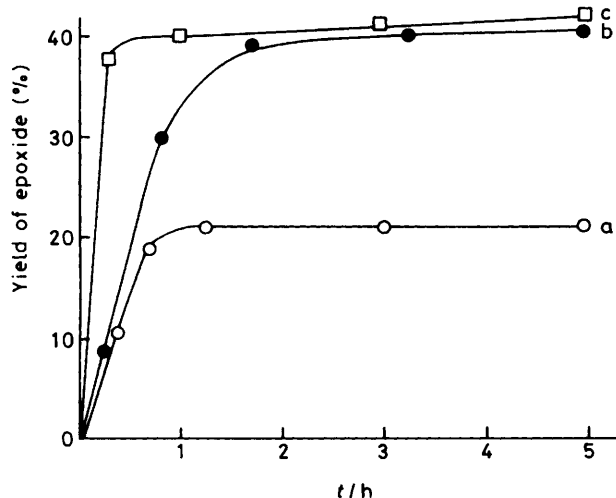


Figure 1. Effect of  $\beta$ -cyclodextrin and 4-methylpyridine on the rates of norbornene epoxidation: (a) without  $\beta$ -cyclodextrin; (b) with  $\beta$ -cyclodextrin; (c) with  $\beta$ -cyclodextrin and 4-methylpyridine (0.15 mmol); conditions as in Table 1.

† All reactions were carried out in a Schlenk tube under nitrogen.  $[\text{Cr}(\text{salen})(\text{H}_2\text{O})_2]\text{Cl}$  (0.05 mmol) dissolved in water (5 ml), the alkene (2.5 mmol) in  $\text{CH}_2\text{Cl}_2$  (4 ml)  $\beta$ -cyclodextrin (80 mg), a suitable internal standard, and iodosylbenzene (0.5 mmol) were taken in the above order and the mixture was stirred at ambient temperature for 5 h. Aliquots (0.1  $\mu\text{l}$ ) from the organic layer were withdrawn and analysed by g.c.

**Table 1.** Epoxidation of alkenes catalysed by  $[\text{Cr}(\text{salen})(\text{H}_2\text{O})_2]\text{Cl}$ : influence of  $\beta$ -cyclodextrin

Substrate	Conditions <sup>a</sup>	Yield of epoxide <sup>b</sup> (%)	Ratio B/A
Norbornene	A	21.0	} 2.1
Norbornene	B	44.0	
Styrene	A	12.0 <sup>c</sup>	} 1.83
Styrene	B	22.0 <sup>c</sup>	
<i>cis</i> -Cyclo-octene	A	4.6	} 1.09
<i>cis</i> -Cyclo-octene	B	5.0	
<i>trans</i> -Hept-2-ene	A	2.6	} 1.23
<i>trans</i> -Hept-2-ene	B	3.2	
<i>trans</i> -Oct-4-ene	A	<0.5	} —
<i>trans</i> -Oct-4-ene	B	<0.5	

<sup>a</sup> A: without  $\beta$ -cyclodextrin; B:  $\beta$ -cyclodextrin added. <sup>b</sup> Based on iodosylbenzene charged. <sup>c</sup> Combined for styrene oxide and phenylacetaldehyde.

gave a mixture of styrene oxide and phenylacetaldehyde. Styrene oxide is known to undergo thermal rearrangement to phenylacetaldehyde in the g.c. injection port.<sup>7</sup> A small amount of phenylacetaldehyde is reported to be formed independently along with styrene oxide in the oxidation of styrene with iodosylbenzene using metalloporphyrins.<sup>4c</sup> *cis*-Cyclo-octene, *trans*-hept-2-ene, and *trans*-oct-4-ene gave the corresponding epoxides selectively. No reaction occurred in the absence of the chromium complex.

The influence of addition of  $\beta$ -cyclodextrin on the yields of epoxides depended on the structure of the alkene. The effect may be expressed in terms of the ratio of yields of epoxide with and without  $\beta$ -cyclodextrin. In the case of norbornene there is about a two-fold increase in the yield of epoxide, whereas the increase is marginal in the case of *cis*-cyclo-octene. The effect of  $\beta$ -cyclodextrin on the yields of epoxides decreased in the following order: norbornene > styrene > *trans*-hept-2-ene > *cis*-cyclo-octene. There was an increase in the rates of epoxidation of norbornene on addition of  $\beta$ -cyclodextrin (Figure 1). Addition of 4-methylpyridine led to further increase in the rates. Pyridine bases co-ordinate to the metal at

an axial position and facilitate the formation of oxo-metal species.<sup>3</sup> Although 85% of the starting iodosylbenzene was converted to iodobenzene, only 44% was utilized in the epoxidation of alkene in 5 h (Table 1, run 2). At this stage the catalyst was still active as indicated by the formation of more epoxide, on adding a further amount of iodosylbenzene.

The system reported here enables water-soluble ionic metal complexes to be used as catalysts for epoxidation of alkenes in the study of mono-oxygenase model systems.

We thank Dr. S. Sivaram for his continued interest in the work and S. D. Chauhan for assistance in carrying out the experiments.

Received, 11th April 1988; Com. 8/01402G

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