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Chiral Mn(III) salen complex-catalyzed enantioselective epoxidation of nonfunctionalized alkenes using urea–H_2O_2 adduct as oxidant

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Abstract

Enantioselective epoxidation of chromenes, indene, and styrene mediated by manganese salen complexes **1a–b**, **2a–b** (1 mol%) as catalysts with urea–H_2O_2 adduct as an oxidant is observed to give excellent epoxide yield (> 99%) in 0.5–4 h with enantiomeric excess (ee) in the range 56–99% except for styrene in which case 23–39% ee was obtained in 20 h. Even with a catalyst loading of 0.4 mol%, the system works efficiently with retention of enantioselectivity, albeit with an increase in reaction time. Kinetic investigations of a representative substrate, indene, with these catalysts indicated a kinetic profile having first-order dependence with respect to the concentrations of the catalyst and oxidant and independent of-initial concentration of the substrate. Based on kinetic, catalytic and experimental evidence, the mechanism of the epoxidation reaction is suggested.

Keywords: Enantioselective; Chiral; Manganese; Nonfunctionalized alkenes; Catalysis; Urea–H_2O_2; Kinetics; Mechanism

1. Introduction

Enantiopure epoxides are highly valuable chiral synthons useful for the synthesis of various biologically active molecules [1,2]. For the preparation of chiral epoxides, the transition metal-catalyzed enantioselective epoxidation of different organic substrates is of the utmost importance and has been widely studied over the past decades [3–9]. However, for its practical application, the catalyst should be easy to synthesize and stored display high reactivity (turnover frequency), selectivity, and durability (turn over number), using inexpensive and environment friendly metals in coordination sphere by means of sterically and electronically tunable chiral ligands [10–12]. The pioneering studies by Katsuki [13] and Jacobsen and co-workers [3–6] have led to a variety of chiral Mn^{III} salen-based catalysts which epoxidized nonfunction alized alkenes with high enantioselectivity with different oxidants [3–9]. As selection of oxidant is also crucial, urea–H_2O_2 adduct (UHP) (an anhydrous source of H_2O_2), being solid and safe, is a particularly attractive source of oxygen [14]. The synthetic utility of Mn^{III} salen catalysts using various oxidants has been a driving source for the elucidation of the mechanisms of the reactions. However, the subject in many cases is mostly speculative. Nevertheless, three main proposals have been presented (Scheme 1) in which (i) alkenes with isolated double bonds have been proposed [15] to react in a concerted manner (path A); (ii) conjugated alkenes have been proposed to react in a stepwise radical process (path B); and (iii) reversible formation of manganaoxetane is applicable to both types of alkenes (path C). Collmann et al. [16] have proposed the formation of oxametallocyclic intermediate during epoxidation for the transfer of oxygen atoms from the metal to the alkenes. Katsuki [13] observed nonlinearity in Eyring plots for the epoxidation of alkenes; on the other hand, Jacobsen and co-workers [17] have demonstrated a linear, temperature/ees relationship, over 100 °C range.

Previously, we have described epoxidation of various nonfunctionalized alkenes using NaOCl as oxidant with complexes **1a–b** and **2a–b** as catalysts under biphasic reaction conditions and demonstrated the formation of Mn^{IV}=O as catalytically active species [18]. The present paper describes enantioselective epoxidation of indene, styrene, and chromenes using complexes **1a–b** and **2a–b** as catalysts, ammonium acetate as cocatalyst, and UHP as oxidant. In order

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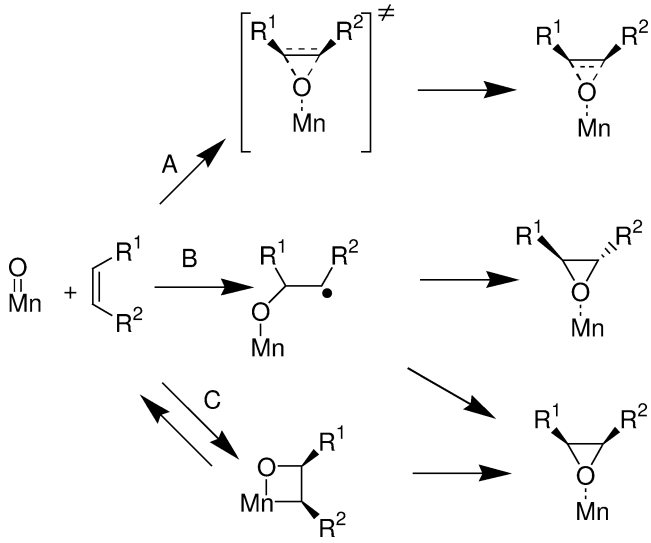


Scheme 1. Mechanisms for the salen Mn-catalyzed epoxidation: A, conserted reaction ($R^1 = R^2 =$ alkyl); B, reaction via a radical intermediate ($R^1 =$ alkyl, $R^2 =$ aryl, alkenyl alkynyl); C, reaction via an oxetane intermediate ($R^1 =$ alkyl, $R^2 =$ alkyl, aryl, alkenyl alkynyl).

to understand the mechanism of epoxidation reaction indene was taken as a representative substrate for detailed kinetic investigations.

2. Experimental methods

All the solvents were purified by a known procedure [19]. Indene and styrene were passed through a pad of neutral alumina before use. 2,2-Dimethylchromene, 6-cyano-2,2-dimethylchromene, 6-nitro-2,2-dimethylchromene, 6-methoxy-2,2-dimethylchromene, spiro[cyclohexane-1,2′-[2H][1] chromene were synthesized by the Bergmann and Gericke procedure [20]. 3-*t*-Butyl-5-chloromethylsalicylaldehyde was synthesized as reported earlier [18].

The purity of the solvents and alkenes and analysis of the product epoxide were determined by gas chromatography (GC) using a Shimadzu GC Model 14B having a stainless-steel column (2 m long, 3 mm i.d., 4 mm o.d.) packed with 5% SE30 (mesh size 60 to 80) and FID detector. Ultrapure nitrogen was used as carriers gas (rate 30 ml/min) and the injection port temperature was kept at 200 °C. For styrene and indene analysis, the column temperature was programmed between 70 and 150 °C while for chromenes it was kept isothermal at 150 °C. Synthetic standards of the products were used to determine conversions by comparison of the peak height and area. The ee for styrene epoxide was determined by GC using chiral capillary column Chiraldex GTA. For chromene and indene epoxides, ees were determined by ^{1}H NMR using chiral shift reagent (+)Eu(hfc)$_3$ as well as HPLC (Shimadzu SCL-10AVP) using Chiralcel column OJ and OB.

2.1. Enantioselective epoxidation of nonfunctionalized alkenes

Enantioselective epoxidation reactions were typically performed according to the established procedure by using 1 mol% of the complexes **1a–b** and **2a–b** with chromenes, styrene, and indene (2.5 mmol) as substrate and UHP adduct (3.0 mmol, added in six equal portions) as an oxidant in 1.6 ml 1:1 dichloromethane:methanol in the presence of a cocatalyst, viz. ammonium acetate, pyridine *N*-oxide, 4-phenylpyridine *N*-oxide, 4-methylmorpholine *N*-oxide, and 1-methylimidazole (0.2 mmol) at 2 °C. The progress of the epoxidation reaction was periodically monitored on GC. After completion of the reaction, the solvent was removed and the residue was extracted with CH_2Cl_2, washed with water, and dried over sodium sulfate. The catalyst was separated from the epoxide by precipitating it with hexane. Enantiomeric excess for the product epoxide was determined as described previously in Experimental.

2.2. Epoxidation reaction for kinetic measurements

Typically, a cooled solution of (0.28×10^{-2}–1.38×10^{-2} M) catalyst in 1.8 ml CH_2Cl_2 was stirred with ammonium acetate (9.16×10^{-2} M) and indene (6.8×10^{-2}–55.4×10^{-2} M). The stirred solution was then interacted with UHP adduct (82.6×10^{-2}–206×10^{-2} M) at 2 °C with constant stirring. To determine the rates of epoxidation, aliquots at an interval of 2 min were drawn from the reaction mixture, quenched with triphenylphosphine, and analyzed on GC.

3. Results and discussion

The syntheses of complexes **1a–b** and **2a–b** (Fig. 1) and their ligand precursors have been reported previously [18]. These complexes (1 mol%) were used as catalysts in the enantioselective epoxidation of a variety of alkenes, namely 2,2-dimethylchromene, 6-cyano-2,2-dimethylchromene, 6-nitro-2,2-dimethylchromene, 6-methoxy-2,2-dimethylchromene, spiro[cyclohexane-1,2′-[2H][1]chromene, styrene, and indene in the presence of ammonium acetate, N, and O coordinating cocatalysts using UHP adduct as oxidant at 2 °C. Product yields, ees, and turnover frequency corresponding to these substrates and catalysts are given in Table 1. Quantitative yields were obtained in all alkenes except styrene (entries 1–4). Reactions were observed to be faster in cases of 2,2-dimethylchromene (entries 13–16), 6-methoxy-2,2-dimethylchromene (entries 17–19), spiro[cyclohexane-1,2′-[2H][1]-chromene (entries 9–12), and 6-nitro-2,2-dimethylchromene (entries 25–28) in comparison to cyanochromene (entries 21, 22). The best enantioselectivities (> 99%) were obtained in cases of electron-deficient nitro- and cyanochromene (entries 21–24 and 25–28). However, in

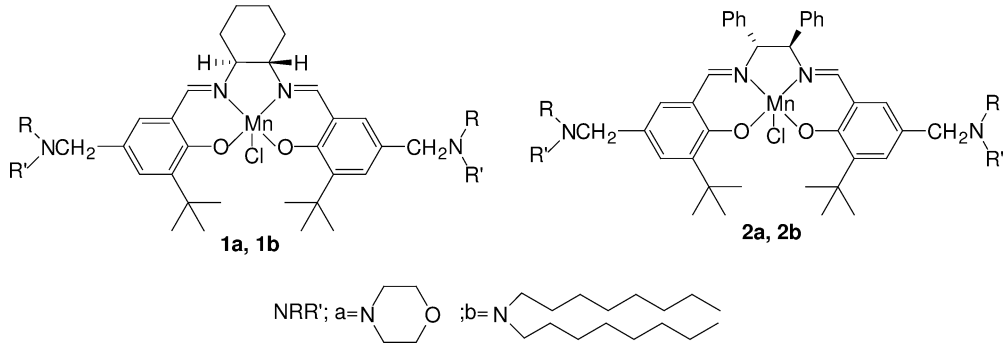


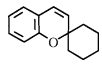
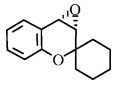
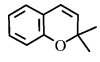
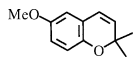
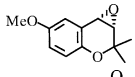
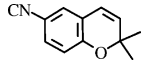
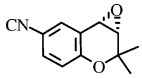
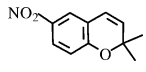
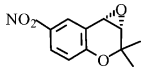
Fig. 1. Structures of the catalysts **1a–b** and **2a–b**.

the case of styrene, ees obtained (23–39%) were not encouraging (entries 1–4) as seen in Fig. 2. We conducted epoxidation of cyanochromene using Jacobsen's complex as a catalyst [3–5] (1 mol%) and UHP as an oxidant under similar reaction conditions and obtained 95% conversion with 98% ee in 15 h. However, complexes **1b** and **2b** gave > 99% conversion and > 99% ee in 1 h (Table 1, entries 23 and 24). The increase in activity and selectivity of catalysts, **1b** and **2b**, reported here may be attributed to an aminoalkyl group at the 5 and 5′ position of the salicylaldehyde moiety. Furthermore, even a catalyst loading of 0.4 mol% was found to be sufficient to achieve similar conversion and selectivity within 8 h in all cases except styrene which took 36 h.

The overall reaction rates are faster with oxidant, UHP adduct, for catalysts **1a–b** and **2a–b** for all the alkenes compared to NaOCl (3.5–10.5 h) as seen in the reaction time of 0.5–4 h for the former compared to 3.5–10.5 h for the later [18,21], except for styrene for which the reaction completes in 20 h (Table 1, entries 1–4).

In order to observe the effect of cocatalysts, namely pyridine *N*-oxide, 4-phenyl pyridine *N*-oxide, 4-methylmorpholine *N*-oxide, and 1-methyl imidazole on the reactivity

Table 1
Product yields, ees, and TOF for enantioselective epoxidation of nonfunctionalized alkenes catalyzed by complexes **1a–b** and **2a–b**[a] in presence of ammonium acetate as cocatalyst with urea–H_2O_2 adduct

Catalyst	Entry	Substrate	Product	Yield[b] (%)	Time (h)	ee[c] (%)	TOF[d] $\times 10^{-3}$	TOF[d] $\times 10^{-3}$ NaOCl
1a(**2a**)	1 (2)			58 (60)	20 (20)	23[e] (25)[f]	0.8 (0.83)	3.06 (9.17)
1b(**2b**)	3 (4)			70 (75)	20 (20)	32[e] (39)[f]	0.97 (1.04)	2.50 (2.29)
1a(**2a**)	5 (6)			> 99 (> 99)	1.5 (1.5)	76[g] (74)[h]	18.3 (18.3)	2.29 (2.75)
1b(**2b**)	7 (8)			99 (> 99)	2.0 (1.0)	76[g] (56)[h]	13.75 (27.5)	2.69 (3.02)
1a(**2a**)	9 (10)			> 99 (> 99)	0.5 (0.5)	68[i] (61)[j]	55 (55)	3.55 (3.22)
1b(**2b**)	11 (12)			99 (> 99)	1.5 (0.5)	62[i] (67)[j]	18.3 (55)	2.95 (2.53)
1a(**2a**)	13 (14)			> 99 (> 99)	1.0 (1.0)	87[i] (67)[j]	27.5 (27.5)	1.89 (1.68)
1b(**2b**)	15 (16)			> 99 (> 99)	0.5 (0.75)	83[i] (64)[j]	55 (36.6)	1.97 (1.86)
1a(**2a**)	17 (18)			> 99 (> 99)	1.0 (1.0)	87[i] (63)[j]	27.5 (27.5)	4.34 (3.44)
1b(**2b**)	19 (20)			> 99 (98)	0.5 (4.0)	92[i] (55)[j]	55 (6.04)	5.11 (3.55)
1a(**2a**)	21 (22)			> 99 (> 99)	4.0 (4.0)	> 99[i] (> 99)[j]	6.87 (6.87)	2.73 (2.53)
1b(**2b**)	23 (24)			> 99 (> 99)	1.0 (1.0)	> 99[i] (> 99)[j]	27.5 (27.5)	2.95 (2.73)
1a(**2a**)	25 (26)			> 99 (> 99)	0.5 (0.5)	> 99[i] (> 99)[j]	55 (55)	8.86 (7.05)
1b(**2b**)	27 (28)			> 99 (> 99)	0.5 (1.0)	> 99[i] (> 99)[j]	55 (27.5)	11.83 (8.86)

[a] Reactions were carried out in CH_2Cl_2:MeOH (1.6 ml) with catalyst (0.025 mmol), substrate (2.5 mmol), cocatalyst (0.2 mmol), oxidant (3.0 mmol) at 2 °C.
[b] Determined on GC.
[c] By ^{1}H NMR using chiral shift reagent (+)Eu(hfc)$_3$/chiral capillary column GTA-type/chiral HPLC column OJ and OB.
[d] Turnover frequency is calculated by the expression [product]/[catalyst] × time s^{-1}.
[e] Epoxide configuration, *S*.
[f] Epoxide configuration, *R*.
[g] Epoxide configuration, 1*S*, 2*R*.
[h] Epoxide configuration, 1*R*, 2*S*.
[i] Epoxide configuration, 3*S*, 4*S*.
[j] Epoxide configuration, 3*R*, 4*R*.

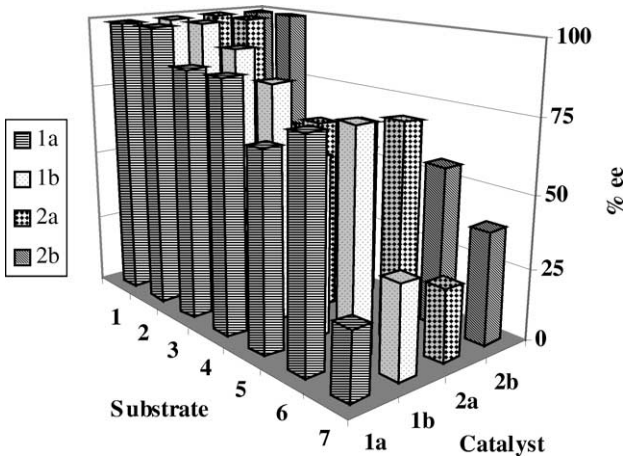


Fig. 2. 3D view showing the % ees versus substrates (1) NO_2CR (nitrochromene) (2) CNCR (cyanochromene), (3) MeOCR (methoxychromene), (4) CR (chromene), (5) IND (indene), (6) CyCR (cyclochromene), and (7) STR (styrene) with catalyst **1a–b** and **2a–b**.

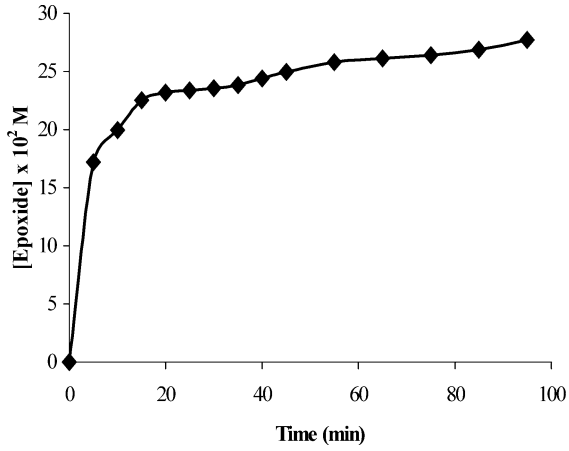


Fig. 3. Time-dependent plot of the formation of epoxide at 2 °C, [**1a**] = [MorCy] = 0.55×10^{-2} M, [oxidant] = 82.60×10^{-2} M, and [indene] = 27.74×10^{-2}.

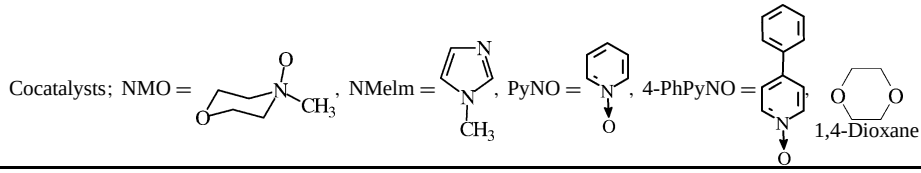
and selectivity for the epoxidation of 2,2-dimethylchromene (a representative substrate), catalytic reactions were carried out in the presence of catalyst **2a** with and without the above-noted cocatalyst. The data are presented in Table 2. In the absence of a cocatalyst a conversion of 37% with 59% ee was obtained in 13 h (entry 34), indicating that cocatalyst has a pronounced effect on the activity and selectivity of the reaction. Of all the cocatalysts, only NMO (Table 2, entry 29) and NmeIm (Table 2, entry 33) worked well with no changes in ees; however, the reaction was slower with PyN-O (Table 2, entry 32). On the other hand, 4-PhPyN-O and 1,4-dioxane did not work at all (Table 2, entries 30 and 31). These results are in agreement with previous reports where NMO and NmeIm were found to be good cocatalysts under anhydrous reaction conditions whereas 4-PhPyN-O, PyN-O, and 1,4-dioxane were suitable under biphasic reaction conditions [22].

In order to understand the mechanism of the epoxidation reaction, the kinetics of epoxidation of a representative substrate, indene, was investigated in detail, using catalysts **1a–b** and **2a–b** in the presence of the oxidant UHP adduct, as a function of the concentrations of catalysts, oxidant, and indene. The plots for formation of epoxide from the epoxidation of indene with time were found to be linear in the beginning of the reaction which attained saturation near completion yielding > 99% epoxide in all the kinetic runs. For the sake of clarity a plot with only one catalyst **1a** is shown in (Fig. 3). Based on this observation, the initial rate constants k_{obs} (up to the linear portion of the graph) were determined by direct estimation of the amount of epoxide formed until completion of the reaction.

3.1. Dependence of the reaction rate on catalyst concentration

The epoxidation of indene was studied by conducting the experiments at different concentrations of catalysts **1a–b** and **2a–b** at constant concentrations of oxidant and indene. A linear increase of the indene epoxide formation with increasing initial concentrations of the catalyst **1a–b** and **2a–b** was observed. The plots of the rate (k_{obs}) of the epoxide formation versus the concentration of the catalyst pass through the origin, indicating that the catalyst is required for the reaction to proceed and is completely catalytic un-

Table 2
Effect of different cocatalysts on enantioselective epoxidation of 2,2-dimethyl chromene catalyzed by complex **2a** with urea–H_2O_2 adduct



Entry	Cocatalyst	Conversion (%)	Time (h)	ee (%)	Configuration
29	NMO	> 99	1	87	3*R*, 4*R*
30	4-PhPyNO	–		–	–
31	1,4-Dioxane	–	–	–	–
32	PyNO	53	7	87	3*R*, 4*R*
33	NMeIm	100	1	87	3*R*, 4*R*
34	–	37	13	59	3*R*, 4*R*

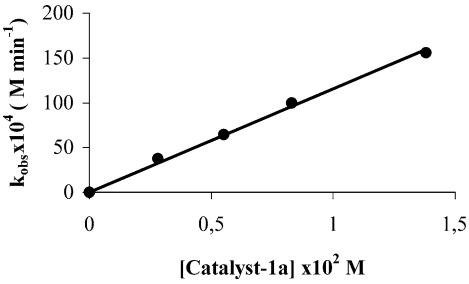


Fig. 4. Plot of catalyst [**1a**] versus k_{obs} at 2 °C, [indene] = 27.74×10^{-2} M and [oxidant] = 82.60×10^{-2} M.

der these experimental conditions. The plots of the $\log k_{obs}$ versus log[catalyst] were found to be linear with unit slopes ($d \log k_{obs}/d \log[\text{catalyst}] = 1$) for catalysts **1a–b** and **2a–b**, indicating that the epoxidation of indene is first order with respect to the concentrations of the catalysts (Fig. 4). Detailed kinetic data for catalyst dependence for epoxidation of indene are given in Table 3.

3.2. Dependence of the reaction rate on the concentration of oxidant

The effect of the concentration of the oxidant (UHP) over a range of 82.6×10^{-2}–206.0×10^{-2} M (3 to 7 equivalents per mole of the substrate) on the rate of epoxidation of the indene was studied, keeping the catalyst and indene concentrations at 0.55×10^{-2} and 27.70×10^{-2} M, respectively. Under the present experimental conditions in the given concentration range, the rate of epoxidation of indene increased with increasing initial concentration of the oxidant. The plots of the rate constants (k_{obs}) versus the concentration of oxidant ($d \log k_{obs}/d \log[\text{oxidant}] \sim 1$) showed first-order dependence (plot for catalyst **1a** is presented in Fig. 5) on oxidant concentration in the epoxidation reaction. The kinetic data for oxidant dependence for epoxidation of indene are given in (Table 4).

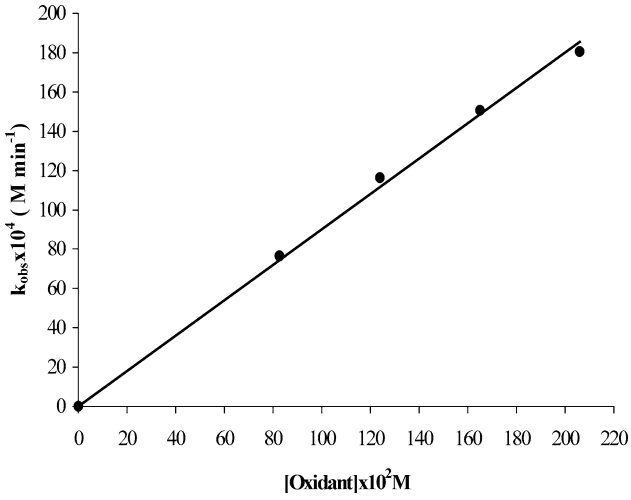


Fig. 5. Plot showing linear dependence of k_{obs} with respect to the concentration of oxidant for epoxidation of indene at 2 °C, [MorCy] = 0.55×10^{-2} M and [indene] = 27.7×10^{-2} M.

3.3. Dependence of the reaction rate on the concentration of alkene

Kinetic experiments conducted at different initial concentrations of indene (Table 5) ranging from 6.8×10^{-2} to 55.4×10^{-2} M, by keeping the concentrations of other reactants and physical conditions constant, indicated a zero-order dependence in terms of the concentrations of the alkene, indene. The tendency of following zero-order kinetics during catalytic epoxidation of alkenes in terms of higher alkene concentrations is also reported in Mn^{III} salen complexes as catalysts and NaOCl [23] and HOCl [24] as oxidants. Dual kinetic behavior [25,26] having zero-order dependence for alkene at higher concentrations and first-order dependence for alkene at lower concentrations has been reported, where the first order dependence at low concentration is explained due to the presence of a competing

Table 3
Catalyst concentration dependence kinetics data for the epoxidation of indene at 2 °C, [indene] = 27.74×10^{-2} M, and [oxidant] = 82.60×10^{-2} M

Catalyst	[Catalyst] $\times 10^2$ M	$k_{obs} \times 10^4$ M min^{-1}
	0.28	37.52
1a	0.55	76.60
	0.83	108.33
	1.38	156.00
	0.28	15.25
2a	0.55	32.80
	0.83	50.11
	1.38	74.22
	0.28	33.33
1b	0.55	62.50
	0.83	85.00
	1.35	150.21
	0.28	14.22
2b	0.55	33.33
	0.83	40.50
	1.38	80.15

Table 4
Dependence of the k_{obs} on the concentration of the oxidant at 2 °C, [catalyst] = 0.55×10^{-2} M and [indene] = 27.74×10^{-2} M

Catalyst	[Oxidant] $\times 10^2$ M	$k_{obs} \times 10^4$ M min^{-1}
1a	82.6	76.60
	124	116.2
	165	150.55
	206	180.42
2a	82.6	32.85
	124	47.54
	165	63.33
	206	75.23
1b	82.6	65.52
	124	95.82
	165	126.66
	206	155.77
2b	82.6	33.30
	124	52.44
	165	62.50
	206	75.80

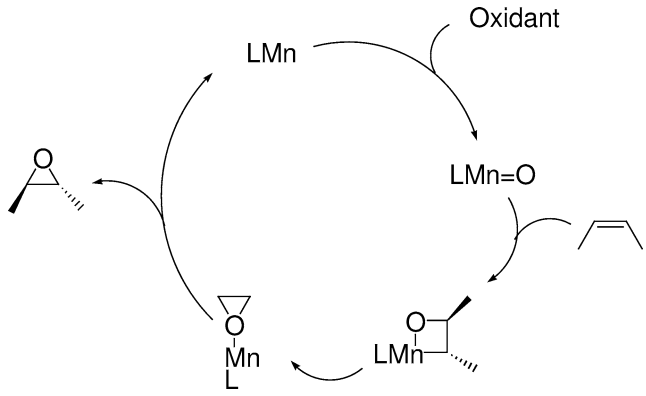
Table 5
Dependence of the k_{obs} on the concentration of indene at 2 °C, [catalyst] = 0.55×10^{-2} M, and [oxidant] = 82.60×10^{-2}

Catalyst	[Indene] $\times 10^2$ M	$k_{obs} \times 10^4$ M min^{-1}
1a	6.8	80.00
	13.6	80.00
	27.4	76.63
	55.4	80.00
1b	6.8	60.00
	13.6	62.50
	27.4	62.50
	55.4	66.00
2a	6.8	30.00
	13.6	30.00
	27.4	32.85
	55.4	35.00
2b	6.8	30.33
	13.6	30.00
	27.4	33.33
	55.4	35.43

side reaction of oxygenation of unknown reductant. However, at higher concentrations of the alkenes the major contribution of the reaction is toward the formation of epoxide from the alkene and contribution toward the side reaction seems to be almost negligible. Only at lower concentrations of the alkenes, the side reaction becomes significant. Under our experimental conditions formation of neat epoxide was also observed without any side product, further supporting the zero-order dependence in indene concentration at reasonably high concentrations.

According to Scheme 1 the epoxidation reaction may proceed via concerted oxygen addition (path A); however, this pathway is reported to be preferred in case of alkyl-substituted alkenes [27]. The radical pathway B is proposed mostly in the case of conjugated alkenes that results in *cis*/*trans* isomerization [28] or aldehyde formation [29]. In all our catalytic epoxidation reactions, exclusive epoxide formation and absence of aldehyde (in case of styrene) and ketone (in case of indene) formation suggest that path C is likely to be operative in this system.

On the basis of kinetics and experimental results the mechanism proposed for the epoxidation of alkene is given in Scheme 2. In the proposed mechanism the catalyst first gets oxidized by the oxidant to form an oxo complex, LMn=O at the rate-determining step. Formation of complex, LMn=O, is proposed on the basis of spectroscopic evidence as well as on kinetic results obtained, which show first-order dependence on catalysts and oxidant concentrations. The interaction of alkene with the oxo complex occurs at faster steps to yield selectively epoxide via the route of oxygen atom transfer at the olefinic bond. The alkene interacts with LMn=O and most viably follows the route of formation of manganaoxetane (path C, Scheme 1) to give selectively epoxide and the catalyst LMn back in its original form. A similar explanation is reported for Mn^{III} salen-catalyzed epoxidation of indene using NaOCl as an oxidant [29].



Scheme 2. Proposed mechanism for Mn^{III} salen complexes **1a–b** and **2a–b**.

Spectroscopic investigations were carried out to show the formation of LMn=O as catalytically active species in Mn^{III} salen-catalyzed epoxidation of alkene. A stepwise overlay of UV–vis spectra for complex **1b** in a mixture of CH_2Cl_2:MeOH at 2 °C is shown in Fig. 6. Wherein (**X**) is the spectrum of catalyst **1b** with ammonium acetate, where a peak at 416 nm is seen which is typically reported for Mn^{III} salen complexes [30]. On addition of the oxidant to this solution the color of the solution changes to dark brown with the development of a new absorption band centered around 500 nm, (**Y**) the maximum of which is obscured by the tailing of strongly absorbing species at $\lambda > 500$ nm, commonly reported with other oxidants, e.g., PhIO, *t*-BuOOOH [30]. This spectral change is attributed to the formation of LMn=O (**Y**). After the addition of the substrate (styrene), it gave spectrum (**Z**) which is very similar to the original complex **1b** (**X**). These events support our observation that LMn=O species is involved at oxygen atom transfer stage and is consistent with earlier reports on Mn^{III} salen complexes [18,30].

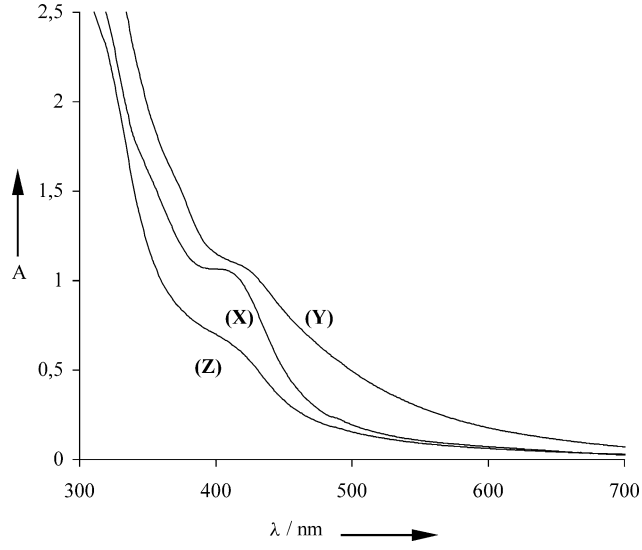


Fig. 6. UV–vis spectra with 0.2 mM solution of **1b** in CH_2Cl_2:MeOH with ammonium acetate (**X**) with oxidant (**Y**) on addition of substrate, styrene (**Z**).

4. Conclusion

Chiral Mn^{III} salen complexes **1a–b**, **2a–b** were investigated for enantioselective epoxidation of chromene derivatives, indene and styrene using UHP as an oxidant in the presence of carboxylato salt, N and O coordinating co-catalysts with excellent conversions for all alkenes except styrene but > 99% ees were obtained only with cyano and nitro chromenes. Ammonium acetate was found to be most suitable co-catalyst under the present epoxidation conditions. Further, a catalyst loading of 0.4 mol% the system works well with some loss of activity, however, ees remain unaltered. The kinetic investigations of a representative substrate indene show first order dependence with respect to the concentrations of the catalyst, oxidant and is independent of initial concentration of the substrate. During the epoxidation, the catalysts first get oxidized to form catalytically active LMn=O species at the rate determining step, which on interaction with alkene gave selectively the product epoxide via the formation of manganaoxetane intermediate.

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