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Epoxidation of Styrene with Molecular Oxygen Catalyzed by Cobalt(II) Salen Complexes

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Cobalt(II) complexes with salen Schiff-base ligands derived from ethylenediamine or (S,S)-1,2-diphenylethylenediamine and salicylaldehyde or 3,5-dibromo and 3,5-di-*t*-butylsalicyladehyde have been tested as catalysts for the epoxidation of styrene with molecular oxygen, in 1,4-dioxane as a solvent. The reaction tests were followed by analyses of gas chromatography and mass spectrometry. Catalytic activities were found to be dependent upon both the electron effects of the substituents on the Co(II) salen complexes and the presence of phenyl substituents on the ethylene moiety. The highest catalytic activity was reached with the Br-substituted complex (2), which was used for further studies on the effects of temperature, time, solvent and additive for epoxidation. The effect of solvent was noted to be critical and the higher reaction temperature (90ºC) was needed. Conversion of styrene reached 97.1 %, with a 59.8 % selectivity of epoxide, when reaction was run at 90ºC for 5 h. Possible reaction mechanism steps were outlined.

Key Words: Co(II) salen complexes, Catalytic epoxidation, Styrene, Oxygen.

INTRODUCTION

Catalytic epoxidation of alkenes has attracted much attention both in industrial processes and in organic syntheses, because epoxides are the most useful synthetic intermediates. Epoxidation of alkenes can be carried out by various techniques with various oxidants. However, stoichiometric (noncatalytic) epoxidation is still widely used and large amounts of byproducts, particularly salts are formed. The utilization of molecular oxygen for a catalytic epoxidation is becoming increasingly important both in industrial and academic researches. Molecular oxygen as a cheap, environmentally clean and readily available oxidant has received much attention in recent years[1-6]. However, when dioxygen was used as an oxidant, in most cases, the reductant should be added into the reactive system. A few ideal homogenous epoxidations of alkenes with molecular oxygen at 1 atm without reducing reagents or radical initiators have been achieved[7-10]. The utilization of dioxygen alone for a catalytic epoxidation is most desirable.

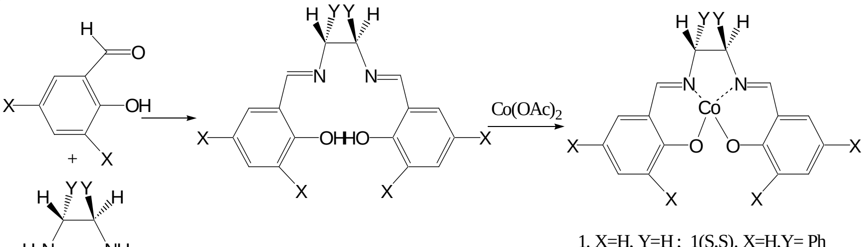
Cobalt ions and complexes are known to catalyze the selective oxidation of alkanes efficiently to organic oxygenates by dioxygen. Budnik and Kochi[11] once reported epoxide formation during the oxidation of *t*-butylethylene, norbornylene and 1,1-dineopentylethylene with dioxygen catalyzed by Co(III) acetylacetonate (acac). Reetz and Töllner[12] showed that $Co(acac)_3$ catalyzed the oxidation of styrene only to benzoic acid and benzaldehyde with dioxygen at 343 K in tetrahydrofuran. When cobalt Schiff base complex[13,14] or bis 1,3-diketonato metal complex[15] was used as catalyst in the oxidation of organic substrates by dioxygen, the reductant, such as isobutyraldehyde, isovalveraldehyde, acetaldehyde or ethyl-2-oxocyclo-pentanecarboxylate was necessary in the catalytic system.

Herein in the present work some of the Co(II) salen complexes, *viz.*, the ethylenediamine and (1S,2S)-1,2-diphenylethylenediamine, have been studied as potential catalysts for epoxidation of styrene by molecular oxygen in 1,4-dioxane as a solvent under mild conditions.

EXPERIMENTAL

(1S,2S)-1,2-Diphenylethylenediamine was purchased from Aldrich. Ethylenediamine (99 %), cobalt(II) acetate tetrahydrate, salicylaldehyde (99 %), styrene (99 %), *t*-butanol and all the solvents were obtained in AR grade of purity.

Preparation of cobalt(II) salen complexes: Cobalt(II) salen complexes 1-3 and 1(S,S)-3(S,S) were synthesized from $Co(OAc)_2$ and the corresponding salen ligands, which were in turn prepared from ethylenediamine or (1S,2S)-1,2-diphenylethylenediamine and corresponding salicyaldehyde, in ethanol under nitrogen atmosphere[16,17]. They were used for epoxidation of styrene without further purification (**Scheme-1**).



1. X=H, Y=H ; 1(S,S). X=H,Y= Ph
2. X=Br,Y=H; 2(S,S). X=Br,Y= Ph
3. X= *t*-Bu,Y=H;3(S,S).X= *t*-Bu,Y=Ph

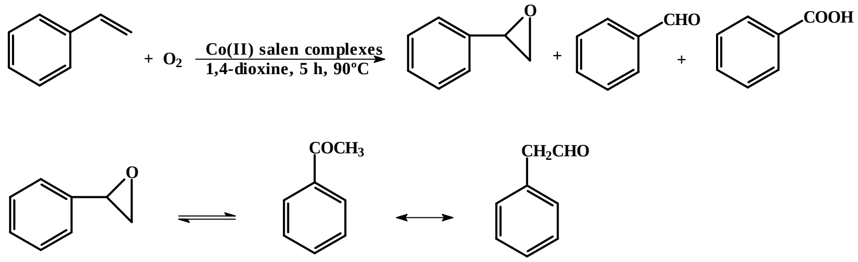
Scheme-1

Oxidation of styrene: The epoxidation of styrene with oxygen was carried out with a three-necked round-bottom flask reactor. In a typical run, 0.01 mmol catalyst was put into the glass reactor which was precharged with styrene (10 mmol) and 8 mL solvent, typically 1,4 -dioxane. The reactant mixture was stirred with bubbling of oxygen at 90ºC for 5 h. The product mixture was analyzed at timed intervals by gas chromatography (SP 6800 A), equipped with a capillary column (SE30 30 M × 0.25 mm × 0.25 µm) and a FID detector, with bromobenzene as internal standard. In most cases, phenyloxirane, benzaldehyde and benzoic acid were obtained as the main products.

The products were identified by Trace-DSQ GC/MS system and quantified by GC. The amount of styrene, benzaldehyde, phenyloxirane and phenylacetaldehyde was calculated from the chromatograms.

RESULTS AND DISCUSSION

Epoxidation of styrene with molecular oxygen catalyzed by cobalt(II) salen complexes were studied. Three main products, namely, benzaldehyde, 2-phenyloxirane (epoxystyrene) and benzoic acid were formed by the aerobic epoxidation of styrene shown in **Scheme-2**. Two minor products: phenylacetaldehyde and 1-phenylethanone are also formed in smaller quantities. They were the result of isomerization of epoxystyrene, the epoxides being known to undergo a tautomeric hydrogen shift with the formation of acyl group[18].



Scheme-2

Effect of substituents on the Cobalt(II) salen complexes: Results obtained for the reactions of styrene with oxygen in the presence of complexes1S-3S and 1-3 were presented in Figs. 2 and 3, respectively. Results for the reactions carried out in the absence of metal complexes were also included for comparison. In these figures, the time course of the reactions has been illustrated in terms of percentage of styrene conversion and epoxide yield. According to these data, in all of the reactions, the conversion of styrene was considerably greater than the yield of epoxide. This fact could be ascribed to the occurrence of side reactions during the epoxidation. Complexes 3 and 3(S,S) appeared to behave rather as inhibitors since they gave rise to styrene conversion rates slower than that of the uncatalyzed reaction. Moreover, both styrene conversion and epoxide yield showed a clear dependence upon the electron withdrawing effects of the substituents on the phenolate moieties. Thus, for both series of cobalt(II) complexes the order Br > H > *t*-Bu was observed (Figs. 1-2).

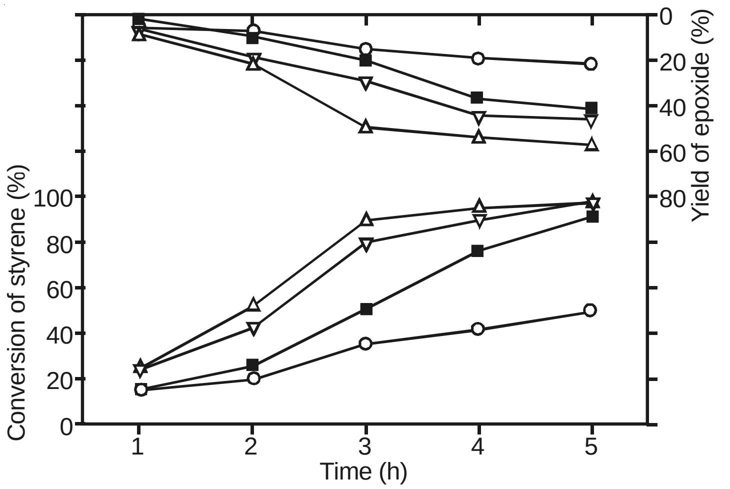


Fig. 1. Reaction profiles for the epoxidation of styrene with oxygen in the presence of complexes 1 (△); 2 (▽); 3 (○). No metal complex (■) Reaction conditions: catalyst, (0.01 mmol); styrene (10 mmol); 1,4-dioxane (8 mL); reaction temperature, 90ºC; flow rate of O_2, 5.0 mL/min

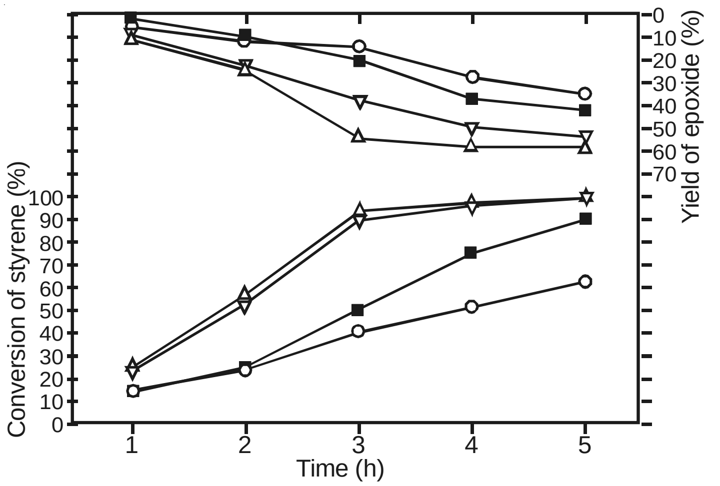


Fig. 2. Reaction profiles for the epoxidation of styrene with oxygen in the presence of complexes 1S (△); 2S (▽); 3S (○). No metal complex (■) Reaction conditions: catalyst, (0.01 mmol); styrene (10 mmol); 1,4-dioxane (8 mL); reaction temperature, 90ºC; flow rate of O_2, 5.0 mL/min

Steric effects were also reviewed on comparing the time profiles of styrene conversion for the reactions mediated by each series of cobalt complexes, *i.e.* ethylenediamine and (1S,2S)-1,2-diphenylethylenediamine derivatives (Figs. 2 and 3). Similar but less conspicuous differences were observed between the styrene conversions and yield of epoxide mediated by complexes 2(S,S) and 2. Accordingly, the styrene conversions mediated by complexes 1(S,S) and 1 occur *ca.* 2.1 and 1.6 times fast than those of the uncatalyzed reaction, respectively (during the first 3 h). Different cobalt complexes showed different catalytic activity under identical reaction conditions. This suggests the direct involvement of the cobalt complexes in the oxygen transfer step. It was assumed that the steric effects arising from the phenyl substituents on the ethylenediamine moiety of the Schiff-base ligand contribute to an appropriate transition state orientation of the styrene molecular towards the oxygen coordinated to the metal ion center.

Influence of reaction temperature: The effects of reaction temperature on the catalytic performances of the complex **2** were summarized in Table-1. At temperatures lower than 90ºC, not only styrene conversion (from 11.8 % at 60ºC to 89.1 % at 90ºC) but also styrene oxide selectivity (from 6 % at 60ºC to 57.8 % at 90ºC) increased remarkably with raising the reaction temperature. On the other hand, selectivity of benzaldehyde decreased (92.9 % at 60ºC to 31.4 % at 90ºC). However, at high temperature (100ºC) selectivity of epoxystyrene decreased to 46.1 % at 3 h. When the temperature was too low, it was difficult to initiate the reaction. While the temperature was too high, the byproducts increased and polymerization of styrene was occurred and caused the drop of selectivity. Hence, the temperature near 90ºC was the optimum one for obtaining a favourable conversion and selectivity of styrene oxide.

TABLE-1
EFFECT OF TEMPERATURE ON THE OXIDATION OF STYRENE IN THE PRESENCE OF COMPLEX **2** AS CATALYST[a]

Reaction temperature (°C)	Conversion of styrene (%)[b]	Selectivity of products (%)[b]			
		Epoxystyrene	Benzaldehyde	Benzoic acid	Others[c]
60	11.8	5.7	92.9	1.4	-
70	28.5	11.3	83.1	3.2	2.4
80	58.1	27.8	64.6	4.6	3.0
90	89.1	57.8	31.4	7.6	3.2
100	98.2	46.1	18.3	24.0	11.6 [d]

[a] Reaction conditions: catalyst **2** (0.01 mmol); styrene (10 mmol); 1,4-dioxane (8 mL); flow rate of O_2, 5.0 mL/min; reaction time, 3 h. [b] Estimated by GC using bromobenzene as an internal standard. [c] Main product is phenylacetaldehyde. [d] phenylacetaldehyde +polymer of styrene.

Effects of time on the epoxidation of styrene catalyzed by complex 2: The time dependence of the oxidation reactions was investigated for complexes **2** and the selectivities for styrene oxide and benzaldehyde with the reaction time were shown in Fig. 3. It might be seen that benzaldehyde was formed at first as the only product, then after some minutes of induction time epoxystyrene appeared. Both the conversion of styrene and the selectivities of products increased slightly in 3 h. And When reaction time over 5h the selectivity of epoxystyrene dropped sharply.

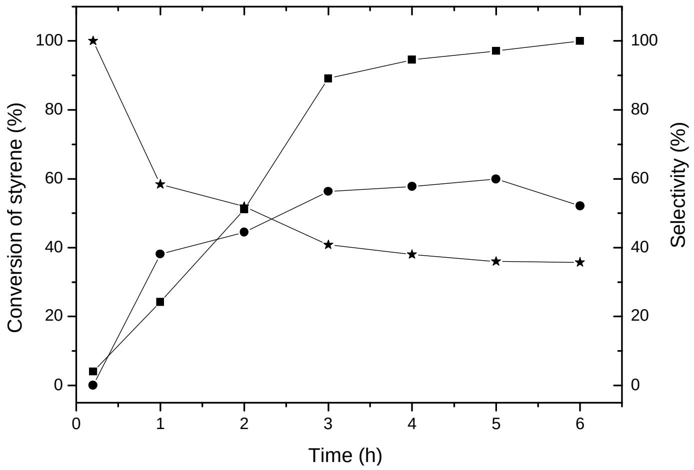


Fig. 3. Effect of reaction time on the oxidation of styrene in the presence of complex **2** as catalyst (■) styrene conversion, (•) epoxide selectivity, (★) benzaldehyde + benzoic acid selectivity Reaction conditions: complex 2, (0.01 mmol); styrene (10 mmol); 1,4-dioxane (8 mL); flow rate of O_2, 5.0 mL/min; reaction temperature, 90ºC.

Effects of solvents on the epoxidation of styrene catalyzed by complex 2: Styrene epoxidation with oxygen catalyzed by complex **2** was taken as a model system to study the influence of the solvent on catalytic activity. Epoxidation was carried out in different solvents. The results as shown in Table-2, indicate the solvent played a crucial role in the epoxidation reactions. It is of significance to note that 1,4-dioxane is particularly efficient in providing both high styrene conversion and high epoxide selectivity. Although high styrene conversion could be obtained when N-methylpyrrolidone and cyclohexanone were used, the selectivity for styrene oxide was low. No reaction occurred when pyridine and DMF were used. It should be noted that *t*-butyl alcohol, a potential co-reductant for the activation of oxygen[19], did not work here. Isopropanol was also used as solvent, only 4.2 % styrene conversion was obtained. Based on the solvent studies, it can be concluded that 1,4-dioxane is the most suitable solvent for this oxidative system.

TABLE-2
EPOXIDATION OF STYRENE BY OXYGEN IN DIFFERENT SOLVENTS WITH COMPLEX **2**[a]

S. No.	Solvent	Conversion (%)[b]	Epoxidation selectivity (%)[b]
1	1,4-Dioxane	97.1	59.8
2	DMF	0.0	-
3	DMSO	Trace	-
4	N-Methylpyrrolidone	71.0	38.0
5	Cyclohexone	63.0	33.0
6	*tert*-Butanol	0.0	-
7	Pyridine	0.0	-
8	Isopropanol	4.2	84.0

[a]Reaction conditions: catalyst **2** (0.01 mmol); styrene (10 mmol); 1,4-dioxane (8 mL); flow rate of O_2, 5.0 mL/min; reaction time, 3 h. [b]Estimated by GC using bromobenzene as an internal standard.

Effect of additives on the reactivity and product selectivity: Katsuki and co-workers[20] had shown that imidazoles and pyridines were very beneficial additives in certain cases in the manganese series. We, therefore, used them in our system. However, when imidazole was added into catalytic oxidation system, the reaction stopped. Pyridine also inhibited the reaction. The addition of acetic acid leads to the decrease of conversion, while the selectivity increased slightly in catalytic oxidation system, shown in Fig. 4.

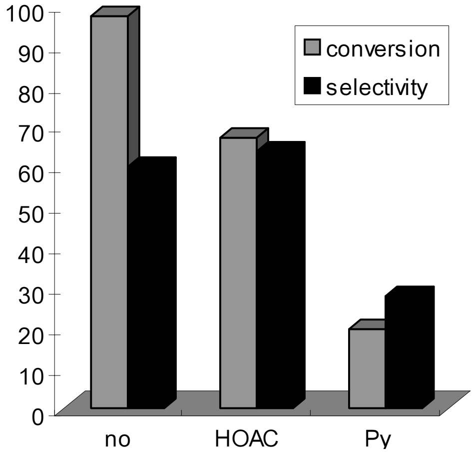
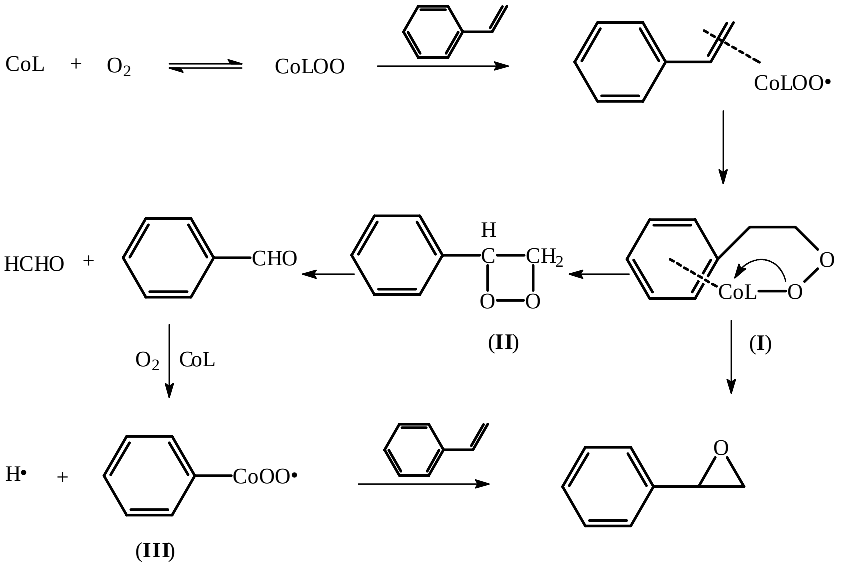


Fig. 4. Effect of HOAc and Py in oxidation of styrene catalyzed by commplex **2**, Reaction conditions: complex 2 (0.01 mmol); styrene (10 mmol); 1,4-dioxane (8 mL); flow rate of O_2, 5.0 mL/min; reaction time, 5 h

Possible reaction mechanism: It is well known that many Co(II) complexes can capture and activate O_2 to form complexes Co(III)-(O_2)[21]. We speculate that, in our case, a similar binding of O_2 to the Co(II) sites may also occur in the initial step. The Co(III)-(O_2) species formed might undergo further reactions to generate an active oxygen species with a radical nature responsible for the epoxidation (**Scheme-3**). First, cobalt-activated molecular oxygen, in the form of a cobalt superoxo complex (CoL-OO) reacts with the alkene to form an intermediate (**I**) having a benzylic radical center. This addition mechanism has been suggested in the literature[22,23]. Then there are two pathways: one is the intermediate (**I**) may collapse to a cyclic peroxide intermediate (**II**) by intramolecular reaction. Then (**II**) is subsequently decomposed to benzaldehyde and formaldehyde under the reaction conditions; another one is the intermediate (**I**) breaks the bond of O-O to form epoxystyrene. It is known that Co(III) ions may catalyze the formation of an acylperoxy radical from benzaldehyde[24] by O_2.The acylperoxy radical may epoxidize alkenes to give epoxides and benzoic acid.



Scheme-3 Reaction mechanism steps to epoxystyrene

This suggest that the reaction is a radical mechanism. To clarify this point, the influence of the addition of a radical scavenger, *p*-benzenediol, on catalytic performances has been investigated. The results revealed that styrene conversion decreased to almost zero after the addition of a small amount of *p*-benzenediol (*ca.* 0.05 mmol) under the reaction conditions mentioned above. This observation confirms the radical nature of the active oxygen species formed by the activation of O_2 over the tetrahedral Co(II) site.

The proposed mechanism can also explain various solvent effects. When the catalytic oxidation was carried out in pyridine or other coordinating solvents might be expected to inhibit the coordination of alkene to the cobalt thereby preventing formation of (**1**). For isopropyl alcohol and *t*-butanol, the cobalt superoxo radical can react the solvent's hydroxy instead of attacking the alkene. 1,4-Dioxane is usually a stable solvent, however, we detected smaller quantities of ethylene dimethyl ester and ethylene monomethyl ester in the reaction mixture by GC-MS in the present of dioxygen, 1,4-dioxane and the Co-salen catalytic system. Therefore, 1,4-dioxine itself may act as a co-reductant in the formation of active oxygen species. Further elucidation of this point and the nature of active oxygen species are needed in future studies.

Conclusions

In this paper we have elucidated the epoxidation of styrene, using Co(II) salen complexes in presence of molecular oxygen and 1,4-dioxine as solvent. The results described above permit some general conclusions to be drawn:

The catalytic activity is dependent upon the electron withdrawing effects of the susbstituents on the Co(II) salen complexes. Activity decreases in the order of: Br > H > *t*-Bu.

The major products of the reaction were epoxystyrene and benzaldehyde. At higher temperature, epoxidation becomes more favored whereas at lower temperature, benaldehyde becomes dominant.

The mechanism of oxidation is a radical chain mechanism. Cobalt(II) salen complexes activate molecular oxygen to generate an active oxygen species with a radical nature responsible for the epoxidation and the solvent (1,4-dioxane) may act as a co-reductant in the formation of active oxygen species.

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