Journal of Molecular Catalysis A: Chemical 421 (2016) 131–137

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Ti-salalen mediated asymmetric epoxidation of olefins with H_2O_2: Effect of ligand on the catalytic performance, and insight into the oxidation mechanism

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ARTICLE INFO

Article history:
Received 12 April 2016
Received in revised form 13 May 2016
Accepted 16 May 2016
Available online 17 May 2016

Keywords:
Asymmetric oxidation
Hydrogen peroxide
Mechanism
Salalen
Titanium

ABSTRACT

The highly enantioselective epoxidation of several conjugated olefins with H_2O_2 in the presence of five chiral titanium(IV) salalen (dihydrosalen) complexes has been studied, with focus on the effects of substituents (electronic and steric) on the epoxide yield and enantioselectivity. The introduction of electron acceptors at the ligand's remote positions enhances the catalytic reactivity, without drastic effect on the stereoselectivity and ultimate catalytic efficiency. In turn, the replacement of Ph substituents of the ligand core with *o*-MeO-Ph and *o*-Et-Ph substituents leads to the enhancement in enantioselectivity (up to 99.8% *ee*), conversion (up to 100%) and efficiency (up to 125 TN). Kinetic and Hammett data provide evidence in favour of a stepwise epoxidation mechanism on Ti-salalen catalysts. As compared to Ti-salan protagonists, Ti-salalen catalysts exhibit much higher activity and efficiency, and in most cases comparable enantioselectivity. Kinetic peculiarities of epoxidations on Ti-salalen and Ti-salan complexes are considered.

1. Introduction

In the last few years, catalytic asymmetric epoxidation of unfunctionalized olefins has been attracting undiminishing interest, owing to the need in novel environmentally friendly catalyst systems based on non-toxic metal complexes (or even metal-free catalysts) and green oxidants (e.g. H_2O_2 and O_2) [1–6]. Within transition-metal based catalysts, complexes of titanium are of great interest due to non-toxicity of this metal (and products of its hydrolysis), and proven ability to activate H_2O_2 molecule, transferring one of its oxygen atoms to olefinic moieties in a highly asymmetric fashion [7]. Katsuki and co-workers pioneered the studies of chiral salan (tetrahydrosalen) [8–12] and salalen (dihydrosalen) [13–16] complexes of titanium(IV) as catalysts for the highly enantioselective epoxidation of conjugated and terminal olefins. Berkessel and co-workers conducted comparative and mechanistic studies of Ti-salalen catalyzed epoxidations [17,18] and developed a library of salalen ligands, derived from optically pure *cis*-1,2-diaminocyclohexane as the chirality source [19,20]. Other groups also contributed a series of works aimed at designing and testing related chiral titanium(IV) catalysts [21–25].

Both salan and salalen type complexes exhibited high to excellent enantioselectivities for the epoxidation of conjugated *cis*-olefins (up to >99% *ee*); furthermore, titanium salalen based catalysts appeared active enough to epoxidize electron-poor terminal olefins [13,20], suggesting a higher intrinsic reactivity of Ti-salalen complexes as compared to their Ti-salan analogs, which may be an important practical advantage. In spite of a plethora of available catalytic data, systematic analyses of effects of substituents on the catalytic reactivity and enantioselectivity of Ti-salalen complexes have been hitherto lacking. In this work, we have undertaken such a study, focusing on the electronic enfluence of remote electron-donating and withdrawing substituents, as well as the effect of introduction of bulky substituents into the ligand structure.

2. Experimental

2.1. Materials and methods

H_2O_2 was used as a commercial analytical grade 30% aqueous solution. Silica gel 60 (0.063–0.200 mm) for column chromatogra-

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http://dx.doi.org/10.1016/j.molcata.2016.05.019
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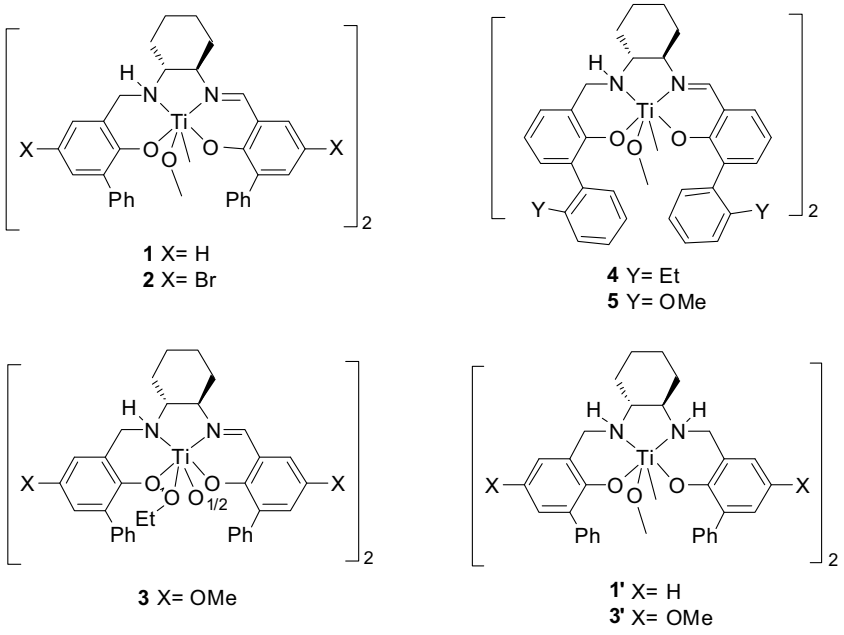


Scheme 1. Titanium(IV) salalen complexes **1**-**5** considered in this work, and titanium(IV) salan catalysts **1**′ and **3**′ [22].

phy was purchased from Panreac. All other chemicals were Aldrich, AlfaAesar, or Acros commercial reagents.

^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance 400 at 400.13 and 100.613 MHz, or on a Bruker DPX-250 at 250.13 and 62.903 MHz, respectively. Chemical shifts were referenced to internal standard tetramethylsilane, with positive values in the low-field direction.

Enantiomeric excess values and absolute configurations of epoxides were measured on a Shimadzu LC-20 HPLC chromatograph equipped with Daicel chiral columns (250 × 4.6 mm). The experimental uncertainty in *ee* measurements did not exceed ±1.0% for *ee*s falling in the range 74–90%, ±0.5% for *ee*s falling in the range 90–98%, and ±0.25% for *ee*s higher than 98%. The chiral HPLC separation details for epoxides and *N*-Boc protected 1,2-aminoalcohols can be found in the Supporting information and references therein.

CCDC 1439962 (**4**) and 1439963 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via ww.ccdc.cam.ac.uk/data_request/cif and from the authors.

2.2. Typical asymmetric epoxidation procedure

A conjugated olefin (0.10 mmol) was added to the Ti-salan or Ti-salalen catalyst (5 μmol or 0.8 μmol, respectively) dissolved in CH_2Cl_2 (0.4 mL), and 0.05 mL of a saturated aqueous NaCl was added. The mixture was thermostatted at the desired temperature (290 K), and 30% aqueous hydrogen peroxide (0.20 mmol of H_2O_2) was then introduced in one portion. Stirring (400 rpm) was continued at that temperature for (typically) 24 h. The reaction mixture was diluted with aqueous NaCl (1 mL), the organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 1 mL). The combined organic extract was dried with $CaSO_4$, diluted with 0.6 mL of CCl_4, and CH_2Cl_2 was carefully removed on a rotary evaporator at room temperature. The remaining solution was diluted with 0.1 mL of $CDCl_3$ and analyzed by ^{1}H NMR to reveal the ratio of olefin, epoxide, and byproduct(s), and by chiral HPLC to measure the *ee* of the epoxide.

For the epoxidation of 1-decene (0.1 mmol), the volumes of CH_2Cl_2 and aqueous NaCl were 0.1 mL and 0.025 mL, respectively; 0.15 mmol of H_2O_2 was introduced at once and the reaction mixture was stirred at 298 K for 24 h. An additional 0.1 mmol of H_2O_2 was added, and the mixture was allowed to stir for additional 48 h at the same temperature. After the standard workup (see above), the reaction outcome was analyzed by ^{1}H NMR; the epoxide *ee* was measured by ^{1}H NMR with c.s.r. Eu(hfc)$_3$. The optical purity of chalcone epoxide was measured by chiral HPLC (SI).

3. Results and discussion

Complexes **1**-**5** (Scheme 1) have been studied as five model catalysts of enantioselective epoxidation of olefins. Complexes **1**-**3** were recently prepared and X-ray characterized, and reported to catalyze the highly enantioselective sulfoxidation of pyridylmethylthiobenzimidazoles to optically pure proton pump inhibitors (*S*)-omeprazole and (*R*)-lansoprazole with hydrogen peroxide [26]. In the solid state, complexes **1**-**3** have dimeric structures, with either two bridging oxygen atoms (complexes **1**, **2**), or with one bridging oxygen (complex **3**) [26,27].

Complexes **4** and **5** have been first synthesized, isolated and X-ray characterized in this work. The chiral ligands for **4** and **5** were prepared starting from commercial precursors (SI). X-ray quality crystals of **4** and **5** were obtained by crystallization from Et_2O/CH_2Cl_2/pentane or from $CHCl_3$/hexane (SI).

The asymmetric units of **4** and **5** contain complexes $[Ti_2O_2(C_{36}H_{38}N_2O_2)_2]$ and $[Ti_2O_2(C_{34}H_{34}N_2O_4)_2]$, respectively. In both complexes, two Ti(IV) cations have distorted octahedral coordination environment formed by two N and two O atoms of an organic ligand and O atoms of two oxo-ligands. The ethyl-groups of **4** are disordered over two orientations in approximate ratio 87:13 and 76:24. Hydrogen atoms of organic ligands were placed geometrically and refined using a riding model except for the (*R*)-amine hydrogen of the **5** which was refined independently. In the asymmetric unit of **4,** the solvent molecule of pentane was also located and isotropically refined because of disordering. Additionally, there are two $CHCl_3$ solvent molecules in the asymmetric unit of **5.**

As compared to the previously reported complexes **1**-**3** [26], **4** and **5** bear additional steric crowd at the aryl rings; their molecular structures are shown in Fig. 1. Curiously, while single-crystalline complex **4** was homochiral (Λ,*R*,*R*,*S*$_N$-Λ,*R*,*R*,*S*$_N$)-**4**, complex **5** exhib-

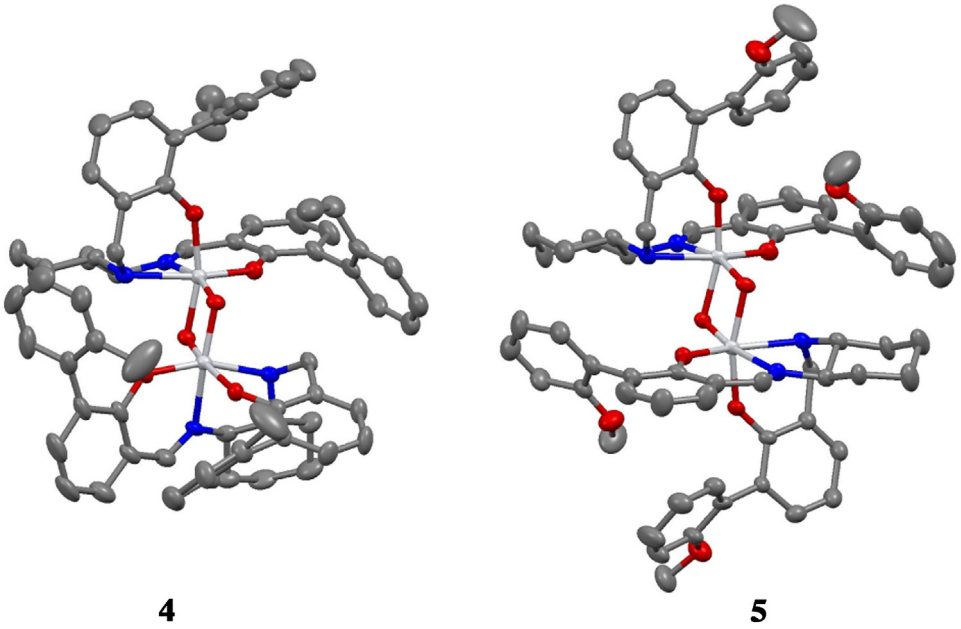


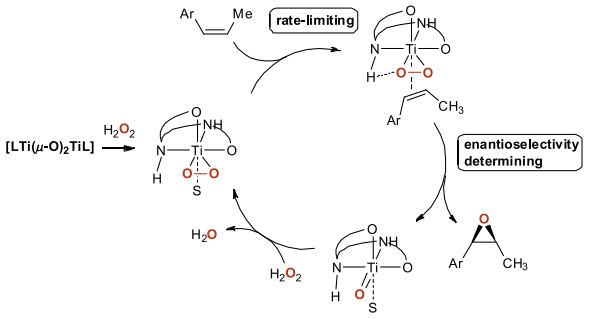
Fig. 1. Molecular structures of complexes (Λ,*R*,*R*,S_N-Λ,*R*,*R*,S_N)-**4** and (Λ,*R*,*R*,S_N-Δ,*R*,*R*,R_N)-**5**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. C grey, Ti white, O red, N blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ited pseudoheterochiral configuration (Λ,*R*,*R*,S_N-Δ,*R*,*R*,R_N)-**5**, the Ti atoms in **5** having different chiralities (Fig. 1). Such sort of isomerism was reported previously for structurally related Ti-salan complexes, where three homo- and heterochiral stereoisomers were isolated for the same Ti-salan species [28]. In catalytic epoxidations, however, all those isomers demonstrated equal enantioselectivities, pointing to the formation of the same active species, apparently, monomeric titanium-peroxo intermediates [7,28].

Complex **4** exhibits hydrogen bonding between the N—H hydrogen of the ligand at one Ti atom and O at the other Ti atom (the H···O distances 2.54, 2.52 Å, SI), and C—H···π interactions between the salalen CH_2 bridge of the ligand at one Ti atom and the phenyl ring of the salalen ligand at the other Ti atom (distances between H to the centers of rings 2.84 and 2.87 Å, SI). Contrariwise, in **5**, only the (*R*)-amine H forms such hydrogen bond (H···O distance 2.18(7) Å).

The catalytic properties of complexes **1**-**5** have been tested in the oxidation of five conjugated olefins (Table 1). Like for previously studied titanium-salan based catalysts [22], the introduction of remote electron-donating or withdrawing substituents (complexes **1**, **2**, **3**) does not dramatically affect the enantioselectivity. This observation is in agreement with the two-stage epoxidation mechanism (previously suggested for titanium-salan catalysts [22]), the oxygen transfer stage occurring in an intramolecular manner, and the enantioselection being virtually unaffected by the presence of EDG and EWG, depending only on the substrate geometry (Scheme 2).

In turn, the introduction of *o*-substituted aryls instead of 3,3′-Ph_2 groups [29] in most cases improved the catalytic efficiency (which was up to 125 TN for indene) and the optical yield of the epoxides. This gain in enantioselectivity was higher for styrene and *cis*-β-methylstyrene and much smaller for cyclic conjugated olefins, which trend is similar to that documented for the epoxidations catalyzed by titanium-salan complexes [22]. For the epoxidations of indene, dihydronaphthalene and 2,2-dimethyl-2H-chromene-6-carbonitrile, the *ee*s obtained with the best catalysts **4** and **5** were good to excellent (96.5–99.8% *ee*). Interestingly, with



Scheme 2. Proposed mechanism of titanium catalyzed olefin epoxidations. S is solvent molecule or vacancy.

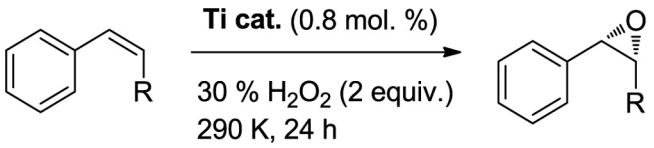
catalysts **4** and **5**, higher product yields (65–76%) were achieved for the epoxidation of styrene, the least electron-rich substrate of the series of conjugated olefins.

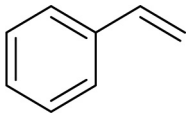
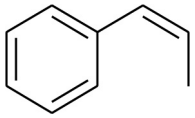
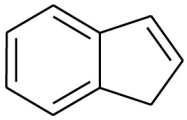
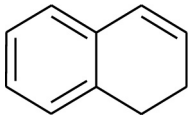
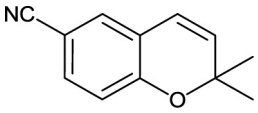
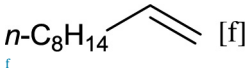
For comparison, catalytic data for the titanium(IV) salan complex **1**′ (used at 5 mol% loading) are given for each substrate. One can see that the salan catalyst demonstrates a slightly higher enantioselectivity than the corresponding salalen complex **1** for the epoxidation of styrene and *cis*-β-methylstyrene (cf. entries 1 vs. 2 and 7 vs. 8), while for cyclic conjugated olefins the enantioselectivities are virtually identical.

The major advantage of the salalen type catalysts appears to be their higher efficiency (in terms of turnover numbers performed): while the epoxidation on titanium-salan based catalysts required 5 mol% catalyst loading, for titanium-salalens, the use of only 0.8 mol% loading ensured comparable epoxide yield and, in most cases, comparable enantioselectivity.

The stepwise mechanism depicted in Scheme 2 assumes that the presence of electron-acceptors should make the titanium center more electrophilic and thus facilitate the rate-limiting olefin coordination step, thus accelerating the overall reaction [22]. Coordination of olefins to the metal centers is extremely widespread in transition metal catalysis. It is an essential, in most cases rate-limiting, step in coordination-insertion olefin polymerization by

Table 1
Epoxidation of conjugated olefins with H_2O_2 in the presence of Ti-salalen catalysts **1**–**5**.[a]



no	substrate	Ti cat.	conversion/selectivity [%][b]	*ee* [%] (config.)[c]
1		**1′**	60[d]	81.5 (S)
2		**1**[e]	50.0/99.5	78.5 (S)
3		**2**[e]	34.0/100	79.0 (S)
4		**3**[e]	25.0/100	75.5 (S)
5		**4**	76.5/99.5	85.5 (S)
6		**5**	65.0/100	81.0 (S)
7		**1′**	73[d]	74.5 (2R,3S)
8		**1**	70.0/100	66.0 (2R,3S)
9		**2**	36.5/100	66.0 (2R,3S)
10		**3**	64.5/95.5	69.0 (2R,3S)
11		**4**	56.0/100	74.5 (2R,3S)
12		**5**	85.0/100	82.0 (2R,3S)
13		**1′**	92[d]	95.0 (1S,2R)
14		**1**	100/90.5	95.5 (1S,2R)
15		**2**	100/89.5	95.5 (1S,2R)
16		**3**	99.0/95.0	96.0 (1S,2R)
17		**4**	98.0/93.5	96.5 (1S,2R)
18		**5**	100/96.0	96.5 (1S,2R)
19		**1′**	94[d]	96.0 (1S,2R)
20		**1**	95.0/98.0	96.5 (1S,2R)
21		**2**	95.5/98.5	96.5 (1S,2R)
22		**3**	95.5/97.5	96.5 (1S,2R)
23		**4**	95.5/98.0	97.5 (1S,2R)
24		**5**	95.5/98.5	97.5 (1S,2R)
25		**1′**	76[d]	99.5 (3S,4S)
26		**1**	88.5/97.5	99.4 (3S,4S)
27		**2**	66.5/99.0	99.3 (3S,4S)
28		**3**	78.0/99.5	98.5 (3S,4S)
29		**4**	80.0/99.0	99.7 (3S,4S)
30		**5**	92.0/99.0	99.8 (3S,4S)
31	 [f]	**2**	6.0/100	68.5[g]
32		**3**	7.0/100	69.0[g]
33		**4**	21.0/100	66.0[g]
34		**5**	11.5/100	70.0[g]

The bold values signifies the numbers of complexes.

[a] Reaction conditions as shown in the sketch unless otherwise noted. Oxidant added in one portion.

[b] Determined by ^{1}H NMR analysis.

[c] Determined by chiral HPLC.

[d] Reported yields from Ref. 22; conditions: At 290 K; $[H_2O_2]/[substrate]/[catalyst] = 150\ \mu mol{:}100\ \mu mol{:}5\ \mu mol$, oxidant was added in one portion and the mixture was stirred for 18 h.

[e] 2 + 1 equiv. H_2O_2, mixture stirred for 48 h (see SI for details).

[f] Conditions reported in Section 2.

[g] Determined by ^{1}H NMR with chiral shift reagent Eu(hfc)$_3$.

group IV metal complexes (Ti, Zr, Hf) as well as by classical Ziegler-Natta titanium-based heterogeneous catalysts [30–32]. We note that Ti-salan and Ti-salalen complexes are well-known catalysts of olefin polymerization [33–42], which obviously implies their ability to coordinate olefin molecules.

Plausible reason for the higher activity of Ti-salalen catalysts (as compared to the salan ones) is the lower electron-donor character of the salalen ligands, owing to the presence of conjugated N=C moiety. The decrease of electron-donor character of the ligand, when passing from Ti-salan to Ti-salalen complexes, should make the latter more electrophilic and facilitate olefin coordination to the titanium centers, thus speeding up the overall process. Contrariwise, the decrease of electron-donor character of the *substrates* would be expected to attenuate the rate of substrate coordination to titanium, thus slowing down the overall process. To illustrate the influence of electronic factors on the relative epoxidation rates, five substituted styrenes were taken to competitive epoxidations with catalyst **4** (Fig. 2). It is seen that the relative epoxidation rates demonstrate good linear correlation with the Hammett substituent parameters σ_p. The slope ρ was found to be −0.52, which is very close to the slope for the epoxidation of substituted styrenes in the presence of salan complex **1′** [22]. At the same time, the enantioselectivity is not visibly affected by the substituents variation, remaining in the range 85. . .87% (with the only exception of *p*-F-styrene for which the *ee* was only 83%). This behavior is identical to that documented for Ti-salan epoxidation catalysts [22], and fully consistent with the stepwise mechanism depicted in Scheme 2, which implies that the epoxidation rate and epoxidation selectivity are determined by two separate reaction steps.

It would be logical to expect that catalyst **2**, bearing Br substituents, should be more active as compared to unsubtituted **1** and OMe-substituted **3**. However, our catalytic data (Table 1) witnessed that for Br-substituted catalyst **2**, the epoxide yields (achieved within 24 h) were in most cases lower than for H- or OMe- containing catalysts **1** and **3**. To disclose the reasons of this apparent discrepancy, we have monitored the kinetics of epoxidation of *cis*-β-methylstyrene in the presence of Ti-salalen catalysts

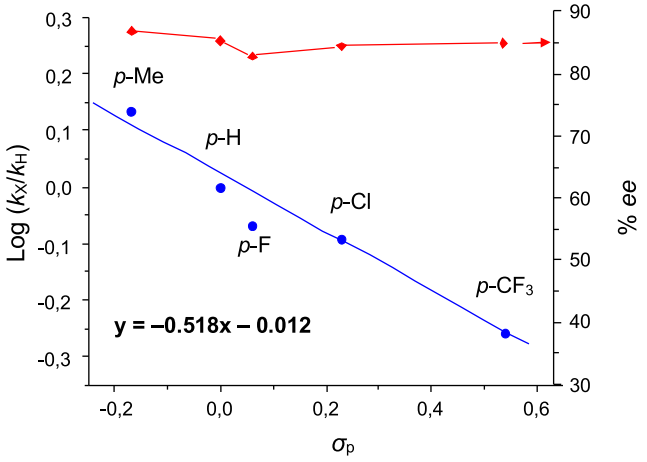


Fig. 2. Hammett plot of Log(k_X/k_H) (blue) and enantiomeric excess (red) vs σ_p for the epoxidation of *p*-substututed styrenes by the **4**/H_2O_2 system. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

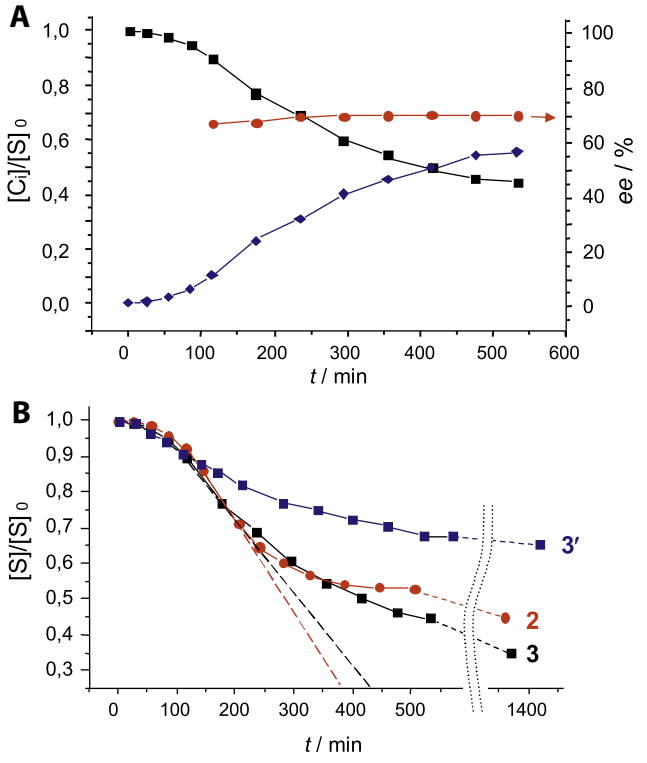


Fig. 3. (A) Kinetics of epoxidation of *cis*-β-methylstyrene (CH_2Cl_2, 290 K, 1.6 mol% of catalyst, [H_2O_2]/[olefin] = 2.0) by catalyst system **3**/H_2O_2: substrate (S) concentration black, epoxide concentration blue, enantiomeric excess brown. (B) Kinetics of epoxidation of *cis*-β-methylstyrene (CH_2Cl_2, 290 K) by catalyst systems **3**/H_2O_2 (black), **2**/H_2O_2 (brown) and **3′**/H_2O_2 (blue). Dashed lines demonstrate the highest slopes of kinetic curves for catalyst systems **3**/H_2O_2 (black) and **2**/H_2O_2 (brown). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2, **3** and (for comparison) Ti-salan catalyst **3′**. The resulting kinetic curves are presented in Fig. 3.

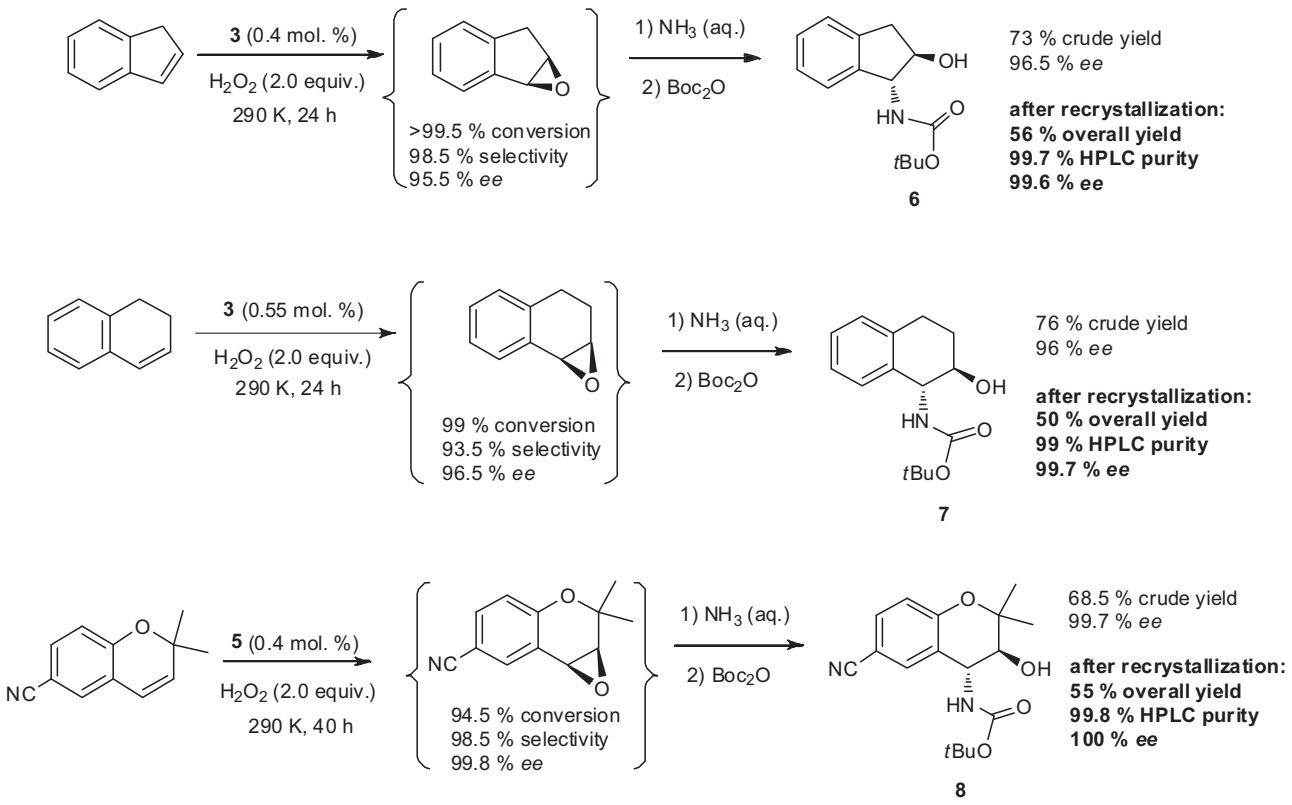
Like for titanium-salan based catalysts [22], there was some initial induction period of ca. 100–120 min (Fig. 3A), which apparently reflects the formation and accumulation of the true catalytically active sites. Also like for titanium-salan based catalysts, during the induction period, the epoxidation enantioselectivity (Fig. 3A) increased to adopt a value which further remained virtually constant during the reaction. At the same time, while for salan systems there was a steady-state regime, resulting in linear ln([S]/[S]$_0$) vs. time dependence [22], for the salalen catalyst **3** the epoxidation kinetics was nonsteady, such that no linear dependence could be observed and no pseudo-first-order rate constants could be derived. At the same time, the slope of the kinetic curve, proportional to the rate of decrement of olefin concentration, may be taken as a measure of relative activities of the active species for different catalyst systems. One can see that the kinetic curve for the system **2**/H_2O_2 (after the induction period) is more steep than for **3**/H_2O_2 (Fig. 3B); however, the former systems deactivates faster. In effect, the system **3**/H_2O_2, which retains its activity for longer, eventually (after 24 h) ensures higher conversion (Fig. 3B). For comparison, titanium-salan catalyst **3′** showed a much lower activity, and deactivated much faster, to end up at only 34% conversion (corresponding to 21 TN) within 24 h.

The nature of this deactivation is most likely complex. On the one hand, adding another 2 equiv. of H_2O_2 to the reaction mixtures in Fig. 3B after 24 h did not affect the olefin/epoxide ratio for the system **3′**/H_2O_2 within the next 24 h. On the other hand, a similar manipulation with the system **2**/H_2O_2 caused an increase of the olefin conversion from 55% to 65% within the next 24 h. Therefore, we believe that the reaction deceleration may be due to (1) titanium catalyst degradation and (2) catalytic decomposition of H_2O_2 which competes with the target epoxidation reaction. The contribution of the latter channel exhibits itself most explicitly in epoxidations of the least electron-rich conjugated olefin, styrene (Table 1, entries 2–5), for which the documented yields were in most cases (except for catalysts **4** and **5**) achievable within only 48 h, with the addition of another 1 equiv. of H_2O_2 after 24 h.

The higher catalytic activity of the Ti-salalen complexes (compared to Ti-salan analogs) was previously exploited for the epoxidation of non-conjugated (especially terminal) olefins [13,14,19,20]. We have conducted the epoxidation of a non-conjugated olefin – 1-decene – (entries 31–34 of Table 1). The enantioselectivities shown by catalysts **2**-**5** did not vary significantly, remaining in the range 66–70%. Under the conditions used, the yields were much lower than for conjugated olefins; with catalyst **4**, the highest epoxide yield of 21% was achieved. In spite of the low yield, we note that the efficiency of **4** (26 TN) was comparable to those demonstrated by the Katsuki's "second-generation" Ti-salalen catalyst in 1-octene epoxidation (23–42 TN) [13,14]. For the epoxidation of a typical electron-deficient olefin, *trans*-chalcone in the presence of catalyst **2** (under the standard conditions of Table 1), only a 2% conversion within 24 h was achieved, with the epoxide having 18% *ee* (2*S*,3*R*).

To exemplify the practical utility of Ti-salalen catalyzed epoxidations, we have attempted the synthesis of optically pure 1,2-aminoalcohols starting from indene, 1,2-dihydronaphthalene and 2,2-dimethyl-2H-chromene-6-carbonitrile, proceeding via ring cleavage of the intermediate epoxide with ammonia (Scheme 3). The nucleophilic attack of NH_3 occurred without deterioration of the enantiomeric excess. Boc-protection provides a practical tool for purification: by recrystallization of the *N*-Boc-protected aminoalcohols, the epoxide HPLC purity and the *ee* can be further increased up to > 99%. After purification, the Boc protecting group can be removed under acidic conditions,

to release the desired optically pure aminoalcohol [41]. This approach to optically pure 1,2-aminoalcohols from chiral epoxides may be a technically easier alternative to that relying on azidolysis of the epoxide, followed by H_2 reduction of the azidoalcohol (over Pd/C), with subsequent Boc-protection, purification by recrystallization, and deprotection [42].



Scheme 3. Synthesis of optically pure 1,2-aminoalcohols.

4. Conclusions

The effects (electronic and steric) of substituents on the product yield and enantioselectivity in the course of epoxidation of conjugated olefins with H_2O_2 in the presence of five chiral titanium(IV) salalen (dihydrosalen) complexes has been studied systematically. The introduction of electron-acceptors at the ligand's remote positions enhances the catalytic reactivity (without significant effect on the stereoselectivity) but causes faster reaction deceleration. The latter is apparently due to (1) irreversible catalyst degradation as well as (2) Ti-promoted decomposition of hydrogen peroxide. In turn, the replacement of Ph substituents of the ligand with *o*-MeO-Ph and *o*-Et-Ph substituents affords more efficient and stereoselective catalysts. The methoxy-substituted catalyst 5 exhibits the highest enantioselectivities (up to 99.8% *ee*) and in most cases the highest yields and efficiencies.

Hammett correlation (Ln of epoxidation rates of *p*-substituted styrenes) provides evidence in favour of an electrophilic active species ($\rho = -0.52$). At the same time, the epoxidation enantioselectivity is virtually independent of the *p*-substituent. This picture is consistent with a stepwise mechanism (previously proposed for epoxidations on similar Ti-salan catalysts [22]), with separate rate-limiting and enantioselectivity-determining steps. As compared with Ti-salan protagonists, Ti-salalen catalysts demonstrate higher activity and efficiency, and, depending on substrate, similar or slightly lower enantioselectivity. Chiral epoxides of cyclic conjugated olefins, obtained with the aid of Ti-salalen catalysts, can be further readily cleaved by ammonia to afford optically active *trans*-1,2-aminoalcohols without deterioration of optical purity.

Acknowledgments

The authors gratefully acknowledge the financial support from the Russian Science Foundation (grant 14-13-00158), and thank the Multi-Access Chemical Service Center SB RAS for providing the equipment for the XRD experiments.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2016.05.019.

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