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Preparation and Characterization of Optically Active Quadridentate Schiff Base-Titanium(IV) Complexes and the Catalytic Properties of These Complexes on Asymmetric Oxidation of Methyl Phenyl Sulfide with Organic Hydroperoxides

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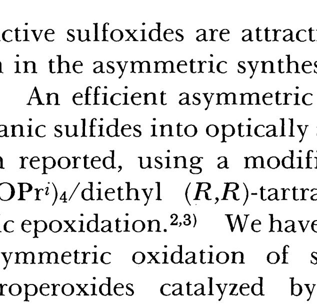
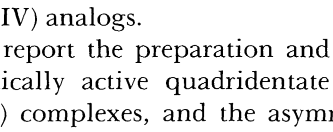
Titanium(IV) complexes, $[\mathrm{TiCl(Schiff\ base)}]_2\mathrm{O}$, with quadridentate Schiff base ligands derived from optically active 1,2-diamines and salicylaldehyde were prepared by treating $\mathrm{TiCl_4}$ with an equimolar amount of the Schiff base ligand in wet pyridine. The complexes were characterized by their ^{13}C NMR, absorption, and circular dichroism spectra, and conductivity measurements. The complexes in dichloromethane take a μ-oxo dinuclear structure, and in methanol the complexes break up into a mononuclear species, [Ti(OMe)(MeOH)(Schiff base)]Cl. The complexes catalyze the asymmetric oxidation of methyl phenyl sulfide into the sulfoxide with organic hydroperoxides; the highest enantiomeric excess (ee) was ca. 60%. The kinetics conform to a rate law which is first order in the concentration of each sulfide, hydroperoxide, and complex catalyst.

Optically active sulfoxides are attracting considerable attention in the asymmetric synthesis of organic compounds.[1] An efficient asymmetric oxidation of prochiral organic sulfides into optically active sulfoxides has been reported, using a modified Sharpless reagent ($\mathrm{Ti(OPr^{\mathit{i}})_4}$/diethyl (*R*,*R*)-tartrate/$\mathrm{Bu^{\mathit{t}}OOH}$) for asymmetric epoxidation.[2,3] We have succeeded in a similar asymmetric oxidation of sulfides with organic hydroperoxides catalyzed by oxovanadium(IV) complexes containing quadridentate Schiff base ligands derived from optically active 1,2-diamines and salicylaldehyde or its derivatives.[4] Thus, it is interesting to study the catalytic properties of titanium(IV) analogs.

Here, we report the preparation and characterization of optically active quadridentate Schiff base-titanium(IV) complexes, and the asymmetric oxidation of methyl phenyl sulfide with organic hydroperoxides catalyzed by these complexes. A part of this study has been reported briefly.[5]



sal-(*RR*)-chxn



$R^1=CH_3$, $R^2=H$; sal-(*R*)-pn
$R^1=R^2=C_6H_5$; sal-(*RR*)-stien

Experimental

(*R*)-1,2-Propanediamine ((*R*)-pn), (*R*,*R*)-1,2-cyclohexanediamine ((*RR*)-chxn), and (*R*,*R*)-1,2-diphenylethylenediamine ((*RR*)-stien) were prepared by the published methods[6,7,8]

(*R*)-pn: $[\alpha]_D$ $-11.0°$ (*c* 1.6, H_2O); lit, $[\alpha]_D$ $-11.0°$ (c 2.5, H_2O).[6]

(*RR*)-chxn: $[\alpha]_D$ $-42.1°$ (*c* 2.0, CH_3OH); lit, $[\alpha]_D$ $-44.1°$ (c 3.0, CH_3OH).[7]

(*RR*)-stien: $[\alpha]_D$ $+104°$ (*c* 0.57, CH_3OH); lit, $[\alpha]_D$ $+106.9°$ (c 1.07, CH_3OH).[8]

Schiff bases were prepared by the methods of Gullotti et al.[9]

Preparation of $[\mathrm{TiCl(Schiff\ Base)}]_2\mathrm{O}$ (Schiff Base=sal-(*R*)-pn, sal-(*RR*)-chxn, sal-(*RR*)-stien). These complexes were prepared by a similar method, and a representative procedure is given for $[\mathrm{TiCl(sal\text{-}(\mathit{R})\text{-}pn)}]_2\mathrm{O}$.

To a pyridine solution (5 cm^3) of $\mathrm{H_2\{sal\text{-}(\mathit{R})\text{-}pn\}}$ (0.56 g, 2 mmol) was added $\mathrm{TiCl_4}$ (0.38 g, 2 mmol) with stirring. The resulting orange solution was cooled in an ice-bath to yield an orange precipitate. It was collected by filtration, and recrystallized from dichloromethane by the addition of acetone. Yield: 0.41 g (56%). Found: C, 54.91; H, 4.55; N, 7.30%. Calcd for $\mathrm{C_{34}H_{32}N_4Cl_2O_5Ti_2}$: C, 54.94: H, 4.34; N, 7.54%. Found: C, 58.79; H, 5.49; N, 6.05%. Calcd for $[\mathrm{TiCl(sal\text{-}(\mathit{RR})\text{-}chxn)}]_2\mathrm{O}\cdot 2(\mathrm{CH_3})_2\mathrm{CO}=\mathrm{C_{40}H_{40}N_4Cl_2O_5Ti_2}\cdot 2\mathrm{C_3H_6O}$: C, 58.80; H, 5.58; N, 5.96%. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$) δ=24.4, 24.5, 28.8, 28.9, 67.2, 67.7, 115.8, 116.4, 119.8, 120.0, 123.4, 124.0, 134.5, 135.1, 135.2, 135.3, 157.9, 158.7, 162.2, and 162.4. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_3OD}$) δ=25.3, 30.1, 70.1, 117.5, 121.9, 124.3, 136.5, 137.8, 163.6, and 164.0. Found: C, 65.75; H, 4.43; N, 5.85%. Calcd for $[\mathrm{TiCl(sal\text{-}(\mathit{RR})\text{-}stien)}]_2\mathrm{O}$ $=\mathrm{C_{56}H_{44}N_4Cl_2O_5Ti_2}$: C, 65.97; H, 4.35; N, 5.49%.

Oxidation of Methyl Phenyl Sulfide by Organic Hydroperoxides with a Catalytic Amount of Schiff Base-Titanium(IV) Complexes. A typical run was performed as

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follows: A methanol solution (20 cm^3) containing [TiCl(sal-(*RR*)-chxn)$]_2$O·2$(CH_3)_2$CO (7.5×10^{-5} mol) and triphenylmethyl hydroperoxide (1.5×10^{-3} mol) was cooled to 0 °C. Methyl phenyl sulfide (1.5×10^{-3} mol) was added and the mixture was kept at 0 °C for 110 h. The solvent was removed under reduced pressure, and the residue was extracted with diethyl ether, which was evaporated under reduced pressure. From the resulting oil, methyl phenyl sulfoxide was isolated and purified by column chromatography on silica gel (eluent: cyclohexane–ethyl acetate (1 : 1 v/v)). Yield: 87%. The enantiomeric excess (ee) was determined on the basis of the reported optical rotation of the pure enantiomer;10) $[\alpha]_D$ +79.7° (*c* 1.9, CH_3OH); 53% ee (*R*).

The progress of the reaction could be checked by high-performance liquid chromatography. Portions of the reaction mixture were withdrawn at intervals and then chromatographed (sample volume, 1—4×10^{-3} cm^3) with a column of Develosil ODS-5 (Nomura Chemical Co., Ltd., ϕ 0.46 cm×25 cm; eluent, acetonitrile-water (6 : 4 v/v)) or JASCO Fine Pack C18S (ϕ 0.46 cm×15 cm; eluent, acetonitrile-water (9 : 1 v/v)). Chromatography was carried out with a JASCO Tri Rotar V system and the components were detected with a JASCO UVIDEC 100 IV spectrophotometric detector at 260 nm. The amounts of sulfide, sulfoxide, and sulfone were determined from the absorption spectra of the collected fractions or by paper cut-outs matching the bands in the elution curve, while taking the molar absorption coefficients into consideration. The ee was determined from the circular dichroism (CD) spectrum of the fraction containing the sulfoxide on the basis of $\Delta\varepsilon_{237}=+13.9$ for the pure (*R*)-isomer.4)

Kinetics Studies. The kinetics of the oxidation reactions was studied by high-performance liquid chromatography as described above. Since triphenylmethyl hydroperoxide is rather unstable, we used stable 1-methyl-1-phenylethyl hydroperoxide as the oxidant. All reactions were carried out under pseudo-first-order reaction conditions.

Spectroscopic Measurements. $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL GX-400 spectrometer using TMS as an internal reference. Optical rotations were measured with a JASCO DIP 4 polarimeter. Absorption and CD spectra were recorded on a Hitachi U-3400 spectrophotometer and a JASCO J-40CS spectropolarimeter, respectively. Conductivity measurements were carried out with a Toa CM-6A conductivity meter.

Results and Discussion

Preparation, Characterization, and Structure of the Schiff Base-Titanium(IV) Complexes. [TiCl(SB)$]_2$O (SB=Schiff base) was prepared by treating $TiCl_4$ with an equimolar amount of the Schiff base ligand in wet pyridine (water content≧0.4%). Although several titanium(IV) complexes with quadridentate Schiff base ligands have been prepared in the same way, they have been formulated differently.11,12) Thus, the structure was determined by X-ray analysis on the sal-(*RR*)-chxn complex (Fig. 1); the details have been reported in a separate paper.13) The structure shows a μ-oxo ligand bridging two TiCl(sal-(*RR*)-chxn) units. It is to be noted that [$TiCl_2$(SB)] is formed instead of [TiCl(SB)$]_2$O when the reaction is carried out in anhydrous solvents. The bridging oxygen atom seems to come from water in wet pyridine (Scheme 1).

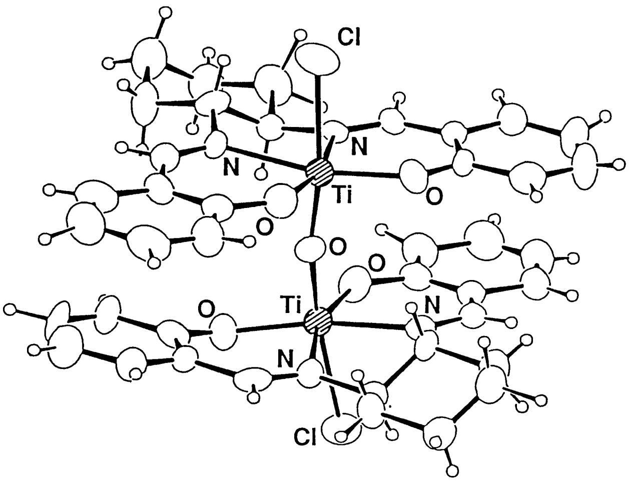
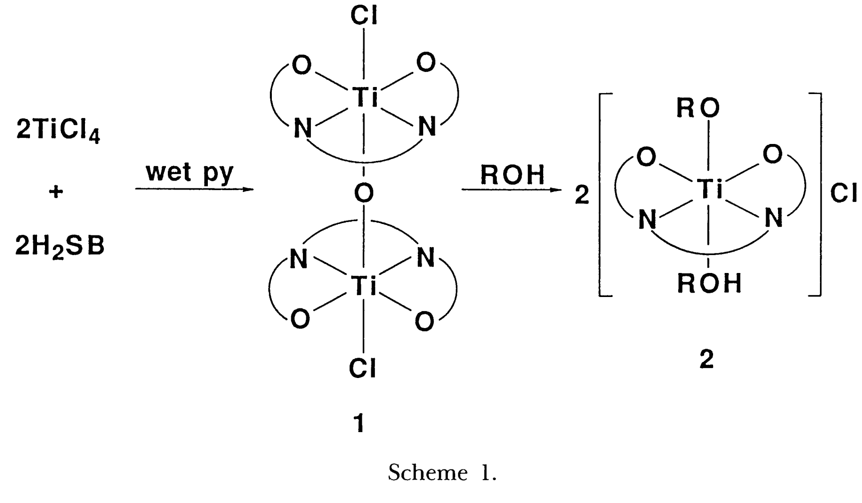


Fig. 1. An ORTEP drawing of [TiCl(sal-(*RR*)-chxn)$]_2$O.



Scheme 1.

Very recently, Mozzanti et al.[14] have reported a μ-oxo dinuclear complex, [TiCl(acen)]$_2$O (acen=N,N'-ethylenebis(4-imino-2-penten-2-olate), the structure of which is very similar to that of [TiCl(sal-(RR)-chxn)]$_2$O.

Conductivity measurement reveals that [TiCl(sal-(RR)-chxn)]$_2$O is a non-electrolyte in dichloromethane, and the ^{13}C{^{1}H} NMR spectrum of the complex in CD$_2$Cl$_2$ shows 20 signals as expected for the crystal structure. On the other hand, the ^{13}C{^{1}H} NMR spectrum in CD$_3$OD shows only 10 signals, suggesting that the complex breaks up into a mononuclear one with a C$_2$ axis. The molar conductivity of 64 S cm^2 mol^{-1} in methanol calculated on the basis of the mononuclear complex, is in the range expected for a 1 : 1 electrolyte.[15] The most probable structure in methanol will be **2** in Scheme 1. Since protons migrate quickly on the NMR time scale, a coordinated methanol molecule and a methoxide ion will be indistinguishable by NMR (pseudo C$_2$). The absorption spectrum of [TiCl(sal-(RR)-chxn)]$_2$O in dichloromethane is quite different from those in methanol, ethanol, or 1-propanol, the spectra in alcohols being similar to each other (Fig. 2). Conductivities in ethanol (28 S cm^2 mol^{-1}) and 1-propanol (12 S cm^2 mol^{-1}) also suggest structure **2** in these solvents.

Figure 3 shows the CD spectra of [TiCl(sal-(RR)-chxn)]$_2$O in dichloromethane, methanol, ethanol, and 1-propanol. Here, again, the spectral pattern in

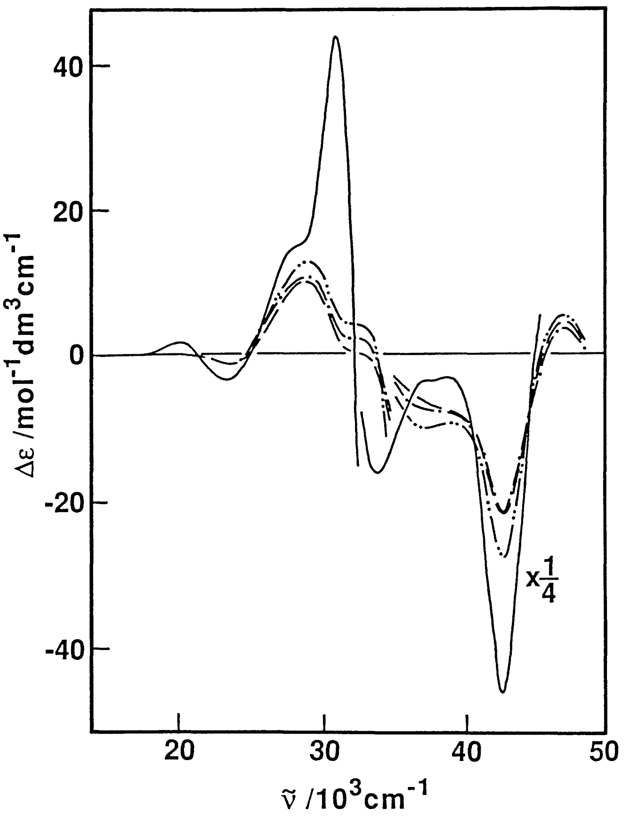


Fig. 3. CD spectra of [TiCl(sal-(RR)-chxn)]$_2$O in dichloromethane (——), methanol (— —), ethanol (— · —), and 1-propanol (—‥—).

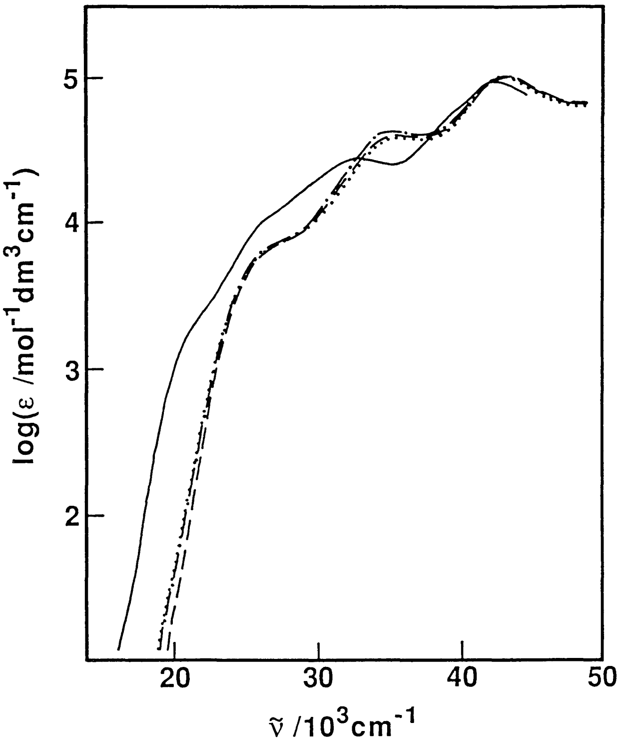


Fig. 2. Absorption spectra of [TiCl(sal-(RR)-chxn)]$_2$O in dichloromethane (——), methanol (— —), ethanol (— · —), and 1-propanol (······).

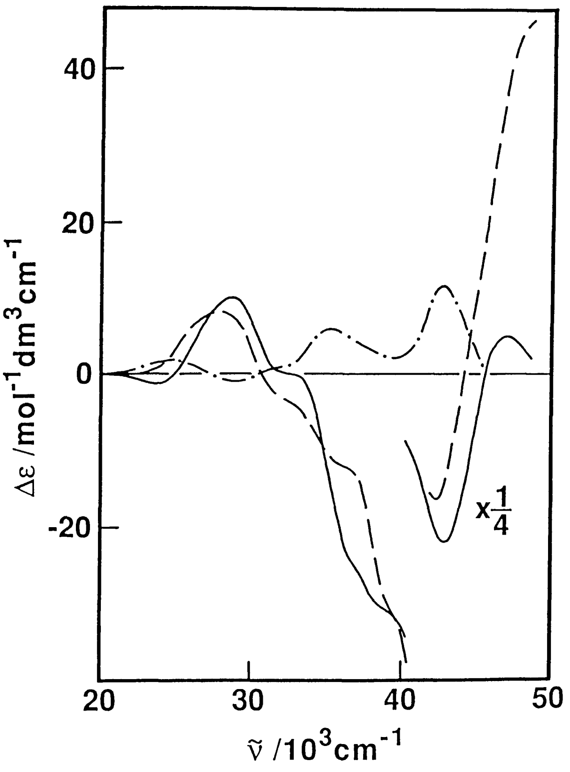


Fig. 4. CD spectra of [TiCl(SB)]$_2$O in methanol, SB=sal-(RR)-chxn (——), sal-(RR)-stien (— —), and sal-(R)-pn (— · —).

Table 1. Rates of Oxidation of Methyl Phenyl Sulfide by 1-Methyl-1-phenylethyl Hydroperoxide in Methanol at 40 °C

$[\mathrm{Cat}]_0/\mathrm{M}^{\mathrm{b)}}$	$[\mathrm{RO_2H}]_0/\mathrm{M}$	$k_{1(\mathrm{obs})}/\mathrm{s}^{-1\,\mathrm{c)}}$	$k_{2(\mathrm{obs})}{}^{\mathrm{d)}}$ $\mathrm{M^{-1}\,s^{-1}}$	$k_{2(\mathrm{obs})}-k_{2(\mathrm{uncat})}$ $\mathrm{M^{-1}\,s^{-1}}$	$k_{3(\mathrm{cat})}{}^{\mathrm{e)}}$ $\mathrm{M^{-2}\,s^{-1}}$
7.5×10^{-3}	0.75	2.34×10^{-4}	3.12×10^{-4}	2.92×10^{-4}	3.9×10^{-2}
7.5×10^{-3}	1.5	5.17×10^{-4}	3.45×10^{-4}	3.25×10^{-4}	4.3×10^{-2}
7.5×10^{-3}	2.25	8.36×10^{-4}	3.71×10^{-4}	3.51×10^{-4}	4.7×10^{-2}
3.75×10^{-3}	0.75	1.09×10^{-4}	1.45×10^{-4}	1.25×10^{-4}	3.3×10^{-2}
1.88×10^{-2}	0.75	5.14×10^{-4}	6.86×10^{-4}	6.66×10^{-4}	3.6×10^{-2}
3.75×10^{-2}	0.75	9.92×10^{-4}	1.32×10^{-3}	1.30×10^{-3}	3.5×10^{-2}

$[\mathrm{Cat}]_0/\mathrm{M}^{\mathrm{b)}}$	$[\mathrm{RO_2H}]_0/\mathrm{M}$	$k_{1(\mathrm{uncat})}=k_{1(\mathrm{obs})}{}^{\mathrm{c)}}$	$k_{2(\mathrm{uncat})}{}^{\mathrm{d)}}$ $\mathrm{M^{-1}\,s^{-1}}$
0	0.75	1.47×10^{-5}	1.96×10^{-5}

a) In all runs $[\mathrm{S}]_0$ was 7.5×10^{-2} M. b) $[\mathrm{Cat}]_0$ denotes the initial concentration of the titanium(IV) complex catalyst calculated as the mononuclear species. c) $k_{1(\mathrm{obs})}$ and $k_{1(\mathrm{uncat})}$ were obtained from the slope of the plot of $\log([\mathrm{S}]_t/[\mathrm{S}]_0)$ vs. time. d) $k_{2(\mathrm{obs})}$ and $k_{2(\mathrm{uncat})}$ were estimated as $k_{1(\mathrm{obs})}/[\mathrm{RO_2H}]_0$ and $k_{1(\mathrm{uncat})}/[\mathrm{RO_2H}]_0$, respectively. e) $k_{3(\mathrm{cat})}$ was estimated as $(k_{2(\mathrm{obs})}-k_{2(\mathrm{uncat})})/[\mathrm{Cat}]_0$.

dichloromethane is quite different from those in alcohols. Figure 4 compares the CD spectra of the titanium(IV) complexes of sal-(*RR*)-chxn, sal-(*RR*)-stien, and sal-(*R*)-pn in methanol. The sal-(*RR*)-stien complex has a CD spectrum similar to that of the sal-(*RR*)-chxn complex. The central chelate ring of sal-(*RR*)-chxn is locked in a λ gauche conformation. The similarity in CD spectra between the two complexes, sal-(*R*)-stien and sal-(*RR*)-chxn, suggests that the sal-(*RR*)-stien complex also takes a λ gauche conformation. Examination of a molecular model indicates that the steric interaction between the phenyl groups and the axial ligands is very severe in the sal-(*RR*)-stien complex when the phenyl groups take axial positions, and the chelate should take the λ form stereoselectively. The CD spectral pattern of the sal-(*R*)-pn complex is almost a mirror image of the others, despite the fact that all parent diamines have the same absolute configuration. The intensity of the sal-(*R*)-pn complex is small compared with the others. Probably the greater part of the sal-(*R*)-pn complex in methanol takes a δ gauche conformation to reduce the steric interaction between the hydrogen on the azomethine carbon and the pn methyl group; the complex will be in an equilibrium mixture of the conformational isomers (δ and λ) with a small preference of the δ form. Similar relationships among the CD spectra have been reported for the corresponding oxovanadium(IV) complexes, VO(sal-(*SS*)-chxn), VO(sal-(*SS*)-stien), and VO(sal-(*S*)-pn).[16)]

Oxidation of Methyl Phenyl Sulfide. The $[\mathrm{TiCl(SB)}]_2\mathrm{O}$ complexes catalyze the oxidation of methyl phenyl sulfide by organic hydroperoxides. Since organic hydroperoxides themselves oxidize sulfides in the absence of any added catalyst, the entire oxidation process must be the result of two independent pathways, catalyzed and uncatalyzed. Uncatalyzed oxidation is known to be first order both in the sulfide concentration ([S]) and in the hydroperoxide concentration ($[\mathrm{RO_2H}]$), $R=k_{2(\mathrm{uncat})}[\mathrm{S}][\mathrm{RO_2H}]$.[17)] In the absence of the complex catalyst, the oxidation of methyl phenyl sulfide by 1-methyl-1-phenylethyl hydroperoxide (CHP) was performed in methanol at 40 °C with the hydroperoxide in large excess over the sulfide. Pseudo-first-order behavior was observed, and the second-order rate constant ($k_{2(\mathrm{uncat})}$) for the uncatalyzed oxidation was calculated as $k_{1(\mathrm{uncat})}/[\mathrm{RO_2H}]_0$; the result is given in Table 1.

In the presence of a complex catalyst, the rate law can be written as

$$-\mathrm{d}[\mathrm{S}]/\mathrm{d}t=k_{2(\mathrm{uncat})}[\mathrm{S}][\mathrm{RO_2H}]+k_{3(\mathrm{cat})}[\mathrm{Cat}]^p[\mathrm{RO_2H}]^q[\mathrm{S}]^r. \quad (1)$$

The first term on the right represents the uncatalyzed oxidation, while the second term the catalyzed one. Figure 5(a) shows the reaction profile for the oxidation of methyl phenyl sulfide (7.5×10^{-2} M, 1 M=1 mol dm^{-3}) with large excess CHP (7.5×10^{-1} M) in methanol in the presence of $[\mathrm{TiCl(sal\text{-}(}RR\mathrm{)\text{-}chxn)}]_2\mathrm{O}$ (3.75×10^{-3} M) at 40 °C. The formation of the sulfone and the decomposition of the catalyst were negligibly small during the reaction. A plot of $\log([\mathrm{S}]_t/[\mathrm{S}]_0)$ vs. time gave a straight line for at least three half-lives (Fig. 5(b)); the pseudo-first-order rate constant ($k_{1(\mathrm{obs})}$) is given in Table 1. Table 1 also shows that at reasonable catalyst concentrations the complex-catalyzed reaction proceeds much faster than does uncatalyzed oxidation. In order to determine the order in CHP, we studied the oxidation with different $[\mathrm{RO_2H}]_0$. The data in Table 1 suggest that $q=1$. Thus, Eq. 1 reduces to Eq. 2 under the conditions given in Table 1.

$$\begin{aligned}-\mathrm{d}[\mathrm{S}]/\mathrm{d}t&=(k_{2(\mathrm{uncat})}+k_{3(\mathrm{cat})}[\mathrm{Cat}]^p)[\mathrm{RO_2H}][\mathrm{S}]\\&=k_{2(\mathrm{obs})}[\mathrm{RO_2H}][\mathrm{S}]\\&=k_{1(\mathrm{obs})}[\mathrm{S}] \qquad (2)\end{aligned}$$

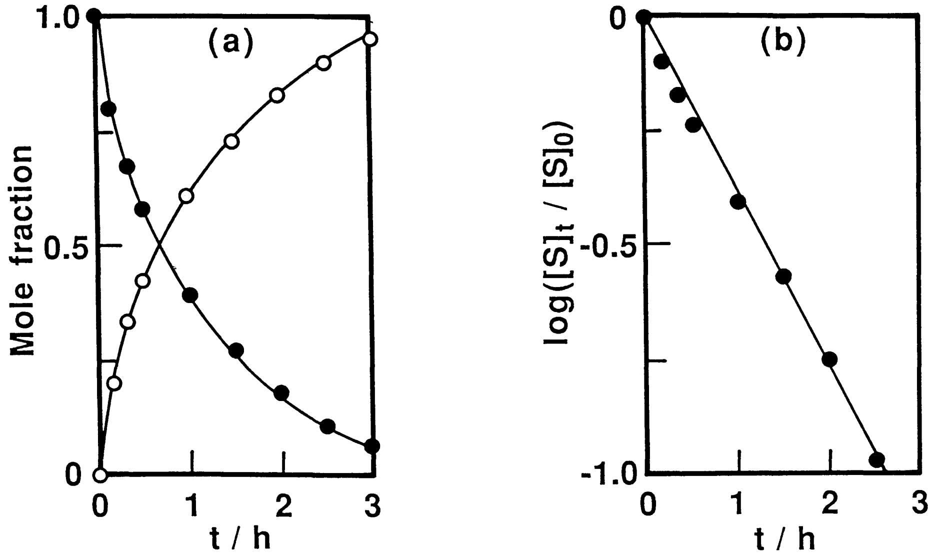


Fig. 5. Oxidation of methyl phenyl sulfide (7.5×10^{-2} M) by 1-methyl-1-phenylethyl hydroperoxide (7.5×10^{-1} M) with the [TiCl(sal-(*RR*)-chxn)]$_2$O (3.75×10^{-3} M) catalyst in methanol at 40 °C. (a) Reaction profile: ●, sulfide; ○, sulfoxide, and (b) the plot of $\log([S]_t/[S]_0)$ vs. reaction time. [S]=sulfide concentration.

At constant CHP and MeSPh initial concentrations, the rates increase upon increasing the catalyst concentration (Table 1). A $\log(k_{2(\mathrm{obs})}-k_{2(\mathrm{uncat})})$-$\log[\mathrm{Cat}]_0$ plot gives a slope of 0.95, indicating that the order in the catalyst is unity ($p=1$). Hence, the catalytic third-order rate constant, $k_{3(\mathrm{cat})}=(k_{2(\mathrm{obs})}-k_{2(\mathrm{uncat})})/[\mathrm{Cat}]$, could be estimated to be 3.9×10^{-2} M^{-2} s^{-1}. The first-order dependence on sulfide, hydroperoxide, and titanium catalyst implies that one molecule of each reactant is involved in the transition state of the rate-determining step. Since the probability of a trimolecular collision would be extremely small, two of the components must have interacted at a prior stage. Neither the addition of CHP nor methyl phenyl sulfide in moderate excess had any effect on the absorption and CD spectra of [TiCl(sal-(*RR*)-chxn)]$_2$O. However, an appreciable CD change was observed upon the addition of a large excess of dibutyl sulfide, which is considered to be a stronger ligand than methyl phenyl sulfide. Coordination of sulfides to Ti(IV) is not an unlikely process, and various titanium complexes with sulfide ligands have been identified.[18,19] We therefore suggest that the mechanism of oxidation involves an external attack by CHP on the coordinated sulfide, as proposed by Colombo et al.[20]

Several optically active Schiff base-titanium(IV) complex catalysts, solvents, and peroxides were used for the asymmetric oxidation of methyl phenyl sulfide; the results are given in Table 2.

Among the four organic hydroperoxides that we used, triphenylmethyl hydroperoxide (THP) gave higher ee's than did the others; the results may be associated with a steric effect of the phenyl groups in THP. In asymmetric catalytic reactions the importance of the orientation of the phenyl groups has been pointed out.[21,22] Recently, it has been reported that a similar oxidation of MeSPh with H_2O_2 catalyzed by titanium(IV) complexes containing optically active Schiff base ligands, such as sal-(*SS*)-chxn, led to low ee's (<20%) of the sulfoxide, the structures of the complexes being not described clearly.[20] The low ee's may result from the use of H_2O_2 in EtOH-H_2O.

Lowering of the temperature results in an enhancement in the enantioselectivity. However, as the temperature is lowered the reactivity decreases, and it takes an extremely long reaction time to oxidize the sulfide below 0 °C. We thus studied most of the oxidation at 0 °C by THP.

The ee shows a remarkable solvent dependence (Table 2); enantioselectivity decreases in the order MeOH>CH_2Cl_2>EtOH>PrOH in the oxidation of MeSPh by THP with the [TiCl(sal-(*RR*)-chxn)]$_2$O catalyst. The results may be partly attributed to a difference in the structure of the complex catalyst in solution. The complex has a dinuclear structure in CH_2Cl_2, while in alcohols it breaks up into a mononuclear species (vide supra). The difference in ee among the alcohols seems to be related to the different reactivities of the catalyst. For example, the oxidation of the sulfide in MeOH for 19 h and in EtOH for 110 h gave the sulfoxide in 73% (58% ee, Entry 6) and 61% (18% ee, Entry 18), respectively, while the same reaction in PrOH took as long as 240 h to yield the sulfoxide in 74% (ca. 0% ee, Entry 19). The oxidation of the sulfide is the result of the catalyzed and uncatalyzed pathways, and chiral discrimination occurs only

Table 2. Asymmetric Oxidation of Methyl Phenyl Sulfide to the Sulfoxide Catalyzed by the Titanium(IV) Complexes

Entry	Peroxide[a]	[TiCl(SB)]$_2$O SB	[Ti]:[O]:[S][b]	Solvent	Temp/°C	Time/h	Yield/%[c]	ee/%[d] (config.)
1	THP	sal-(*RR*)-chxn	0.25:20:10	MeOH	0	15	58	43 (*R*)
2	THP	sal-(*RR*)-chxn	0.25:20:10	MeOH	0	70	81[e]	46 (*R*)
3	THP	sal-(*RR*)-chxn	0.5:20:10	MeOH	0	14	75	56 (*R*)
4	THP	sal-(*RR*)-chxn	0.5:20:10	MeOH	0	70	54[f]	58 (*R*)
5	THP	sal-(*RR*)-chxn	1:20:10	MeOH	0	15	98	62 (*R*)
6	THP	sal-(*RR*)-chxn	1:11:10	MeOH	0	19	73	58 (*R*)
7	THP	sal-(*RR*)-chxn	1:11:10	MeOH	0	44	98	61 (*R*)
8	THP	sal-(*RR*)-chxn	2:11:10	MeOH	0	16	89	63 (*R*)
9	THP	sal-(*RR*)-chxn	4:11:10	MeOH	0	1.5	42	58 (*R*)
10	THP	sal-(*RR*)-chxn	4:11:10	MeOH	0	3	59	60 (*R*)
11	THP	sal-(*RR*)-chxn	4:11:10	MeOH	0	7	77	62 (*R*)
12	THP	sal-(*RR*)-chxn	4:11:10	MeOH	0	9	84	58 (*R*)
13	THP	sal-(*RR*)-chxn	4:11:10	MeOH	0	15	95[g]	61 (*R*)
14	THP	sal-(*RR*)-chxn	1:10:10	MeOH	40	20	86[h]	22 (*R*)
15	THP	sal-(*RR*)-chxn	1:10:10	MeOH	20	70	86[h]	48 (*R*)
16	THP	sal-(*RR*)-chxn	1:10:10	CH_2Cl_2	20	64	60[h]	12 (*R*)
17	THP	sal-(*RR*)-chxn	1:10:10	CH_2Cl_2	0	170	46[h]	26 (*R*)
18	THP	sal-(*RR*)-chxn	1:10:10	EtOH	0	110	61[h]	18 (*R*)
19	THP	sal-(*RR*)-chxn	1:10:10	PrOH	0	240	74[h]	ca. 0
20	TBHP	sal-(*RR*)-chxn	1:10:10	CH_2Cl_2	0	144	61[h]	8 (*R*)
21	TMBHP	sal-(*RR*)-chxn	1:10:10	CH_2Cl_2	0	141	68[h]	12 (*R*)
22	CHP	sal-(*RR*)-chxn	1:10:10	CH_2Cl_2	0	170	32[h]	19 (*R*)
23	THP	sal-(*RR*)-stien	0.2:10:10	MeOH	0	71	95[h]	14 (*R*)
24	THP	sal-(*R*)-pn	0.2:10:10	MeOH	0	65	83[h]	9 (*S*)
25	THP	—	0:11:10	MeOH	0	19	16	—
26	THP	—	0:11:10	MeOH	0	46	38	—
27	THP	—	0:20:10	MeOH	0	15	30	—
28	THP	—	0:20:10	MeOH	0	70	66	—

a) Peroxide: THP, triphenylmethyl hydroperoxide; TBHP, *t*-butyl hydroperoxide; TMBHP, 1,1,3,3-tetramethylbutyl hydroperoxide; CHP, 1-methyl-1-phenylethyl hydroperoxide. b) [Ti]:[O]:[S] denotes molar ratio of [TiCl(SB)]$_2$O (calculated as the mononuclear species): organic hydroperoxide: methyl phenyl sulfide (8.0×10^{-2} M). c) Analyzed by high-performance liquid chromatography unless otherwise stated. d) Based on the CD spectral data or the optical rotation of the pure enantiomer (see Experimental). e) In addition there is 12% sulfone. f) In addition there is 36% sulfone. g) In addition there is 5% sulfone. h) Isolated yield, based on the sulfide.

in the former. Hence, the ee becomes lower as the reactivity of the catalyst decreases. The greater part of the oxidation in PrOH may result from the uncatalyzed process. The solvent plays an important role in the present catalyzed reaction. Entries 25—28 show that the uncatalyzed oxidation of the sulfide with THP proceeds rather fast, even in MeOH; we therefore carried out the oxidation with different catalyst concentrations in order to estimate the contribution of the uncatalyzed pathway to the entire oxidation. At reasonably high catalyst concentrations, $[Ti]/[S]>0.05$, the ee stayed almost constant (ca. 60% ee), suggesting that the catalyzed process dominates the uncatalyzed one under these conditions. The ee did not change appreciably during the oxidation.

The complex catalysts containing an (*RR*)-chxn moiety or an (*RR*)-stien moiety gave the (*R*)-sulfoxide, while that containing an (*R*)-pn moiety gave the (*S*)-sulfoxide (Entry 24). These results can be understood if we assume that the catalytically active species has a conformational chirality similar to that of the added complex. As described before, the central chelate rings of the sal-(*RR*)-chxn and sal-(*RR*)-stien complexes take a λ gauche conformation. On the other hand, [TiCl(sal-(*R*)-pn)]$_2$O in solution is suggested to be an equilibrium mixture of the conformational isomers (δ and λ) with a small preference of the δ form. Such a difference in conformational chirality among the complexes should be responsible for the enantioselectivity. It should be noted that oxovanadium(IV) complex catalysts give the antipode in a similar oxidation; for example, VO(sal-(*RR*)-chxn) gives the (*S*)-sulfoxide. Although the reason is not clear it may be related to a difference in mechanism between the two systems. As described above, we suggested coordination of sulfur to titanium prior to oxidation. Prochiral sulfides become chiral upon coordination, and chiral induction occurs at this stage. On the other hand, in a similar reaction with the VO(SB) complex catalyst, the catalytically active species was suggested to be a vanadium peroxide complex and the activated peroxide will oxidize sulfides.[4]

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References

1) For example, G. Solladié, *Synthesis,* **1981**, 185.

2) P. Pitchen and H. B. Kagan, *Tetrahedron Lett.,* **1984**, 1049; P. Pitchen, M. Deshmukh, E. Duñach, and H. B. Kagan, *J. Am. Chem. Soc.,* **106**, 8188 (1984); H. B. Kagan, E. Duñach, C. Nemecek, P. Pitchen, O. Samuel, and S. Zhao, *Pure Appl. Chem.,* **57**, 1911 (1985); E. Duñach and H. B. Kagan, *Nouv. J. Chim.,* **9**, 1 (1985); S. H. Zhao, O. Samuel, and H. B. Kagan, *Tetrahedron,* **43**, 5135 (1987).

3) F. Di Furia, G. Modena, and R. Seraglia, *Synthesis,* **1984**, 325.

4) K. Nakajima, K. Kojima, M. Kojima, and J. Fujita, *Bull. Chem. Soc. Jpn.,* **63**, 2620 (1990).

5) K. Nakajima, C. Sasaki, M. Kojima, T. Aoyama, S. Ohba, Y. Saito, and J. Fujita, *Chem. Lett.,* **1987**, 2189.

6) F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Am. Chem. Soc.,* **81**, 290 (1959) and "Shin-Zikken Kagaku Koza," Maruzen, Tokyo (1977), Vol. 8, p. 1429.

7) R. G. Asperger and C. F. Liu, *Inorg. Chem.,* **4**, 1429 (1965).

8) K. Saigo, N. Kubota, S. Takebayashi, and M. Hasegawa, *Bull. Chem. Soc. Jpn.,* **59**, 931 (1986).

9) M. Gullotti, A. Pasini, P. Fantucci, R. Ugo, and R. D. Gillard, *Gazz. Chim. Ital.,* **102**, 855 (1972).

10) J. Jacobus and K. Mislow, *J. Am. Chem. Soc.,* **89**, 5228 (1967).

11) P. Pfeiffer and H. Thielert, *Chem. Ber.,* **71**, 119 (1938).

12) M. Gullotti and A. Pasini, *Inorg. Chim. Acta,* **15**, 129 (1975).

13) T. Aoyama, S. Ohba, Y. Saito, C. Sasaki, M. Kojima, J. Fujita, and K. Nakajima, *Acta Cryst., Sect. C,* **44**, 1309 (1988).

14) M. Mazzanti, J.-M. Rosset, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Chem. Soc., Dalton Trans.,* **1989**, 953.

15) W. J. Geary, *Coord. Chem. Rev.,* **7**, 81 (1971).

16) A. Pasini, M. Gullotti, and R. Ugo, *J. Chem. Soc., Dalton Trans.,* **1977**, 346.

17) G. Modena, *Gazzetta,* **89**, 834 (1959); M. A. P. Dankleff, R. Curci, J. O. Edwards, and H.-Y. Pyun, *J. Am. Chem. Soc.,* **90**, 3209 (1968).

18) O. Bortolini, F. Di Furia, and G. Modena, *J. Mol. Catal.,* **16**, 61 (1983); O. Bortolini, C. Campello, F. Di Furia, and G. Modena, *J. Mol. Catal.,* **14**, 63 (1982).

19) G. W. A. Fowles, D. A. Rice, and J. D. Wilkins, *J. Chem. Soc. A,* **1971**, 1920.

20) A. Colombo, G. Marturano, and A. Pasini, *Gazz. Chim. Ital.,* **116**, 35 (1986).

21) B. Bosnich and N. K. Roberts, *Adv. Chem. Ser.,* **196**, 337 (1982).

22) J. M. Hawkins and K. B. Sharpless, *Tetrahedron Lett.,* **28**, 2825 (1987).