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Insight into the Mechanism of Oxidative Kinetic Resolution of Racemic Secondary Alcohols by Using Manganese(III)(Salen) Complexes as Catalysts

Zhen Li, Zhong H. Tang, Xiao X. Hu, and Chun G. Xia*[a]

Abstract: The oxidative kinetic resolution of various racemic secondary alcohols with $PhI(OAc)_2$ catalyzed by chiral [Mn^{III}(salen)] complexes in the presence of KBr was studied in a water/organic solvent mixture. The dramatic, synergetic effect of additives, organic solvent, and the substituents of chiral salen ligands on the enantioselectivities of the reactions is reported. Results from UV/Vis spectroscopy and ESI-MS studies provide evidence that these reactions are induced by the formation of a high-valent manganese intermediate.

Keywords: alcohols · manganese · mass spectrometry · oxidative kinetic resolution · UV/Vis spectroscopy

Introduction

The oxidation of alcohols to carbonyl compounds is a key transformation in organic chemistry, and has attracted much attention, especially in the search for versatile and selective regents in catalytic reactions.[1] Recently, the oxidizing properties of hypervalent iodine reagents have been of increasing interest, as these species have low toxicity, are readily available, and are easy to handle.[2] Adama found that Cr(salen) complexes were effective catalysts for the oxidation of secondary alcohols to ketones with iodosobenzene (PhI=O) and diacetoxyiodobenzene ($PhI(OAc)_2$) as oxidants,[3] and we also reported [Mn^{III}(salen)] complexes to be effective catalysts for the oxidation of secondary alcohols to ketones in the presence of the co-oxidant $PhI(OAc)_2$.[4] We wanted to extend the scope of this potentially useful reaction to asymmetric catalysis and its application to the oxidative kinetic resolution of secondary alcohols; the kinetic resolution of which has been accomplished through acylation[5,6] and oxidation.[7]

We recently developed a method for the oxidative kinetic resolution of alcohols in water, catalyzed by chiral [Mn(salen)] complexes and the phase-transfer catalyst (PTC) tetraethylammonium bromide, with $PhI(OAc)_2$ as the co-oxidant.[8] Here we report a more efficient and simple method for the enantioselective oxidation of alcohols catalyzed by chiral [Mn(salen)] complexes and either PTC or the inexpensive inorganic salt KBr, with $PhI(OAc)_2$ as co-oxidant. We also elucidated the mechanism of the oxidative kinetic resolution by conducting electrospray ionization mass spectrometry (ESI-MS) and UV-visible spectroscopy.

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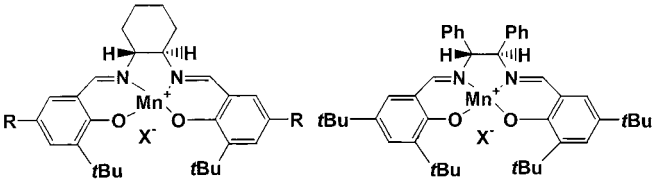
Results and Discussion

Effect of additive: To explore the effect of cation and haloid anion we performed an additive screen using the [Mn^{III}(salen)] complex **1a** (the highly enantioselective epoxidation Jacobsen catalyst[9]) as catalyst and α-methylbenzyl alcohol as a model test substrate.



1a: R=*t*Bu, X=Cl
1b: R=*t*Bu, X=Br
1c: R=*t*Bu, X=OAc^-
1d: R=*t*Bu, X=PF_6^-
2: R=Me, X=PF_6^-

3a: X=Cl
3b: X=PF_6^-

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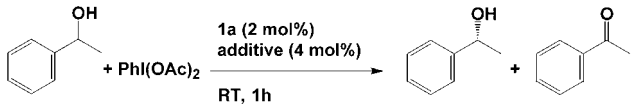
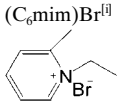
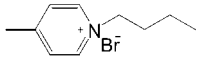
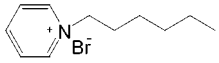
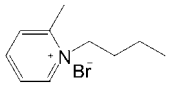
Table 1. Screen with various additives.[a]



Entry	Additive	Conversion [%][b]	*ee* [%][c]	k_{rel}[d]
1	–	12.0	0	1
2	$N(CH_3)_4Br$	65.0	>99	>15.6
3	$N(C_2H_5)_4Br$	63.2	>99	>18.0
4	$N(C_4H_9)_4Br$	62.0	53.7	3.2
5	CTAB[f]	41.5	15.4	1.8
6	$(C_2mim)Br$[g]	57.4	92.9	17.9
7	$(C_4mim)Br$[h]	56.6	92.9	19.6
8	$(C_6mim)Br$[i]	11.6	3.3	1.7
9		62.2	94.1	12.3
10		68.5	99.9	17.4
11		62.1	99.9	28.4
12		59.1	93.0	15.0
13	NaBr	58.5	95.7	19.3
14	LiBr	73.4	92.0	5.7
15	KBr	64.0	96.0	12.2
16[e]	KBr	62.8	95.9	13.2
17	KCl	9.0	0	1
18	KI	9.9	0.93	1.2

[a] Reactions performed at room temperature with Jacobsen catalyst (2 mol%), additive (4 mol%), substrate (0.25 mmol), $PhI(OAc)_2$ (0.175 mmol), and H_2O/CH_2Cl_2 (1 mL/0.5 mL). [b] Determined by performing GC analysis using an internal standard. [c] Determined by performing GC analysis using a CP-Chirasil-Dex CB capillary column. [d] $k_{rel}=\ln[(1-C)(1-ee)]/\ln[(1-C)(1+ee)]$. [e] After 30 min. [f] Hexadecyltrimethylammonium bromide. [g] 1-ethyl-3-methylimidazolium. [h] 1-butyl-3-methylimidazolium. [i] 1-hexyl-3-methylimidazolium.

As shown in Table 1, in the absence of additive, the (*R, R*) Jacobsen catalyst is inactive in the resolution of α-methylbenzyl alcohol (Table 1, entry 1). The addition of bromide salts leads to a substantial increase in enantioselective activity (Table 1, entries 2, 3, 6, 7, 9–11). The most dramatic effect was observed upon addition of the inexpensive inorganic salt KBr (4 mol%); 99.9% *ee* was obtained in just 0.5 h.

In this system, it is unclear if bromide is acting as a counterion in the catalyst. To investigate this, [Mn^{III}(salen)Br] **1b** was added to the standard reaction conditions in the absence of KBr. Consequently, a surprisingly low level of catalysis was observed (Table 2, entry 1). However, upon addition of KBr (4 mol%), catalytic activity was re-established and good conversion and *ee* values were obtained (Table 2, entry 2). This data suggests that KBr is necessary for oxidation, and that the bromide ion does not coordinate to the manganese atom.

We also investigated the relationship between conversion, *ee*, the selectivity factor k_{rel}, and reaction time, in the kinetic resolution of α-methylbenzyl alcohol. Figure 1 reveals that, although the highest conversion and *ee* values were obtained after ten minutes, k_{rel} remained at a value of around 15 during the course of reaction.

Table 2. Oxidative kinetic resolution of α-methylbenzyl alcohol with various [Mn^{III}(salen)] complexes[a]

Entry	Catalyst	Conversion [%][b]	*ee* [%][c]	k_{rel}[d]
1[e]	**1b**	18.7	0	1
2	**1b**	63.0	99.8	23.9
3	**1c**	68.0	99.9	23.2
4	**1d**	68.4	29.1	2.0
5	**2**	33.2	2.8	1.1
6	**3a**	66.1	81.2	5.6
7	**3b**	57.5	30.8	2.1

[a] Reaction conditions as in Table 1. [b] Determined by performing GC analysis using an internal standard. [c] Determined by performing GC using a CP-Chirasil-Dex CB capillary column. [d] $k_{rel}=\ln[(1-C)(1-ee)]/\ln[(1-C)(1+ee)]$. [e] In the absence of KBr.

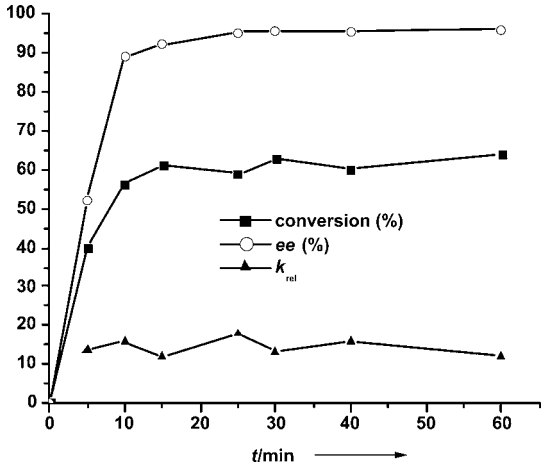


Figure 1. Plot of conversion, *ee*, and k_{rel} versus reaction time for the oxidative kinetic resolution of α-methylbenzyl alcohol.

Effect of counterion: Use of the manganese(III)(salen) complex with a nonligating counterion, such as PF_6^- (**1d**), yielded a conversion of 68.4% and a low k_{rel} value of only 2. Species **1c**, which has OAc^- as a counterion, also resolved effectively; a conversion of 68.0%, an *ee* value of 99.9%, and a k_{rel} of 23.2 were observed (Table 2, entry 3). Substitution of the *tert*-butyl groups at the 5,5′-positions of the Jacobsen catalyst **1a** by methyl substituents (**2**) resulted in low conversion and enantioselectivity (Table 2, entry 5). This indicates that the steric hindrance at the 5,5′-positions was favourable for the catalytic activity of the [Mn^{III}(salen)] complex. Complex **3b**, derived from (*R, R*)-diphenylethylenediamine, displayed an activity similar to complex **1d**; however, in the case of Cl^- as a counterion (**3a**), a moderate result was obtained (Table 2 entry 6).

Effect of organic solvents: Before turning to other substrates, attempts were made to improve the process and to make it more general. The oxidative kinetic resolution of α-methylbenzyl alcohol catalyzed by **1a** (2 mol%) and $PhI(OAc)_2$ with KBr (4 mol%) was studied by using a varie-

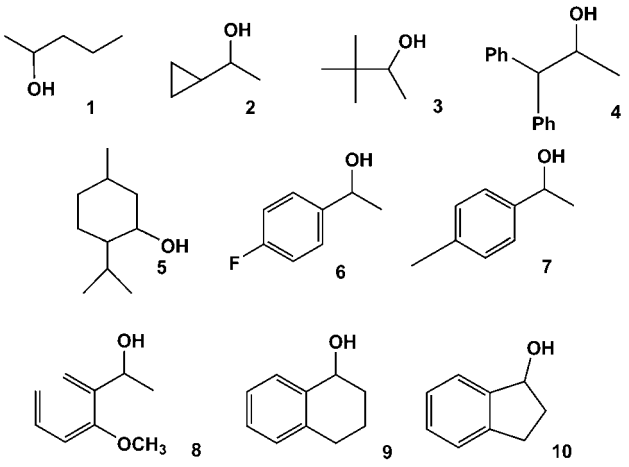
Table 3. The effect of organic solvent on oxidative kinetic resolution.[a]

Entry	Solvent system	Conversion [%][b]	*ee* [%][c]	k_{rel}[d]
1	H_2O/hexane	64.5	99.3	17.3
2	H_2O/toluene	61.6	99.9	29.7
3	H_2O/acetone	53.0	91.6	30.8
4	H_2O/1,4-dioxane	55.8	91.1	19.2
5	H_2O/CH_2Cl_2	64.0	96.0	12.2
6	H_2O/DCE	69.0	99.2	12.4
7	H_2O/MeCN	43.2	1.4	1.05
8	H_2O/$CHCl_3$	68.4	79.5	4.8
9	H_2O/ethyl acetate	41.3	19.7	2.1
10	H_2O/DMF	59.2	20.3	1.6
11	H_2O/THF	54.6	52.9	4.1
12	H_2O/*t*BuOH	–[e]	–	–

[a] Reactions performed at room temperature with catalyst (2 mol%), KBr (4 mol%), substrate (0.25 mmol), $PhI(OAc)_2$ (0.175 mmol), and H_2O/organic solvent (1 mL/0.5 mL). [b] Determined by performing GC analysis using an internal standard. [c] Determined by performing GC analysis using a CP-Chirasil-Dex CB capillary column. [d] $k_{rel} = \ln[(1-C)(1-ee)]/\ln[(1-C)(1+ee)]$. [e] No oxidation.

ty of organic solvents. As shown in Table 3, the k_{rel} of the reaction depends strongly upon the organic solvent used. In the case of H_2O mixed with less polar solvents, the oxidative kinetic resolution reaction exhibited moderate to high enantioselectivity (*ee* of >90%) (Table 3). No reaction was observed when the protic solvent *t*BuOH was used. Dipolar aprotic solvents, including MeCN, $CHCl_3$, ethyl acetate, DMF, and THF, gave low k_{rel} values (Table 3, entries 7–11).

Effect of substrates: The scope of the oxidative kinetic resolution of some other *rac*-secondary alcohols was explored by using KBr (4 mol%) as an additive together with **1a** (2 mol%) (Table 4).



Notably, most of the examples produced enantiomeric excesses of over 99%. Interestingly, H_2O/hexane is the best solvent system for the asymmetric oxidation of aliphatic racemic *sec*-alcohols, such as (±)-**1**, (±)-**3**, (±)-**4**, and (±)-**5** (DL-menthol), and resulted in the kinetic resolution of these substrates with extremely high enantioselectivity. On the other hand, hexane and toluene are not applicable to (±)-**2**. Aryl-substituted alcohols are generally good substrates under these modified conditions, in which the optimal solvent is dependent on the substrate. Substrates with a large substituent group at the *ortho* site undergo relatively poor oxidation and kinetic resolution (Table 4, entries 19–21). This observation is in line with the view that the difference in size of the substituents plays a significant role in the overall efficiency of the kinetic resolution.

To verify the efficiency of catalyst **1a** in the kinetic resolution of α-methylbenzyl alcohol, analysis was performed on a 1:500 molar ratio of catalyst/

Table 4. Data for the kinetic resolution of *rac*-secondary alcohols by the **1a**/$PhI(OAc)_2$/KBr system[a]

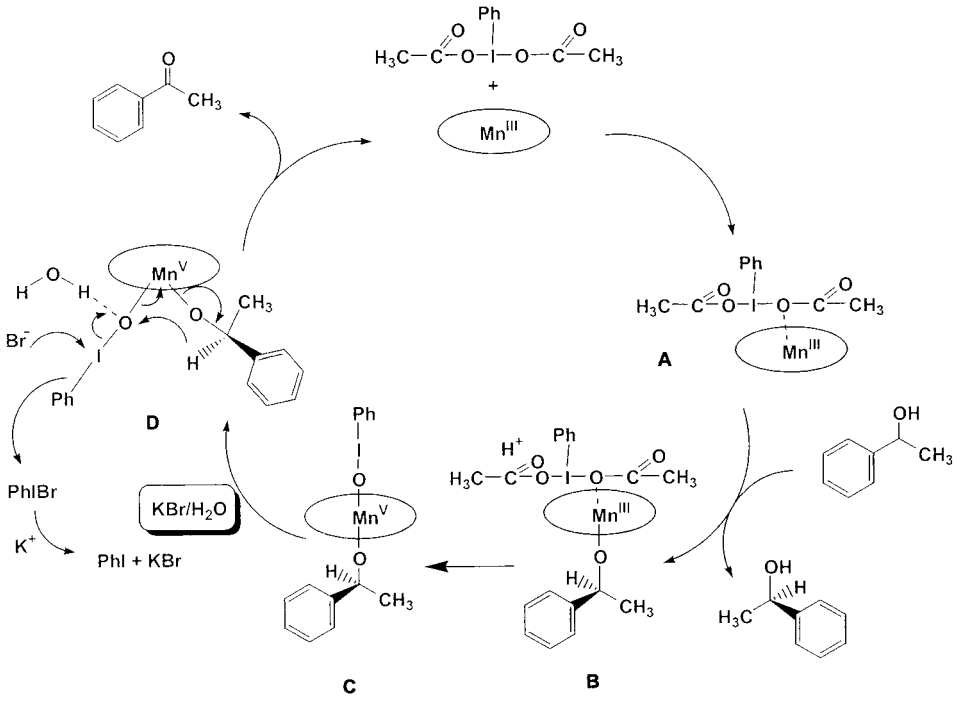
Entry	Substrate	Solvent	Conversion [%][b]	*ee* [%][c]	k_{rel}[d]
1	(±)-**1**	H_2O/CH_2Cl_2	66.1	95.3	10.0
2		H_2O/hexane	66.4	>99.0	>14.2
3		H_2O/toluene	29.7	21.7	3.8
4[e]	(±)-**2**	H_2O/CH_2Cl_2	55.1	91.2	21.2
5	(±)-**3**	H_2O/CH_2Cl_2	69.2	>99.9	>16.7
6		H_2O/hexane	53.4	>99.9	>108
7	(±)-**4**	H_2O/CH_2Cl_2	60.6	>99.9[g]	>32.8
8		H_2O/hexane	55.1	>99.9[g]	>71.3
9		H_2O/toluene	59.5	>99.9[g]	>37.0
10	(±)-**5**[i]	H_2O/CH_2Cl_2	50.4	93.5	83.6
11		H_2O/hexane	50.8	>99.9	>458.0
12		H_2O/toluene	58.8	>99.9	>40.2
13	(±)-**6**	H_2O/CH_2Cl_2	72.2	96.7	7.8
14		H_2O/hexane	67.3	99.5	15.0
15		H_2O/toluene	69.6	99.9	16.3
16[e]	(±)-**7**	H_2O/CH_2Cl_2	61.3	92.5	12.0
17[e]		H_2O/hexane	57.1	74.3	7.6
18[e]		H_2O/toluene	62.5	97.7	15.9
19[f]	(±)-**8**	H_2O/CH_2Cl_2	8.2	–	–
20		H_2O/hexane	14.0	–	–
21		H_2O/toluene	31.2	–	–
22	(±)-**9**	H_2O/CH_2Cl_2	63.4	97.8	14.9
23[e]		H_2O/hexane	56.6	>99.9	>54.5
24		H_2O/toluene	70.2	99.9	15.7
25	(±)-**10**	H_2O/CH_2Cl_2	52.2	99.5[h]	127.1
26		H_2O/hexane	68.9	99.4[h]	13.1
27		H_2O/toluene	71.6	99.6[h]	11.9

[a] Reactions were performed at room temperature with catalyst (2 mol%), KBr (4 mol%), substrate (0.25 mmol), $PhI(OAc)_2$ (0.175 mmol), H_2O/organic solvent (2:1, v/v), for 1 h. [b] Determined by performing GC analysis using decane as an internal standard. [c] Determined by performing GC analysis using a CP-Chirasil-Dex CB capillary column. [d] $k_{rel} = \ln[(1-C)(1-ee)]/\ln[(1-C)(1+ee)]$. [e] After 0.5 h. [f] KBr 8 mol%. [g] Determined by using HPLC with a Chiralcel OJ column (Hex/IPA = 75:25). [h] Determined by using HPLC with a Chiralcel OD-H column (Hex/IPA = 95:5). [i] The remaining alcohol is L-menthol according to the MS spectrum.

substrate. This larger scale reaction required a slightly longer reaction time of 2 h and showed a slight decrease in k_{rel} values (9.8 compared to 12.2) and a reasonable *ee* of 92%.

Reaction mechanism: Kita and co-workers reported the oxidation of alcohols by using iodosobenzene (PhI=O) as a co-oxidant and KBr as a catalyst in water, and thought that PhI=O and KBr formed a reactive intermediate in water [Eq. (1)].[10] Electrospray ionization mass spectrometry (ESI-MS) analysis of the behavior of PhI=O–KBr in aqueous solution suggested that the highly reactive iodine species ($PhIBrO^-$) was formed.[11]

$$PhI{=}O + KBr \xrightarrow{H_2O} PhIBrO^- + K^+ \quad (1)$$



Scheme 1. Possible mechanism of the oxidative kinetic resolution of *sec*-alcohols catalyzed by [Mn^{III}(salen)] complexes and $PhI(OAc)_2$ in the presence of KBr.

This hypervalent iodine(III) species may not, however, be the active intermediate in our reaction system. In fact, the in situ treatment of α-methylbenzyl alcohol and **1a** with $PhIBrO^-$, which had been generated from iodosobenzene diacetate (IBDA) and KBr in water, resulted in zero enantioselectivity. This differs from Kita's conclusion that the formation of $PhIBrO^-$ is very rapid and, once formed, reacts immediately with alcohol. To clarify this discrepancy, we considered a possible mechanism involving a ternary compound, which was generated by combining catalyst, $PhI(OAc)_2$, and substrate.

We assumed that the adduct **A** of complex **1a** with $PhI(OAc)_2$ is formed in the first step, as proposed during the reaction of [(salen)Cr^{III}] with $PhI(OAc)_2$,[12] after which this adduct coordinates with the substrate molecule to form the ternary compound **B**. Subsequent electronic reorganization, with elimination of the $CH_3(O)C^{\bullet}$ radical and an acetate group, generates the high-valent manganese intermediate **C**. This hypothesis was supported by the results of UV-visible and ESI-MS spectroscopic analysis and a possible, plausible reaction mechanism is proposed in Scheme 1.

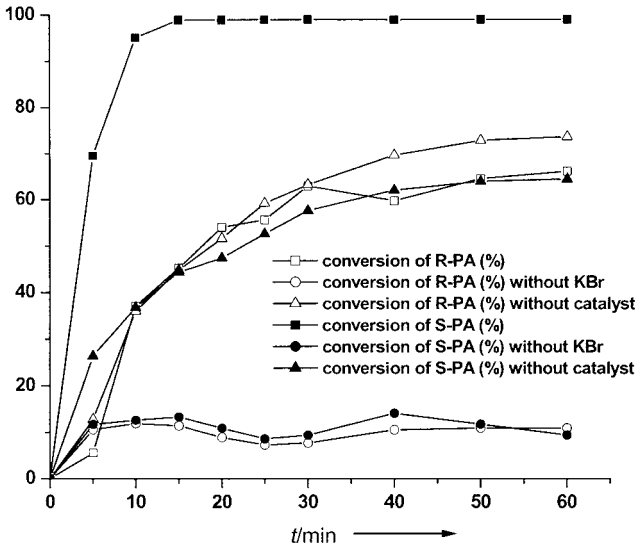


Figure 2. Relationship between the conversion and reaction time under different reaction conditions.

Control experiment: The results of a control experiment with the enantiomerically enriched α-methylbenzyl alcohol showed that the (*S*)-α-methylbenzyl alcohol enantiomer was oxidized preferentially to the ketone by the (*R, R*)-Jacobsen catalyst **1a**, with a conversion of 99.0% in 15 min (Figure 2). In contrast, the (*R*)-α-methylbenzyl alcohol enantiomer exhibited only 45.2% conversion after the same reaction time and 66.0% conversion after 1 h. Reactions performed in the absence of KBr resulted in a poor conversion for both (*R*)- and (*S*)-α-methylbenzyl alcohol, whereas in the absence of catalyst, two enantiomers were transformed to ketone with similar conversions of ~60–70%.

This discrepancy may be explained in terms of thermodynamic or kinetic differences. Initially, as the substrate combines with the catalyst, the binding of the (*S*)-enantiomer is favored, which is in accordance with the observation above that substrates with a bulky group next to the carbonyl carbon atom do not undergo oxidative kinetic resolution

under the present conditions. This suggests that coordination of a hydroxyl group is essential for oxidation and that this occurs within the coordination sphere of the manganese ion.

UV-visible spectroscopy of reaction intermediates: To identify the reactive intermediates in the oxidative kinetic resolution of racemic *sec*-alcohols using **1a**/$PhI(OAc)_2$/KBr, we recorded UV/Vis spectra at room temperature by using toluene as the solvent.

The UV/Vis spectra of **1a** in the presence of substrate are shown in Figure 3. An initial increase in absorbance at 431 nm and a broad band between 600 and 700 nm were observed within 25 min of addition of $PhI(OAc)_2$ to the solution. This indicates that a compound with a broad absorption band of around 600 nm was formed. The spectra changed as the reaction proceeded (Figure 3B). An isosbestic point at 583 nm implies that the initially formed compound is converted to another species, which was assumed to be the high-valent manganese intermediate **C**.

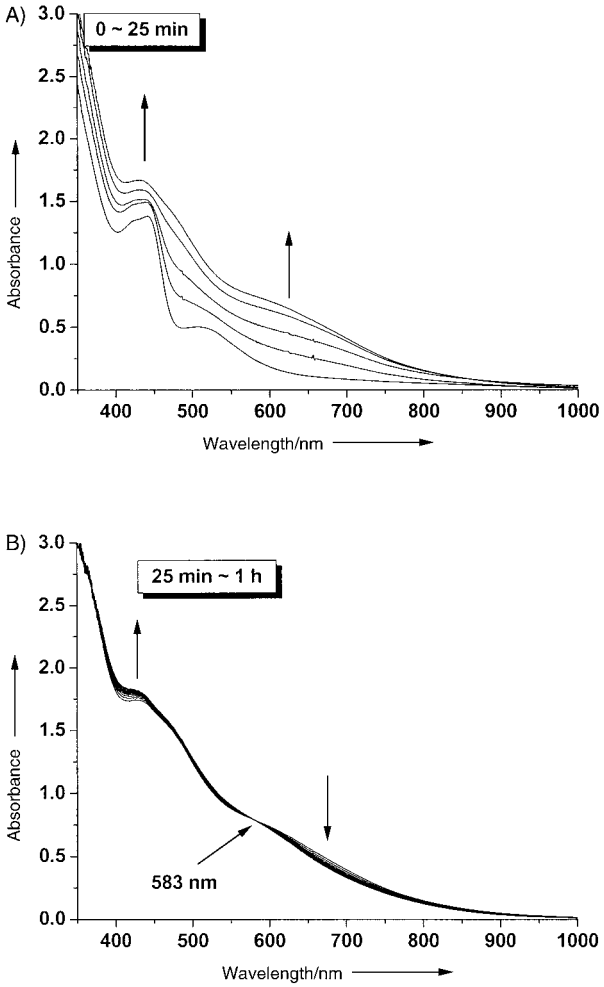


Figure 3. Variation in UV/Vis spectra of **1a**/α-methylbenzyl alcohol/$PhI(OAc)_2$ (molar ratio = 1:6.7:20) in toluene with time.

Figure 4 shows the UV/Vis spectra of the organic phase following the addition of KBr/H_2O to toluene containing complex **1a**, α-methylbenzyl alcohol, and $PhI(OAc)_2$. In contrast to spectrum 2, spectrum 3 shows the decrease in absorbance at about 600 nm. Therefore, it can be concluded that the key step of this kinetic resolution reaction is the attachment of the Br^- ion to the high-valent manganese intermediate **C**.

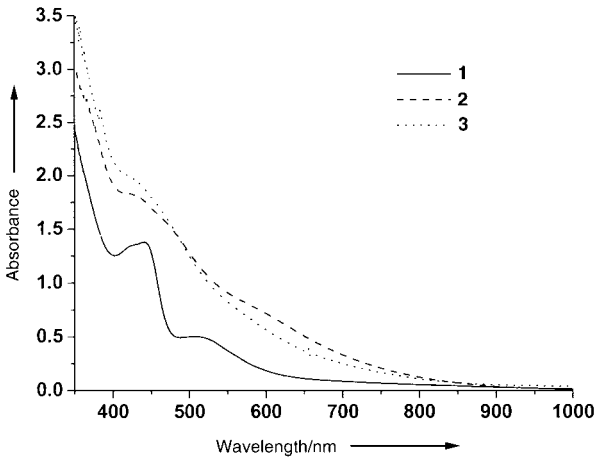


Figure 4. UV/Vis spectra of the organic phase following the addition of KBr/H_2O (1.68×10^{-2} M) to **1a**/α-methylbenzyl alcohol/$PhI(OAc)_2$ (molar ratio = 1:6.7:20) in toluene. Spectrum 1: catalyst **1a**/α-methylbenzyl alcohol; spectrum 2: catalyst **1a**/α-methylbenzyl alcohol/$PhI(OAc)_2$ (after 1 h); spectrum 3: the organic phase following the addition of KBr/H_2O to **1a**/α-methylbenzyl alcohol/$PhI(OAc)_2$ in toluene (after 30 min).

ESI-MS studies of reaction intermediates: The addition of a solution of complex **1a** in toluene to a solution of $PhI(OAc)_2$ in toluene resulted in the disappearance of the molecular ion $[Mn^{III}(salen)]^+$ (m/z: 599.7). Instead, the molecular ions $[O{=}Mn^{V}(salen)(PhIO)]^+$ (m/z: 836.8), $[Mn^{V}(salen)(OPhIOAc)]^+$ (m/z: 878.6), and $[Mn^{III}(salen)\{PhI(OAc)_2\}]^+$ (adduct **A**) (m/z: 921.7) dominated (Figure 5A).

Results of collision-induced dissociation (CID) experiments performed on the solution showed that the $[Mn^{III}(salen)\{PhI(OAc)_2\}]^+$ ion is stable. The fragment ion $[O{=}Mn^{V}(salen)]^+$ (m/z: 615.7) is produced by increasing the cone energy from 10 V to 20 V, which suggests that this ion is a product of the dissociation of $[O{=}Mn^{V}(salen)(PhIO)]^+$ and $[Mn^{V}(salen)(OPhIOAc)]^+$ (Figure 5B).

Addition of α-methylbenzyl alcohol led to the disappearance of the molecular ion $[Mn^{III}(salen)\{PhI(OAc)_2\}]^+$ (m/z: 921.7) and the appearance of a new ion (m/z: 941.6), which was assigned to the $[PhIOMn^{III}(salen)\{OCH(CH_3)Ph\}]^+$ ion **C**, formed from the $[Mn^{III}(salen)\{PhI(OAc)_2\}]^+$ ion (Figure 6A). A solution of KBr in H_2O was then added to the above solution and, after being stirred for 5 min, the organic phase was analyzed by using ESI-MS. The resulting spectrum (Figure 6B) is consistent with the data described above; the catalyst **1a** was recovered and the ion (m/z: 283.6) was assigned to the PhIBr cation.

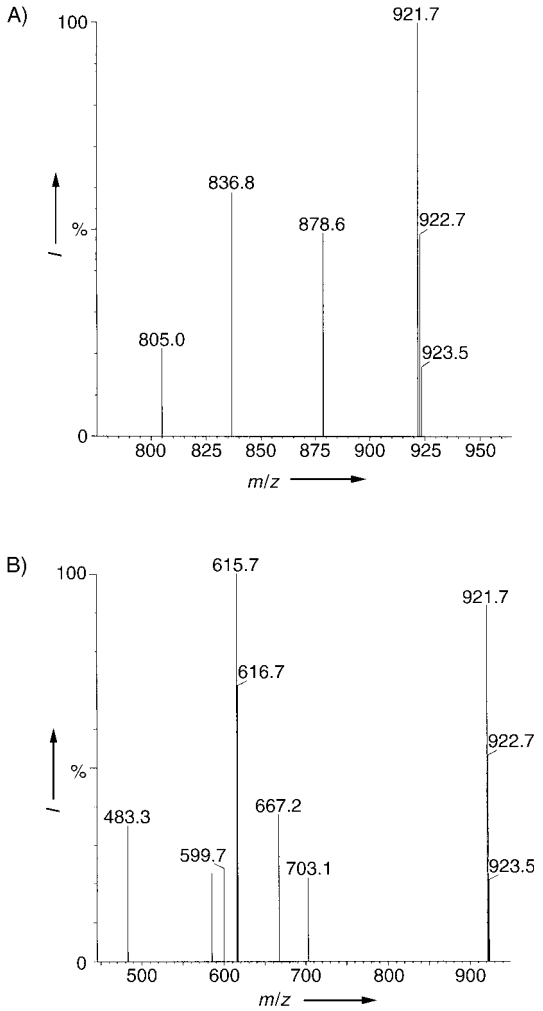


Figure 5. Electrospray ionization mass spectrum of the reaction mixture of **1a** with $PhI(OAc)_2$ in toluene. A) cone voltage 10 V; B) cone voltage 20 V.

Conclusion

We have demonstrated a clean and efficient system for the enantioselective oxidative kinetic resolution of secondary alcohols catalyzed by [Mn^{III}(salen)] complexes and $PhI(OAc)_2$ with KBr as an additive. Analysis of the system by using ESI-MS enabled us to characterize the detailed mechanism of oxygen transfer from $PhI(OAc)_2$ to the [Mn^{III}(salen)] complex and to identify for the first time the oxomanganese species formed during oxidative kinetic resolution. The results clearly show that the bromide ion plays a key role in the enantioselective oxidative reaction.

Experimental Section

Materials: The Jacobsen ligand, α-methylbenzyl alcohol, 4-methyl-*sec*-phenethyl alcohol, 4-fluoro-*sec*-phenethyl alcohol, 1,2,3,4-tetrahydro-1-naphthol, DL-2-methoxy-α-methylbenzyl alcohol, DL-2-pentanol, 1,1-diphenyl-2-propanol, 1-indanol, DL-menthol, 3,3-dimethyl-2-butanol, cyclopropylmethyl carbinol, (*R*)-(+)-*sec*-phenethyl alcohol, (*S*)-(+)-*sec*-phenethyl alcohol, $PhI(OAc)_2$, and derivatives of benzaldehyde were purchased from Acros Chemical Company and used as received. The other secondary alcohols were prepared from derivatives of benzyldehyde and CH_3MgI or C_2H_5MgBr and were subjected to GC-MS analysis. The imidazolium bromine and pyridinium bromine were prepared according to known procedures.[13] Complexes **1b**–**1d**, **2**, **3a**, and **3b** were prepared according to reported procedures.[7b,9b,14]

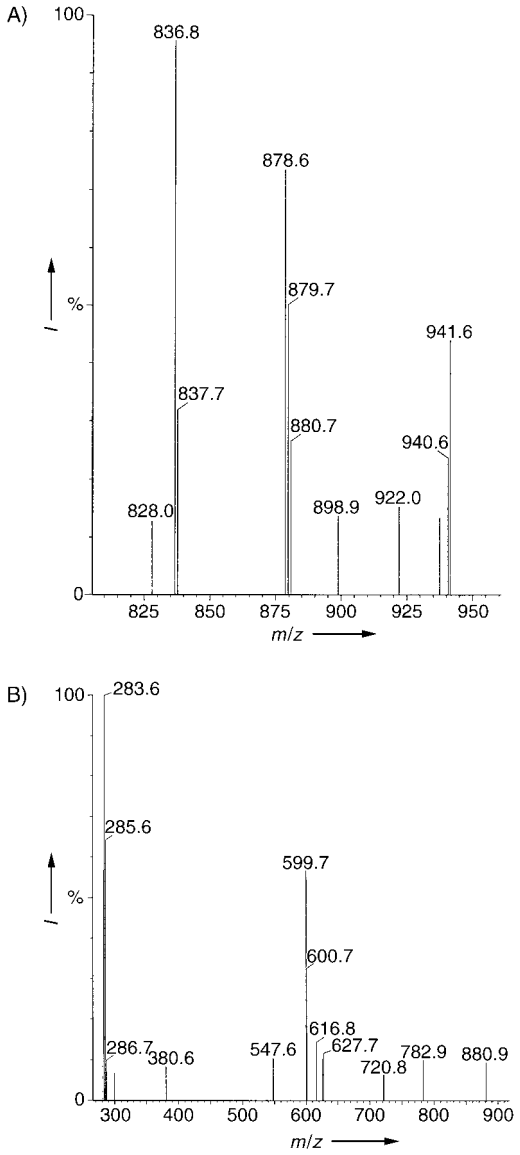


Figure 6. A) Electrospray mass spectrum of a solution of **1a**, α-methylbenzyl alcohol, and $PhI(OAc)_2$ in toluene, showing the formation of cation **C**. B) Electrospray mas spectrum of a toluene solution after oxidative kinetic resolution of α-methylbenzyl alcohol.

Equipment: GC analysis was performed by using an HP 6890 gas chromatograph with a CP-Chirasil-Dex CB column (25 m long, 0.25 mm inner diameter), helium as a carrier gas, and a flame ionization detector (see Supporting Information). The UV/Vis spectra were recorded by using an HP 8453 UV/Vis spectrometer. ESI-MS analysis was performed by using a Waters micromassZQ alliance spectrometer with acetonitrile/H_2O (0.2 mL min^{-1}, 80:20). GC-MS measurements were obtained by using an Agilent 6890N/5973N apparatus. Analytical chiral HPLC was performed by using an HP1090 instrument equipped with Chiralcel OJ and OD-H

columns (each 25 cm long, inner diameter of 0.46 cm) obtained from Daicel Chemical Industries, Ltd (see Supporting Information).

General procedure for the kinetic resolution of secondary alcohols catalyzed by [Mn^{III}(salen)] complexes: A mixture of the substrate (0.25 mmol), catalyst (0.005 mmol), additive (0.02 mmol), CH_2Cl_2 (0.5 mL), and water (1 mL) was stirred in a 5 mL tube for a few minutes at room temperature. The oxidant $PhI(OAc)_2$ (0.175 mmol) was then added and the system was stirred for a further 1 h until completion of the reaction. The products were extracted by using diethyl ether and the conversion and *ee* values were determined by performing GC analysis.

Control experiments: A mixture of the (*R*)- or (*S*)-(+)-*sec*-phenethyl alcohol (0.125 mmol), **1a** (0.005 mmol), KBr (0.02 mmol), CH_2Cl_2 (0.5 mL), and water (1 mL) was stirred in a 5 mL tube for a few minutes at room temperature. The oxidant $PhI(OAc)_2$ (0.175 mmol) was then added. Aliquots (2 μL) of the organic phase were removed during the course of the reaction by using a syringe and were diluted with diethyl ether in preparation for GC analysis.

UV/Vis measurements: Electronic spectra were recorded by using a Hewlett Packard HP 8453 diode array spectrometer under ambient conditions (25 °C) and with a wavelength range of 190–1100 nm. For kinetic studies, a solution of complex **1a** and α-methylbenzyl alcohol in toluene was poured into 10 mm quartz cuvettes, $PhI(OAc)_2$ was added in a 20-fold excess, and the spectra were recorded.

Electrospray solutions: The stock solution of **1a** containing substrate (10 equivalents) was diluted with toluene, then a solution of $PhI(OAc)_2$ (20 equivalents) in toluene was added. The reaction mixture was shaken for 10 s and a sample of the solution was subjected to ESI-MS analysis. Next, a solution of KBr in H_2O was added, and a sample from the organic phase was analyzed by using ESI-MS.

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