Sulfoxidation with hydrogen peroxide catalyzed by $[SeO_4\{WO(O_2)_2\}_2]^{2-}$†

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Received 3rd February 2010, Accepted 13th April 2010
First published as an Advance Article on the web 7th May 2010
DOI: 10.1039/c002318c

The selenium-containing dinuclear peroxotungstate, $[(n\text{-}C_4H_9)_4N]_2[SeO_4\{WO(O_2)_2\}_2]$ (**I**), acts as a homogeneous catalyst for the selective oxidation of various kinds of cyclic mono- and disulfides with 30% aqueous H_2O_2. The cyclic disulfides were selectively oxidized to the corresponding monosulfoxides with one equivalent of H_2O_2 with respect to the sulfides. In the presence of two equivalents of H_2O_2, the oxidation of dibenzothiophene gave the corresponding sulfone in 98% yield under the mild conditions. The negative Hammett ρ value (−0.62) for the competitive oxidation of *p*-substituted thioanisoles and the low X_{SO} (X_{SO} = (nucleophilic oxidation)/(total oxidation)) value of 0.14 for the **I**-catalyzed oxidation of thianthrene 5-oxide (SSO) revealed that **I** is a strong electrophilic oxidant. The reactivities of the di- and tetranuclear peroxotungstates with XO_4^{n-} ligands (X = Se(VI), As(V), P(V), S(VI), and Si(IV)) were strongly dependent on the kinds of hetero atoms. The reaction rates for the sulfoxidation decreased with an increase in the X_{SO} values and a peroxotungstate with a stronger electrophilicity was more active for the sulfoxidation. The kinetic and mechanistic investigations showed that the electrophilic attack of the peroxo oxygen at the sulfur atom is a key step in the sulfoxidation. The computational investigation supported the high chemoselectivitiy for the sulfoxidation of diallyl sulfide.

Introduction

The development of the highly efficient catalytic systems for the oxidation of sulfides to sulfoxides and sulfones has received much attention because they are important as intermediates of biologically significant molecules,[1] ligands in asymmetric catalysis,[2] and oxo-transfer reagents.[3] In addition, the oxidative desulfurization is a promising method for the removal of sulfur compounds from fuels and industrial effluents.[4] In contrast with the conventional methods using stoichiometric oxidants such as peracids, dioxiranes, $NaIO_4$, MnO_2, CrO_3, SeO_2, and PhIO,[5] the catalytic oxidation of sulfides with H_2O_2 is much more desirable from the standpoints of green-sustainable chemistry. Although many H_2O_2-based sulfoxidation systems with homogeneous and heterogeneous organocatalysts,[6] acid catalysts,[7] enzymes,[8] and metal catalysts such as Sc,[9] Ti,[10] V,[11] Cr,[12] Mn,[13] Fe,[14] Cu,[15] Zr,[16] Nb,[17] Mo,[18] Ru,[19] Ta,[20] W,[21] Re,[22] Pt,[23] Au,[24] and polyoxometalates[25] have been reported. Most systems have disadvantages; the use of excess H_2O_2 (1.1–8.0 equiv) with respect to substrates and narrow applicability to a limited number of substrates for example. Therefore, there are only a few reports on catalytic sulfoxidation, which uses an equimolar amount of H_2O_2, showing wide substrate scope; *e.g.*, Ti-,[10] V-,[11] and Fe-based[14] catalytic systems.

Recently, the chemistry of tungsten complexes has attracted considerable attention because of the applications to the catalytic oxidation of various organic substances with H_2O_2.[26] Tungsten catalysts such as WO_3, H_2WO_4, $W(CO)_6$, polyoxotungstates, peroxotungstates, Na_2WO_4, and other tungsten complexes with various quaternary ammonium cations have been used for the oxidation of sulfides.[21,25] We have preliminarily reported the highly efficient epoxidation of various homoallylic and allylic alcohols with H_2O_2 catalyzed by a selenium-containing dinuclear peroxotungstate, $[(n\text{-}C_4H_9)_4N]_2[SeO_4\{WO(O_2)_2\}_2]$ (**I**) (Fig. 1).[27] In addition, **I** is the most active homogeneous catalyst for the selective oxidation of sulfides among the di- and tetranuclear peroxotungstates with XO_4^{n-} ligands (X = Se, As, P, S, Si, *etc.*)

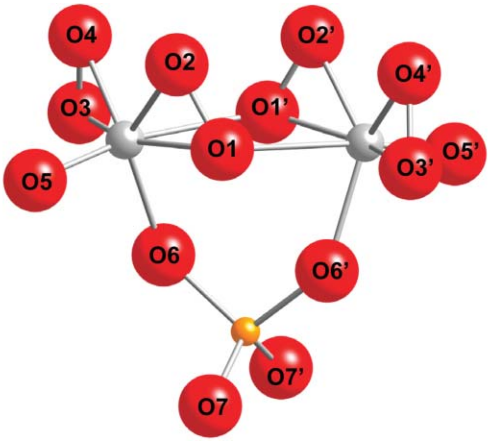

Fig. 1 Proposed structure of the anion part of **I**. The structure of $[SeO_4\{WO(O_2)_2\}_2]^{2-}$ was calculated with DFT using Gaussian03 program package. Theory: B3LYP; basis sets: 6-31+G(d,p) (O atoms) and LanL2DZ (Se and W atoms). Orange, grey, and red balls represent selenium, tungsten, and oxygen atoms, respectively.

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† Electronic supplementary information (ESI) available: Experimental details, kinetic derivation, data of products, Tables S1–S3, and Fig. S1–S3. See DOI: 10.1039/c002318c

and selenium complexes (ESI, Table S1).† Various kinds of acyclic aryl and alkyl sulfides containing vinyl, allyl, and hydroxyl groups can chemoselectively be oxidized into the corresponding sulfoxides or sulfones in excellent yields with one or two equivalents of H_2O_2 with respect to the sulfides, respectively (eqn (1) and Table S2). The present system is applicable to a larger-scale oxidation of thioanisole (100 mmol scale) and the turnover frequency (TOF) and the turnover number (TON) reached up to 70 800 h^{-1} and 19 500, respectively. These values are the highest among those reported for the artificial catalytic systems and the TOF value is comparable to that of the natural enzyme *chloroperoxidase*. While **I** showed the high activity and chemoselectivity for the sulfoxidation, the reaction mechanism is still unclear. In this paper, we extend the scope of the present catalytic system by carrying out the oxidation of cyclic mono- and disulfides with H_2O_2. In addition, the reaction mechanism of the **I**-catalyzed sulfoxidation including the electronic nature of the active oxygen species are investigated in detail on the basis of the catalyst effects, kinetics, and DFT calculation.

(1)

Experimental

General

GC analyses were performed on Shimadzu GC-17A with a flame ionization detector equipped with an InertCap Pure-WAX capillary column (internal diameter = 0.25 mm, length = 30 m). HPLC analyses were performed on Agilent 1100 series LC with a UV-vis detector using an Inertsil ODS-3 column (5 μm × 4.6 mmϕ × 250 mm). Mass spectra were recorded on Shimadzu GCMS-QP2010 equipped with a TC-5HT capillary column (internal diameter = 0.25 mm, length = 30 m). NMR spectra were recorded at 298 K on a JEOL JNM-EX-270 (^1H, 270.0 MHz; ^{13}C, 67.80 MHz; ^{77}Se, 51.30 MHz; ^{183}W, 11.20 MHz) spectrometer. IR spectra were measured on JASCO FT/IR-460 Plus using KCl disks. UV-vis spectra were recorded on a JASCO V-570 spectrometer with a Unisoku thermostatic cell holder (USP-203). Acetonitrile, dichloromethane, and toluene (Kanto Chemical) were purified by The Ultimate Solvent System (GlassContour Company).[28] The other solvents and sulfides were obtained from TCI or Aldrich (reagent grade) and purified prior to the use.[29] Peroxotungstates were synthesized and characterized according to the literature procedures (see ESI).†[30]

Synthesis and characterization of $[(n\text{-}C_4H_9)_4N]_2[SeO_4\{WO(O_2)_2\}_2]$ (I)

The TBA salt derivative of $[SeO_4\{WO(O_2)_2\}_2]^{2-}$ was synthesized according to the reported procedure.[27] Full details of synthesis and characterization of **I** are shown in ESI.†

Procedure for catalytic oxidation of sulfide

The catalytic oxidation of various sulfides was carried out in a 30 mL glass vessel containing a magnetic stir bar. All products were identified by the comparison of GC retention time, mass spectra, and NMR spectra with those of the authentic samples. A typical procedure for the catalytic oxidation was as follows: Thioanisole (1 mmol), acetonitrile (5.9 mL), and 30% aqueous H_2O_2 (1 mmol) were charged in the reaction vessel. The reaction was initiated by the acetonitrile solution containing **I** (1 μmol; [**I**] = 10 mM, 0.1 mL) and the reaction solution was periodically analyzed. Before the GC analysis, the remaining H_2O_2 was decomposed at 273 K by the addition of $Ru(OH)_x/Al_2O_3$.[31] It was confirmed that the oxidation of sulfides did not proceed at all in the presence of $Ru(OH)_x/Al_2O_3$ during the decomposition of H_2O_2. The sulfoxides and sulfones were identified by comparison of their ^1H and ^{13}C NMR signals with the literature data (see ESI).†

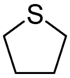
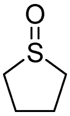
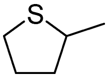
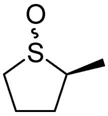
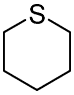
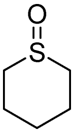
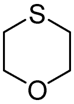
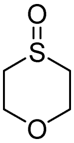
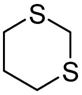
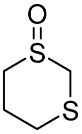
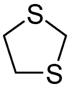
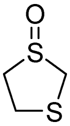
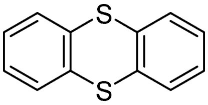
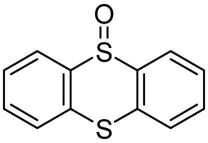
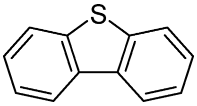
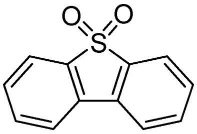
Procedure for oxidation of thianthrene 5-oxide

Thianthrene 5-oxide (SSO) was synthesized by the oxidation of thianthrene (Aldrich) with HNO_3 according to the reported procedure.[32] *cis*-Thianthrene 5,10-dioxide (*cis*-SOSO) and *trans*-thianthrene 5,10-dioxide (*trans*-SOSO) were synthesized by the oxidation of SSO using H_2O_2/HCl, and thianthrene 5,5-dioxide (SSO_2) was synthesized by the oxidation of SSO using $KMnO_4$ as previously reported.[33] Thianthrene 5,5,10-trioxide ($SOSO_2$) was synthesized by the oxidation of SSO_2 catalyzed by $[(n\text{-}C_4H_9)_4N]_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$ with 30% aqueous H_2O_2.[34] SSO and the oxidation products were purified by using silica gel column chromatography. The oxidation products were quantitatively analyzed by HPLC: CAPCELL PAK MG C18-reverse phase column (5 μm × 3 mmϕ × 250 mm, SHISEIDO FINE CHEMICALS), eluent (CH_3OH–CH_3CN–H_2O = 60 : 15 : 25), flow rate (0.4 mL min^{-1}), column temperature (303 K), detection at λ = 254 nm, retention times (3.57, 4.69, 4.93, 5.72, 7.73, and 10.7 min for *trans*-SOSO, $SOSO_2$, *cis*-SOSO, SSO_2, SSO, and naphthalene (internal standard), respectively). The reaction conditions (*i.e.*, concentration of substrate, substrate to oxidant ratio, reaction temperature, *etc.*) were controlled to minimize the over oxidation to $SOSO_2$ and then to estimate the true electronic nature of the oxidant.[35] The X_{SO} value was calculated according to the following equation reported,[35] X_{SO} = (nucleophilic oxidation)/(total oxidation) = (SSO_2 + $SOSO_2$)/(SSO_2 + SOSO + 2$SOSO_2$).

Quantum chemical calculations

The calculations were carried out at the B3LYP level theory[36] with 6-31+G(d,p) basis sets for H, C, O, and S atoms and the double-ξ quality basis sets with effective core potentials proposed by Hay and Wadt[37] for Se and W atoms. The entire structure of peroxotungstates was used as a model in the calculations and the overall charge of the system was –2. Dimethyl sulfide and diallyl sulfide were used as model substrates. The all geometries were optimized without the symmetry restrictions. Transition-state structures were searched by numerically estimating the matrix of second-order energy derivatives at every optimization step and by requiring exactly one eigenvalue of this matrix to be negative. The zero-point vibrational energies were not included. The computed enthalpy, entropy, and free enthalpy were converted

Table 1 Oxidation of various cyclic sulfides with 30% aqueous H_2O_2 catalyzed by **I**[a]

Entry	Substrate	Time/min	Yield (%)	Product (Selectivity (%))	H_2O_2 Efficiency (%)
1		60	96	 (96)	96
2		60	>99	 (96) *trans*/*cis* = 84/16	>99
3		90	>99	 (92)	>99
4		60	99	 (91)	99
5		70	98	 (96)	98
6		30	>99	 (80)	>99
7[b]		30	>99	 (80)	>99
8[c]		90	98	 (>99)	98

[a] Reaction conditions: **I** (0.1 mol% relative to substrate and H_2O_2), sulfide (1 mmol), 30% aqueous H_2O_2 (1 mmol), CH_3CN (6 mL), 293 K. Yield and selectivity were determined by GC and NMR. Remaining H_2O_2 after reaction was estimated by potential difference titration of Ce^{3+}/Ce^{4+} (0.1 M of aqueous $Ce(NH_4)_4(SO_4)_4\cdot 2H_2O$. Yield (%) = (sulfoxide (mol) + sulfone (mol) × 2)/H_2O_2 used (mol) × 100. H_2O_2 efficiency (%) = (sulfoxide (mol) + sulfone (mol) × 2)/consumed H_2O_2 (mol) × 100. [b] **I** (0.5 mol%), CH_3CN–toluene (4/4 mL). [c] **I** (1.0 mol%), 30% aqueous H_2O_2 (2 mmol).

from the 1 atm standard state into the standard state of molar concentration (ideal mixture at 1 mol L^{-1} and 1 atm).[38] The solvent (acetonitrile) effect was introduced by using the CPCM model at the B3LYP/6-311+G** + LanL2DZ level.[39] All calculations were performed with the Gaussian03 program package.[40] The reactivities of four kinds of peroxo oxygen atoms (O1, O2, O3, and O4) in **I** were compared for sulfoxidation of dimethyl sulfide (ESI, Fig. S1).† The calculated activation barriers of sulfide attacks at O2 (69–82 kJ mol^{-1}) were lower than those of sulfide attacks at O1 (110–122 kJ mol^{-1}), O3 (83–88 kJ mol^{-1}), and O4 (76–86 kJ mol^{-1}), suggesting that a sulfide attack at O2 is the most favorable. A similar reactivity order was also observed for the epoxidation.[27] Therefore, the transition-state structures and activation barriers for the oxidation of diallyl sulfide with only O2 in **I**. The cartesian coordinates of the optimized geometries are shown in Table S3.

Results and discussion

The oxidation of various kinds of cyclic mono- and disulfides was investigated and the results are shown in Table 1. Cyclic sulfides were also effectively oxidized to the corresponding sulfoxides with 80–96% selectivity (Table 1, entries 1–7). The *trans* diastereoselectivity (*trans*/*cis* ratio = 84/16) for the oxidation of 2-methyltetrahydrothiophene was higher than that (62/38) of the *m*-chloroperbenzoic acid (*m*-CPBA) system[41] and comparable to that (84/16) of the CrO_3/pyridine system (Table 1, entry 2).[42] The cyclic disulfides such as 1,3-dithiane, 1,3-dithiolane, and thianthrene were selectively oxidized to the monosulfoxides (Table 1, entries 5–7). For the oxidation of dibenzothiophene which has been used as a model compound of organic sulfur in fossil fuels for the oxidative desulfurization, the corresponding sulfone was obtained in 98% yield by using two equivalents of H_2O_2 under the mild conditions (Table 1, entry 8).

Thioanisoles with various kinds of *p*-substituents were oxidized to the corresponding sulfoxides and the reaction rates were dependent on the electronic effects of the substituents on the aromatic rings. The Hammett plots ($\log(k_X/k_H)$ *versus* σ) for the competitive oxidation of thioanisole and *p*-substituted thioanisoles are shown in Fig. 2. The good linearity suggests that the present sulfoxidation proceeds *via* a single mechanism. The negative ρ value (–0.62) indicates the electrophilic active oxygen species. Similar negative ρ values have been reported for the oxidation of aryl sulfides with H_2O_2 catalyzed by d^0-transition metal peroxo complexes such as Mo, W and Re.[43]

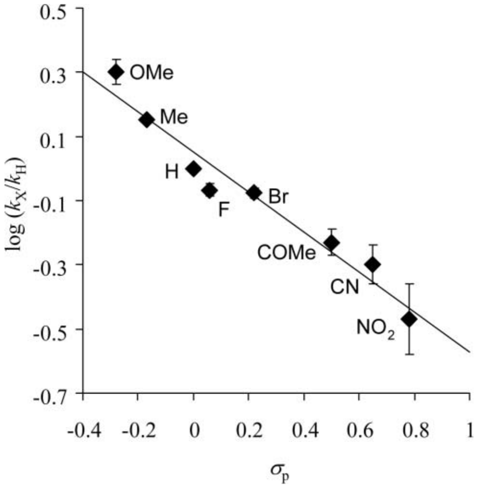


Fig. 2 Hammett plots for the competitive oxidation of thioanisole and *p*-substituted thioanisoles with H_2O_2 catalyzed by **I**. Reaction rates were estimated by the conversion of substrates. Reaction conditions: thioanisole (0.5 mmol), *p*-substituted thioanisole (0.5 mmol), **I** (0.1 mol% relative to H_2O_2), 30% aqueous H_2O_2 (1 mmol), CH_3CN (6 mL), 293 K. Slope = –0.62 (R^2 = 0.95).

The electronic character of the active oxygen species in **I** was further investigated by using thianthrene 5-oxide (SSO) that has been used as a probe of the electronic character of an oxidant (Table 2).[33,44] The oxidation did not proceed without **I** under the present conditions (Table 2, entry 9). The results for the oxidations of SSO by the tungsten complexes showed relatively low X_{SO} values (0.14–0.35, X_{SO} = (nucleophilic oxidation)/(total oxidation) = $(SSO_2 + SOSO_2)/(SSO_2 + SOSO + 2SOSO_2)$) and the sulfide site of SSO was much more selectively oxidized, showing the electrophilic nature of the active oxygen species (Table 2, entries 1–8). The X_{SO} value (0.14) of **I** was lower than those of the other peroxotungstates (0.15–0.35), suggesting that **I** has the most electrophilic active oxygen species among these peroxotungstates. In addition, the reaction rates and X_{SO} values of the dinuclear peroxotungstates with XO_4^{n-} ligands (X = Se, S, P, As, and Si) decreased in the order of Se (25.0 mM min^{-1}, X_{SO} = 0.14) > S (16.0 mM min^{-1}, 0.15) > As (4.1 mM min^{-1}, 0.16) > P (3.7 mM min^{-1}, 0.18) > Si (0.5 mM min^{-1}, 0.30) (Fig. 3).[27] The pK_a values of H_nXO_4 decrease in the same order.[45] Since the pK_a values of ligands can be an index of the Lewis acidity of transition metal complexes,[46] the Lewis acidity of W atoms has an important role in the sulfoxidation.[47]

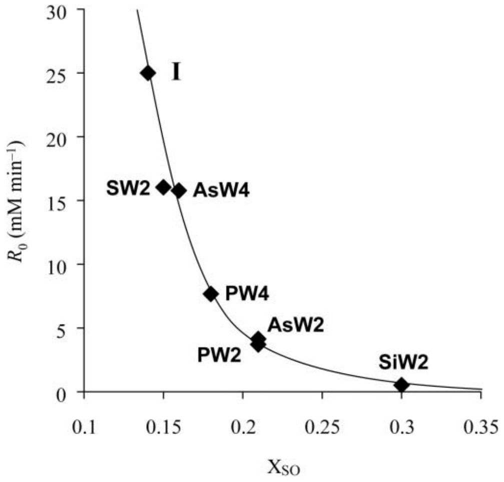


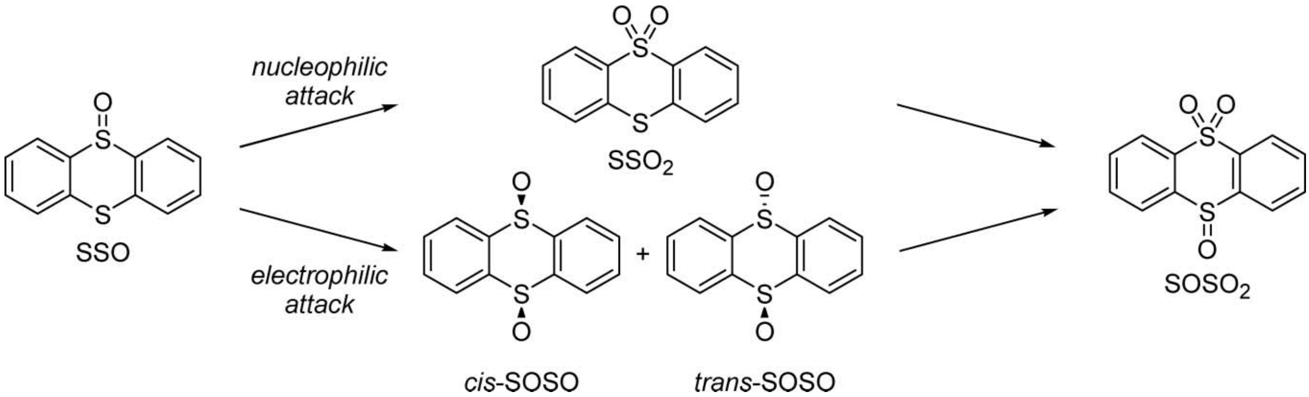
Fig. 3 Correlation between reaction rates for the oxidation of thioanisole and X_{SO} values for the oxidation of SSO. Abbreviations of peroxotungstates were shown in Table 2.

The initial rates of the **I**-catalyzed oxidation of six representative sulfides, ary1 alkyl sulfide, diaryl sulfide, dialkyl sulfide, diallyl sulfide, dihydroxylalkyl sulfide, and aryl vinyl sulfide, are shown in Table 3. The reaction rates decreased in the order of di(2-hydroxylethyl) sulfide (49.1 mM min^{-1}) > methyl *n*-octyl sulfide (43.2 mM min^{-1}) > diallyl sulfide (37.8 mM min^{-1}) > thioanisole (12.1 mM min^{-1}) > phenyl vinyl sulfide (1.5 mM min^{-1}) > diphenyl sulfide (1.3 mM min^{-1}). The correlation was not observed between the reaction rates and the HOMO energies of the corresponding sulfides (*i.e.*, the lone pair orbital energies of a sulfur atom).[48] This is probably because the other factors such as steric and structural effects play significant roles in the present sulfoxidation. For the epoxidation of allylic and homoallylic alcohols, the intermolecular oxygen transfer was assisted by the hydrogen bonding, where the oxo and/or peroxo species act as hydrogen bond acceptors and HOR as hydrogen bond donors.[27] In the present sulfoxidation system, such a stabilization of the transition-state by the hydrogen bonding between **I** and the substrates also results in the highest reactivity of di(2-hydroxylethyl)sulfide among various sulfides.

In the $H_5PV_2Mo_{10}O_{40}$/TBHP system for which a radical mechanism has been proposed,[49] the reaction rate of thioanisole was about six times lower than that of diphenyl sulfide. In contrast, the reaction rate of thioanisole was much higher than that of diphenyl sulfide in the present system. The addition of a radical scavenger (2,6-di-*tert*-butyl-4-methylphenol, two equivalents with respect to **I**) did not change the reaction rates, profiles, and selectivity to methyl phenyl sulfoxide for the **I**-catalyzed oxidation of thioanisole under the conditions in the ESI, Table S1.† These results suggest that free-radical intermediates are not involved in the present sulfoxidation.

The stoichiometric oxidation of diphenyl sulfide (3.12 mM) with **I** (0.31 mM) at 233 K produced 0.60 mM of the corresponding products (ESI, Fig. S2(b)),† suggesting that **I** has two equivalents of active oxygen for the sulfoxidation.[50] Upon the addition of H_2O_2 (3.12 mM, 10 equivalents with respect to **I**) after one equivalent of the active oxygen with respect to **I** was transferred, the oxidation of diphenyl sulfide proceeded catalytically (Fig. S2(c)).† Upon the addition of 10 equivalents of H_2O_2 with respect to **I** to the reaction solution after two equivalents of active oxygen with respect to **I**

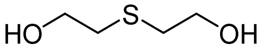
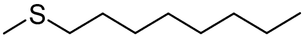
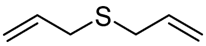
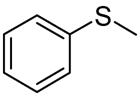
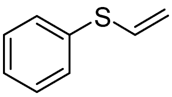
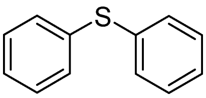
Table 2 Oxidation of SSO with H_2O_2 catalyzed by various peroxotungstates[a]



Entry	Catalyst	Time/min	Yield (%)	Selectivity (%)				X_{SO}
				SSO_2	*cis*-SOSO	*trans*-SOSO	$SOSO_2$	
1	**I**	5	>99	7	29	55	9	0.14
2	**W2**	60	97	22	19	40	18	0.35
3	**SW2**	15	>99	8	28	56	9	0.15
4	**AsW4**	20	>99	7	43	39	11	0.16
5	**PW4**	40	>99	8	37	43	12	0.18
6	**AsW2**	45	>99	9	37	39	15	0.21
7	**PW2**	60	>99	9	35	41	15	0.21
8	**SiW2**	1440	88	13	31	31	25	0.30
9	Without	1440	<1	—	—	—	—	—

[a] Reaction conditions: Catalyst (W: 20 μmol), SSO (200 μmol), CH_3CN (5 mL), 30% aqueous H_2O_2 (50 μmol), 298 K. Yield and selectivity were determined by HPLC analysis with an internal standard technique. Yield (%) = products (mol)/oxidant used (mol) × 100. X_{SO} = (SSO_2 (mol) + $SOSO_2$ (mol))/(SOSO (mol) + SSO_2 (mol) + 2 × $SOSO_2$ (mol)). Peroxotungstates were abbreviated as follows: $[(n\text{-}C_4H_9)_4N]_2[\{WO(O_2)_2\}_2(\mu\text{-}O)]$ (**W2**), $[(n\text{-}C_6H_{13})_4N]_3[AsO_4\{WO(O_2)_2\}_4]$ (**AsW4**), $[(n\text{-}C_4H_9)_4N]_2[SO_4\{WO(O_2)_2\}_2]$ (**SW2**), $[(n\text{-}C_6H_{13})_4N]_3[PO_4\{WO(O_2)_2\}_4]$ (**PW4**), $[(n\text{-}C_4H_9)_4N]_2[HAsO_4\{WO(O_2)_2\}_2]$ (**AsW2**), $[(n\text{-}C_4H_9)_4N]_2[HPO_4\{WO(O_2)_2\}_2]$ (**PW2**), and $[(n\text{-}C_4H_9)_4N]_2[Ph_2SiO_2\{WO(O_2)_2\}_2]$ (**SiW2**).

Table 3 Initial rates for the oxidation of various sulfides with H_2O_2 catalyzed by **I**[a]

Entry	Sulfide	HOMO Energy of sulfide [b]/eV	R_0/mM min^{-1}
1		−9.19	49.1
2		−9.03	43.2
3		−9.19	37.8
4		−8.12	12.1
5		−8.43	1.5
6		−8.16	1.3

[a] Reaction conditions: **I** (0.01 mol% relative to substrate and H_2O_2), sulfide (1 mmol), 30% aqueous H_2O_2 (1 mmol), CH_3CN (1 mL), 293 K. R_0 values were determined from the reaction profiles at low conversions (≤10%) of both substrates and H_2O_2. [b] Calculated at the HF/6-311G(d,p) level.

were transferred, the catalytic oxidation rate (≤0.1 mM s^{-1}) was much smaller than that (13.1 mM s^{-1}) under the stoichiometric conditions (Fig. S2(d)).† Similar phenomena were observed in the **I**-catalyzed epoxidation of olefins and the following results are reported:[27] (i) **I** has two equivalents of active oxygen. (ii) The subsequent peroxo species (**II**) such as $[SeW_mO_n]^{o-}$ (m = 1 and 2) are formed by the reaction of **I** with an olefin (*i.e.*, one equivalent of the active oxygen with respect to **I** is transferred). (iii) While **I** is regenerated by the reaction of **II** with H_2O_2, the further epoxidation with **II** leads to irreversible catalyst inactivation. Therefore, the present sulfoxidation also includes the following two steps: (i) the formation of **II** and a sulfoxide by the reaction of **I** with a sulfide and (ii) the regeneration of **I** by the reaction of **II** with H_2O_2.[51]

On the basis of these results, the present oxidation of sulfides possibly proceeds as follows (Scheme 1): first, the sulfide directly attacks the peroxo oxygen groups in **I** to form the corresponding sulfoxide and **II** (steps 1 and 2). Then, the subsequent peroxo species **II** is regenerated by the reaction with H_2O_2 (step 3). The successive oxidation of the sulfoxide to the corresponding sulfone is also catalyzed by **I** (steps 4 and 5).[52] The kinetics for the oxidation of thioanisole with H_2O_2 catalyzed by **I** were investigated. The reaction profiles for the catalytic oxidation of thioanisole are shown in Fig. 4. The catalytic oxidation proceeded smoothly and the induction periods were not observed. The plots of the reaction rates against the concentrations of **I**, thioanisole, and H_2O_2 are shown in Fig. 5. Saturation kinetics were observed

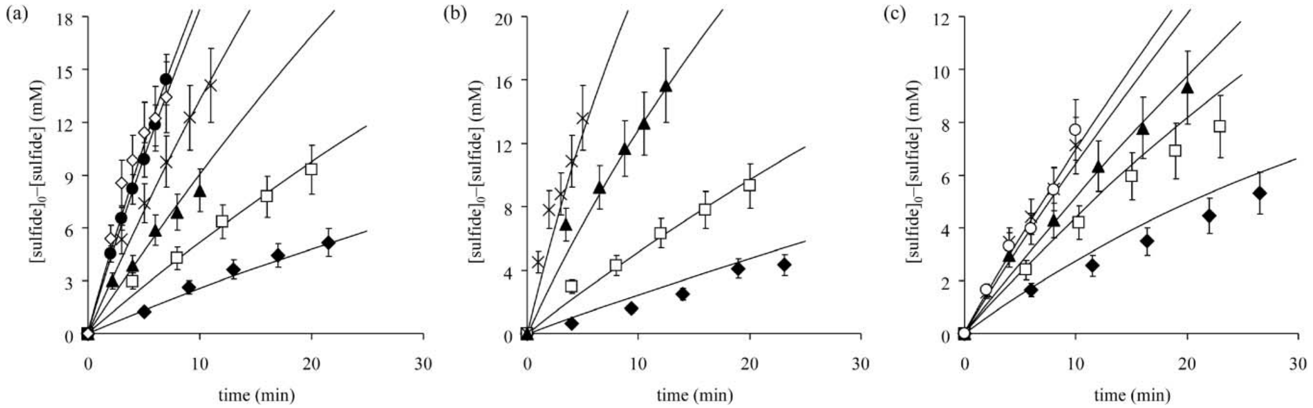
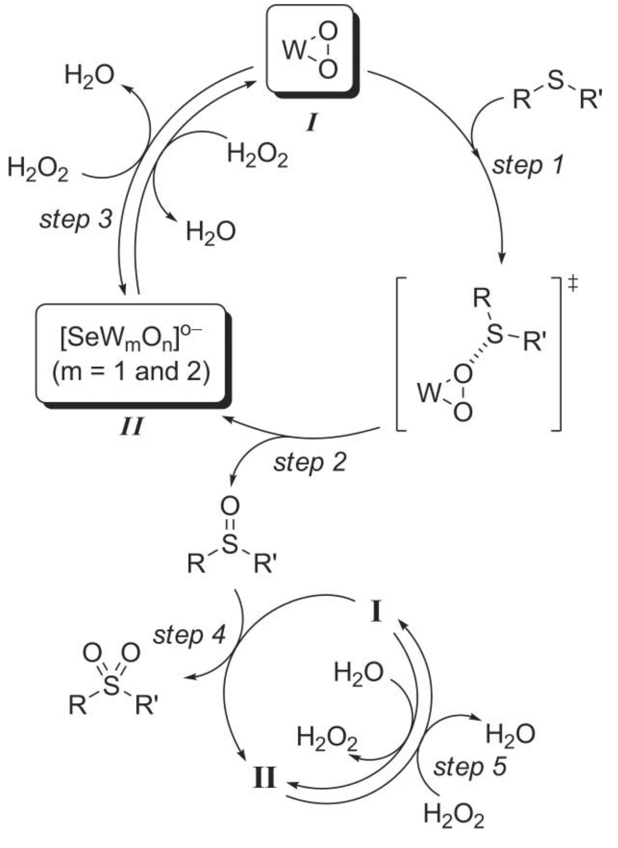
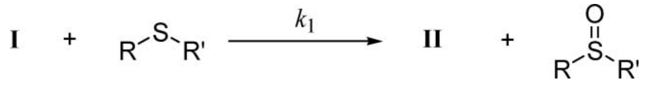


Fig. 4 Reaction profiles for the oxidation of thioanisole with H_2O_2 catalyzed by **I**: (a) **I** (0.10 mM), thioanisole (50 mM), H_2O_2 (20–955 mM), H_2O (250 mM), CH_3CN (6 mL), 273 K; (b) **I** (0.04–0.50 mM), thioanisole (50 mM), H_2O_2 (50 mM), H_2O (250 mM), CH_3CN (6 mL), 273 K; (c) **I** (0.10 mM), thioanisole (10–200 mM), H_2O_2 (50 mM), H_2O (250 mM), CH_3CN (6 mL), 273 K. R_0 values were determined from the reaction profiles at low conversions (<20%) of both thioanisole and H_2O_2. Solid lines are simulation curves using eqn (4).



Scheme 1 Proposed mechanism of **I**-catalyzed oxidation of sulfide and sulfoxide with H_2O_2.

for the dependence of the reaction rate on the concentrations of thioanisole (10–200 mM) and H_2O_2 (20–955 mM), respectively (Fig. 5(a) and 5(c)).[53] The first-order dependence of the reaction rate on the concentration of **I** (0.04–0.50 mM, Fig. 5(b) and ESI, Fig. S3)† was observed. The proposed mechanism is divided into the following two elementary processes (eqn (2) and (3)).



$$\mathbf{I} + RSR' \xrightarrow{k_1} \mathbf{II} + RS(=O)R' \quad (2)$$

$$\mathbf{II} + H_2O_2 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathbf{I} + H_2O \quad (3)$$

From the steady-state approximation on **I** and **II** and the mass balance ($[\mathbf{I}]_t = [\mathbf{I}] + [\mathbf{II}]$), the overall sulfoxidation rate is expressed by eqn (4) (see details in ESI). When the k_1, k_2, and k_{-2} values in eqn (4) are 9.3, 2.6, and 2.0 × 10^{-1} $M^{-1}s^{-1}$, respectively, the dependencies of the reaction rates on the concentrations of **I**, thioanisole, and H_2O_2 calculated using eqn (4) (shown by the solid lines in Fig. 5(a), 5(b), and 5(c)) fairly well reproduced the experimental results.[53,54] In addition, the time course of oxidation calculated by the numerical integration of eqn (4) (shown by the solid lines) fairly well reproduced the experimental results of the sulfide conversions as a function of time (Fig. 4(a), 4(b), and 4(c)), supporting Scheme 1. The slight deviation of the observed yields from the calculated ones at a higher conversion (especially under the conditions with the low ratio of the sulfide to H_2O_2) is probably explained by the over oxidation to the corresponding sulfone. The reaction constant ($k = 4.3 \times 10^{-3}$ $M^{-1}s^{-1}$, $R_0 = k[\mathbf{I}][\text{cyclooctene}]$ at 273 K) for the epoxidation of cyclooctene by **I** is much smaller than those (k_1, k_2, and k_3) for the present sulfoxidation, supporting that the oxygen transfer from **I** to the C=C double bond is the rate-determining step for the epoxidation.[27,55]

$$R_0 = \frac{d[\text{sulfoxide}]}{dt} = \frac{k_1 k_2 [\mathbf{I}]_t[\text{sulfide}][H_2O_2]}{k_1[\text{sulfide}] + k_2[H_2O_2] + k_{-2}[H_2O]} \quad (4)$$

In order to investigate the proposed reaction mechanism, the density functional theory calculations were carried out at the B3LYP/LanL2DZ + 6-31+G(d,p) level. The energies of the reaction steps were calculated according to Scheme 1 and the results are summarized in Fig. 6. The formation of the subsequent peroxo species (**B**) and dimethylsulfoxide by the reaction of dimethyl sulfide with the selenium-containing dinuclear peroxotungstate (**A**) was calculated to be exothermic by −81 kJ mol^{-1}. The transition-state structure was found to exhibit spiro orientations in which the sulfur groups is almost orthogonal to the plane formed by the peroxo group and the tungsten center. The activation

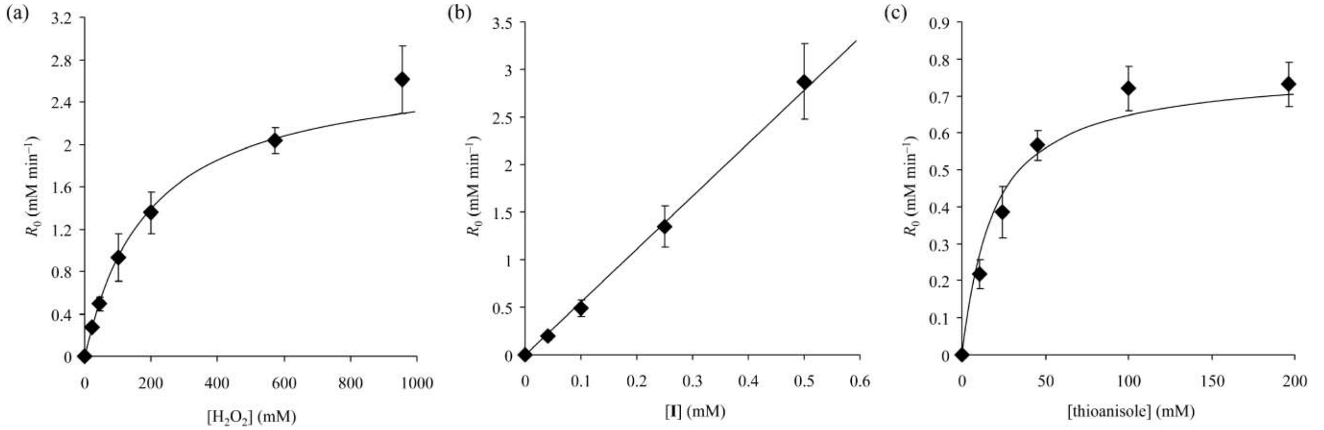


Fig. 5 Dependencies of the reaction rates on the concentrations of (a) H_2O_2, (b) **I**, and (c) thioanisole: (a) **I** (0.10 mM), thioanisole (50 mM), H_2O_2 (20–955 mM), H_2O (250 mM), CH_3CN (6 mL), 273 K; (b) **I** (0.04–0.50 mM), thioanisole (50 mM), H_2O_2 (50 mM), H_2O (250 mM), CH_3CN (6 mL), 273 K; (c) **I** (0.10 mM), thioanisole (10–200 mM), H_2O_2 (50 mM), H_2O (250 mM), CH_3CN (6 mL), 273 K. Solid lines are simulation curves using eqn (4).

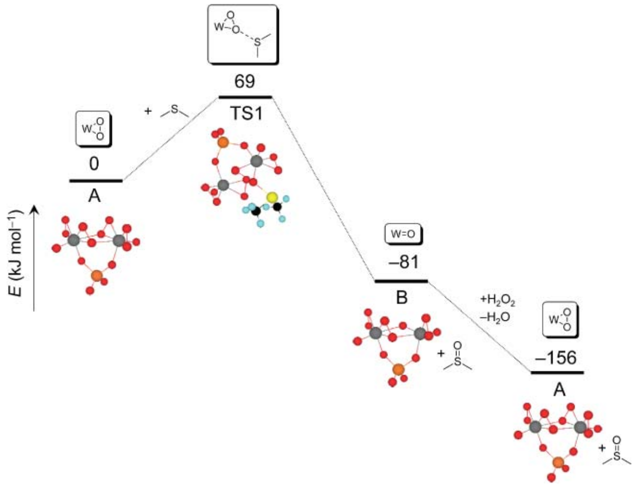


Fig. 6 Calculated energy diagram of the oxidation of dimethyl sulfide to dimethyl sulfoxide by **I** in the gas phase (energies in kJ mol^{-1}). Orange, grey, red, yellow, black, and light blue balls represent selenium, tungsten, oxygen, sulfur, carbon, and hydrogen atoms, respectively.

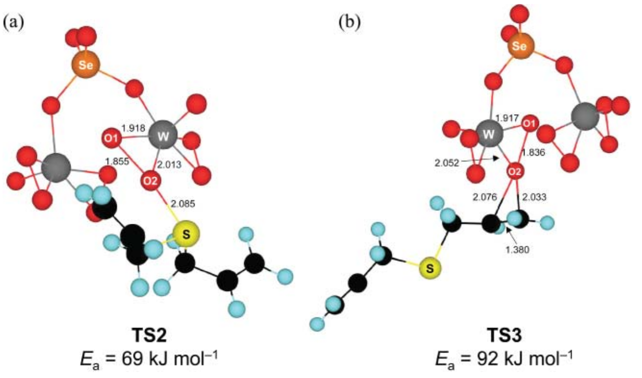


Fig. 7 Transition-state structures and the corresponding activation barriers for (a) the sulfoxidation and (b) the oxidation of diallyl sulfide by **I** in the gas phase (bond lengths in Å).

energy for the oxygen transfer reaction (**TS1**) was calculated to be 69 kJ mol^{-1} and the following computed thermodynamic activation parameters of **TS1** were afforded: $\Delta H^{\ddagger}_{298\,K}$ = 73.1 kJ mol^{-1}, $\Delta S^{\ddagger}_{298\,K}$ = −147.6 J mol^{-1} K^{-1}, and $\Delta G^{\ddagger}_{298\,K}$ = 117.1 kJ mol^{-1}.[56,57] The H_2O_2 molecule reacted with **B** to form **A** and water, establishing the catalytic cycle. This step was calculated to be exothermic by −75 kJ mol^{-1}.

The present chemoselectivity for the oxidation of diallyl sulfide was also investigated by the DFT calculation (Fig. 7). The peroxo species attack the sulfur atom (**TS2**) or the double bond (**TS3**) to form the corresponding sulfoxide or epoxide, respectively. The activation energy (69 kJ mol^{-1}) of **TS2** was much lower than that (92 kJ mol^{-1}) of **TS3**, showing that the sulfur atom was oxidized much more preferentially than the C=C double bond. The order is consistent with the experimental results that the diallyl sulfoxide was only formed without the epoxidation.

Conclusion

In conclusion, the selenium-containing dinuclear peroxotungstate of **I** could efficiently catalyze the oxidation of sulfides to the corresponding sulfoxides and sulfones. The high reactivity for the sulfoxidation, the negative ρ value of the Hammett plots for the competitive oxidation of *p*-substituted thioanisoles, and the low X_{SO} value for oxidation of SSO in comparison with those of various peroxotungstates showed that **I** is a strong electrophilic oxidant. The kinetic and mechanistic investigations show that the electrophilic attack of the peroxo oxygen at the sulfur atom is a key step in the sulfoxidation. The computational studies support the high chemoselectivity to the sulfoxide for the oxidation of diallyl sulfide.

Acknowledgements

This work was supported by the Core Research for Evolutional Science and Technology (CREST) program of the Japan Science and Technology Agency (JST), the Global COE Program (Chemistry Innovation through Cooperation of Science and Engineering), the Development in a New Interdisciplinary Field

Based on Nanotechnology and Materials Science Programs, and a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Science, Sports, and Technology of Japan. We are grateful to Mr S. Kuzuya (University of Tokyo) for his help in experiments.

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52 The oxidation of methyl phenyl sulfoxide with H_2O_2 catalyzed by **I** was carried out under the same conditions in ESI, Table S1.† The oxidation proceeded to form the corresponding sulfone in 91% yield for 3 h, suggesting that the successive oxidation of the sulfoxide to the corresponding sulfone is also catalyzed by **I**. The reaction rate (2.3 mM min^{-1}) for the oxidation of methyl phenyl sulfoxide was much lower than that (25.0 mM min^{-1}) of methyl phenyl sulfide. Such a difference of the reactivities resulted in the control of the product selectivity by changing the amount of H_2O_2 with respect to the sulfides.

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55 The large equilibrium constant ($K = k_2/k_{-2} =$ *ca.* 13) of eqn 3 supports that **I** is a dominant species during the epoxidation.

56 The experimental reactivity decreased in the order of thioanisole (>200) $\gg$ 2-methyl-2-propen-1-ol (4.8) > 2-methyl-1-pentene (1.0). This order was not consistent with that of the activation barriers calculated at the B3LYP/6-31+G** + LanL2DZ level for the oxidation in the gas phase (2-methyl-1-pentene (98 kJ mol^{-1}) > dimethyl sulfide (69 kJ mol^{-1}) > 2-methyl-2-propen-1-ol (56 kJ mol^{-1})). The calculation levels and solvent effects have an important role on the theoretical investigation on the hydrogen bonding effects for the mechanism of olefin epoxidation and the high level calculations including solvent effects well reproduce the experimental data.[57] Therefore, the solvent (acetonitrile) effect was considered with the CPCM model at the B3LYP/6-311+G** + LanL2DZ level. The activation barrier for the oxidation of dimethyl sulfide was much decreased to 27.8 kJ mol^{-1}, while the transition state structures for the epoxidation of 2-methyl-1-pentene and 2-methyl-2-propen-1-ol could not successfully be optimized.

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