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Highly efficient utilization of H_2O_2 for oxygenation of organic sulfides catalyzed by $[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]^{4-}$

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Abstract—Remarkable efficiency of hydrogen peroxide utilization is reported for oxygenation of four organic sulfides catalyzed by a divacant lacunary silicotungstate, $(Bu_4N)_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$ (**1**), under mild conditions. The addition of imidazole, phosphate, or carboxylates significantly enhances the rate of organic sulfide oxygenation. Most notably, use of **1** and imidazole, both at 1% molar concentration, resulted in the quantitative conversion of phenylsulfide to sulfoxide with 1 equiv of H_2O_2 in 3 h, and to sulfone with 2 equiv of H_2O_2 in 6 h.

Catalyzed oxygenation of organic sulfide remains a topical interest due to the versatile utility of both sulfoxide and sulfone in organic synthesis.[1–4] While a plethora of oxygen donors ([O]) are available, use of 'green' oxygen donors such as H_2O_2, O_2, and ^{t}BuOOH have become increasingly prominent.[5–7] Recent examples of effective catalysts for oxygenation of sulfide by H_2O_2 include peroxycarbonate,[8,9] $MnSO_4$,[10] Mn-TACN,[11] molybdate/tungstate,[12,13] polyoxometalates,[14] and methyloxorhenium.[15] A number of polyoxometalates have been used as effective catalysts for oxygenation of alkanes[16] and alkenes[17] by H_2O_2. Recently, Mizuno and co-workers reported the synthesis of $(Bu_4N)_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$ (**1**, Fig. 1), which displays remarkable regioselectivity in olefin epoxidation and quantitative utility of hydrogen peroxide.[18,19]

Oxygenation of organic sulfides may proceed in a stepwise fashion: sulfide to sulfoxide and sulfoxide to sulfone as indicated in Eq. 1.

$$RSR' \xrightarrow{[O]} RS(O)R' \xrightarrow{[O]} RS(O)_2R' \qquad (1)$$

Our current interest in the oxygenation of organic sulfides and the desire to limit oxygenation at the sulfoxide formation prompt us to employ **1** as a catalyst to activate H_2O_2. Organic sulfides studied herein, shown in Scheme 1, include phenyl sulfide (PPS), methyl phenyl sulfide (MPS), ethyl phenyl sulfide (EPS), and 2-chloro-ethylphenyl sulfide (CEPS). Additives such as cyclic imines and carboxylates have been shown to increase reaction rates for catalytic olefin epoxidation, as reviewed by Lane and Burgess.[6] Six additives from Burgess's tabulation, namely benzoate, ascorbate, oxalate, phosphate, acetate, and imidazole, are evaluated for their effects on the oxygenation of organic sulfides. The efficiency of the catalytic system is judged from

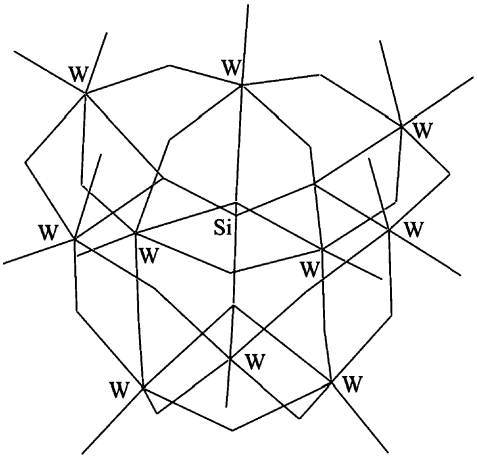

Figure 1. Wire-frame representation of $\gamma\text{-}[SiW_{10}O_{34}(H_2O)_2]^{4-}$; unlabeled corners/termini are oxygen atoms (based on the CIF file courtesy of Professor N. Mizuno, see Ref. 18 for details).

Keywords: Organic sulfide; Catalytic oxygenation; Imidazole; Hydrogen peroxide; $[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]^{4-}$.

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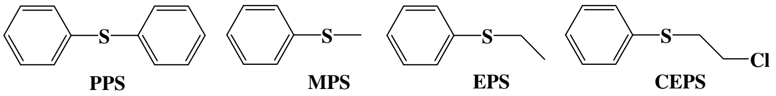

Scheme 1. Organic sulfide substrates.

the following criteria: (i) ability to oxygenate organic sulfides, (ii) product composition of sulfoxide or sulfone, (iii) capability of complete transfer of active oxygen from H_2O_2 to organic sulfide, and (iv) effect of additives.

Table 1 lists the results obtained from the oxygenation of PPS with hydrogen peroxide catalyzed by **1** both with and without additives. In the absence of an additive, conversion of PPS to the corresponding sulfoxide is slow, producing only 38% after 3 h with 1 equiv of H_2O_2 (entry 1). Use of 2 equiv of H_2O_2 resulted in a quantitative conversion to sulfoxide in 4 h (entry 8) followed by a slower conversion to sulfone (19% in 6 h, entry 15). In comparison, all six additives significantly accelerate the conversion of PPS to sulfoxide or sulfone with 1 or 2 equiv of H_2O_2, respectively (entries 2–7, 9–14 and 16–21). The addition of imidazole resulted in 100% sulfoxide or sulfone formation using either 1 or 2 equiv of H_2O_2, respectively, demonstrating a 100% utility of active oxygen from H_2O_2 in each case (entries 7 and 21).

Oxygenation of PPS catalyzed by **1** also proceeds in a well-defined stepwise fashion: no sulfone product was detected prior to the complete sulfoxide formation with the use of 2 equiv of H_2O_2, even in the presence of an additive (entries 8–14). Addition of 2 equiv of H_2O_2 resulted in the partial conversion to sulfone within 6 h without (entry 15) or with additives other than imidazole (entries 16–20). In contrast, the use of imidazole led to the complete conversion to sulfone (entry 21), reaffirming the efficiency in utilizing H_2O_2 by **1** in conjunction with imidazole.

The activity of **1** has been further assessed using MPS and EPS as substrates in conjunction with imidazole at 1:1 or 1:2 molar ratio of the substrate and H_2O_2. As shown in Table 2, the oxygenation of MPS and EPS catalyzed by **1** progress from sulfide to sulfoxide to sulfone sequentially, though disulfide oxidation products were detected as intermediates for EPS. The formation of disulfides through catalytic reactions with H_2O_2 has been documented in literature.[20]

As shown by the entries in Table 3, catalyst **1** is also effective in the H_2O_2 oxygenation of 2-chloro-ethylphenyl sulfide (CEPS), a model compound for mustard gas.[9,21] Notably, use of 1 equiv of H_2O_2 both without and with imidazole resulted in the complete consumption of CEPS in 6 h (entry 1) and 2 h (entry 2), respectively, while sulfones were not detected among the products. Prevention of sulfone formation is signifi-

Table 1. Results for oxygenation of phenyl sulfide (PPS) in CH_3CN catalyzed by **1**[a]

Entry	Additive	H_2O_2 (equiv)	Reaction time (h)	Sulfide	Sulfoxide	Sulfone
1	None	1	3.0	62	38	0
2	Benzoate	1	3.0	49	51	0
3	Ascorbate	1	3.0	39	61	0
4	Oxalate/oxalic acid	1	3.0	19	81	0
5	$(NH_4)_3PO_4$	1	3.0	14	86	0
6	Acetate	1	3.0	12	88	0
7	Imidazole	1	3.0	0	100	0
8	None	2	4.0	1	99	0
9	Benzoate	2	3.5	0	100	0
10	Ascorbate	2	3.0	2	98	0
11	Oxalate/oxalic acid	2	2.5	2	98	0
12	$(NH_4)_3PO_4$	2	2.5	2	98	0
13	Acetate	2	2.0	0	100	0
14	Imidazole	2	1.5	0	100	0
15	None	2	6.0	0	81	19
16	Benzoate	2	6.0	0	68	32
17	Ascorbate	2	6.0	0	53	47
18	Oxalate/oxalic acid	2	6.0	0	39	61
19	$(NH_4)_3PO_4$	2	6.0	0	34	66
20	Acetate	2	6.0	0	16	84
21	Imidazole	2	6.0	0	0	100

[a] All data reported are an average of two runs. Reaction conditions: PPS (5 mmol), catalyst (**1**, 0.05 mmol), additive (sodium benzoate, sodium ascorbate, sodium oxalate/oxalic acid (1:1), $(NH_4)_3PO_4$, sodium acetate, or imidazole, 0.05 mmol), CH_3CN (5 mL). The reaction was initiated by the addition of 1 equiv or 2 equiv of 11.96 M H_2O_2 (concentration established by iodometric analysis). All reactions were performed at room temperature (23 ± 2 °C). At the indicated time, the reaction was stopped by the addition of saturated NaCl solution, forcing the catalyst into the aqueous layer and the remaining organic layer was analyzed by GC–MS. Percentages determined by GC–MS. Product identities were confirmed through their MS by the NIST Standard Reference Database (NIST98 and Search Program v. 1.7, Chem SW, Inc. version, 1999).

Table 2. Results for oxygenation of methyl phenyl sulfide (MPS) and ethyl phenyl sulfide (EPS) catalyzed by **1**[a]

Entry	Substrate	Imidazole present	H_2O_2 (equiv)	Reaction time (h)	Sulfide	Sulfoxide	Sulfone	Others[b]
1	MPS	No	1	2.5	0	100	0	0
2	MPS	Yes	1	0.8	0	100	0	0
3	MPS	No	2	1.5	0	91	9	0
4	MPS	Yes	2	0.5	0	100	0	0
5	MPS	No	2	7.5	0	0	100	0
6	MPS	Yes	2	2.5	0	0	100	0
7	EPS	No	1	8	0	62	0	38
8	EPS	Yes	1	3	0	59	0	41
9	EPS	No	2	1	0	16	7	77
10	EPS	Yes	2	1	0	17	14	69
11	EPS	No	2	8	0	9	45	46
12	EPS	Yes	2	8	0	0	100	0
13	EPS	No	2	24	0	0	100	0

[a] Reaction conditions similar to those in Table 1. Results depicted are an average of two runs.

[b] Disulfides (PhSSPh) and their respective oxidation products [PhS(O)SPh or PhS(O)S(O)Ph and $PhS(O)_2SPh$].

Table 3. Results for oxygenation of 2-chloro-ethylphenyl sulfide (CEPS) catalyzed by **1**[a]

Entry	Imidazole present	H_2O_2 (equiv)	Reaction time (h)	Sulfide	Sulfoxide	2-Chloro-ethylphenyl sulfone	Phenyl vinyl sulfone	Others
1	No	1	6	0	67	0	0	33[b]
2	Yes	1	2	0	73	0	0	27[b]
3	No	2	6	0	0	82	13	5[c]
4	Yes	2	3	0	0	72	27	1[c]
5	No	2	24	0	0	75	25	0
6	Yes	2	24	0	0	70	30	0

[a] Reaction conditions similar to those in Table 1. Results depicted are an average of two runs.

[b] Disulfides (PhSSPh) and its respective oxidation products [PhS(O)SPh].

[c] PhS(O)S(O)Ph or $PhS(O)_2SPh$.

cant in the decontamination of mustard gas since its sulfone is also highly toxic.[21] Final products of oxygenation of CEPS with 2 equiv of H_2O_2 were identified as phenyl vinyl sulfone (25–30%) and 2-chloro-ethylphenyl sulfone (70–75%) (entries 4 and 5). Similar product distribution was observed in both the presence and absence of imidazole, although a longer reaction time is required for quantitative conversion for the latter. Allowing the reaction to continue for several hours does not affect the established product distribution (entries 4 and 6). Previous studies of CEPS oxygenation catalyzed by various metal-based catalysts also found either phenyl vinyl sulfone[11] or 2-chloro-ethylphenyl sulfone[22] as the final product, but not a combination of these products. The rate of sulfide oxygenation is much faster in comparison with the rate of sulfoxide oxygenation for each substrate.

In summary, $(Bu_4N)_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$ (**1**) is remarkably efficient with its utilization of hydrogen peroxide in the oxygenation of organic sulfides. The addition of carboxylates, phosphate, or most notably imidazole, enhances the rate of organic sulfide oxygenation. Product distribution of phenyl vinyl sulfone and 2-chloro-ethylphenyl sulfone was not significantly altered by the addition of imidazole. Results reported herein reveal a 100% utilization of H_2O_2 by catalyst **1**, enabling synthetic control of organic sulfide oxygenation to form either sulfoxide or sulfones with 1 or 2 equiv of H_2O_2, respectively.

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