Journal of Catalysis **182,** 285–288 (1999)
Article ID jcat.1998.2369, available online at http://www.idealibrary.com on IDEAL®

RESEARCH NOTE

Selective Oxidation of Alkenes Catalyzed by *di*-Iron-Substituted Silicotungstate with Highly Efficient Utilization of Hydrogen Peroxide

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Received October 28, 1998; revised November 24, 1998; accepted November 26, 1998

Oxidation reactions of alkenes with hydrogen peroxide were catalyzed by *di*-iron-substituted silicotungstate, $\gamma\text{-SiW}_{10}\{\text{Fe(OH}_2)\}_2\text{O}_{38}^{6-}$, with a high efficiency of hydrogen peroxide utilization. The efficiency of hydrogen peroxide utilization reached up to ca. 100% for the epoxidation of cyclooctene catalyzed by the *di*-iron-substituted silicotungstate. Not only cyclooctene but also 2-octene and cyclohexene were oxidized with a high efficiency of hydrogen peroxide utilization. The $\gamma\text{-SiW}_{10}\{\text{Fe(OH}_2)\}_2\text{O}_{38}^{6-}$ silicotungstate showed the highest efficiency of hydrogen peroxide utilization and conversion among *di*-transition-metal- and iron-substituted silicotungstates.

Key Words: di-**iron-substituted silicotungstate; epoxidation; high efficiency; hydrogen peroxide.**

INTRODUCTION

Stoichiometric oxidation is still widely used and large amounts of by-products are formed. These oxidation processes require new catalytic, low-salt technologies. Oxidation of alkenes is especially important both industrially and in organic synthesis. Among products, epoxides are useful synthetic intermediates both industrially and in organic synthesis. Many complexes of ruthenium, molybdenum, and titanium have been reported to be active for epoxidation reactions with peracids or peroxides (1–3). Among oxidants, hydrogen peroxide is a preferable oxidant because of its simplicity of handling; the environmentally friendly nature of its coproduct, water; its high oxygen atom efficiency; and its versatility (1, 4, 5–8). Therefore, the development of highly efficient catalysts for selective oxidation of alkenes with hydrogen peroxide is very attractive (9–14).

Recently, we have reported that *di*-iron-substituted silicotungstate, $\gamma\text{-SiW}_{10}\{\text{Fe(OH}_2)\}_2\text{O}_{38}^{6-}$, can specifically catalyze the selective oxidation of alkanes with highly efficient utilization of hydrogen peroxide, reaching up to ca. 100% for oxidations of cyclohexane and adamantane (15). To date, almost 100% efficiency in the epoxidation of cyclooctene with hydrogen peroxide has also been achieved for the Mn(TDCPP)Cl/Im system ($\text{H}_2\text{TDCPP} = 5,10,15,20$-tetrakis-2′,4′,6′-terimethylphenyl)porphirin, where Im is imidazole) (11), TS-1, and Ti-beta (12–14). These catalysts show the characteristic reactivities as follows: TS-1 and Ti-beta show high efficiency of hydrogen peroxide utilization for alkene oxidations, but low efficiency for alkane oxidations. The Mn(TDCPP)Cl/Im system shows high selectivity to epoxide and high efficiency of hydrogen peroxide utilization for alkene oxidations, but low efficiency for alkane oxidations. The Gif system, which shows high efficiency and conversion for alkane oxidations, is inactive for alkene epoxidations (15–17). Therefore, little is known about the effective catalytic systems, which catalyze oxidation of both alkanes and alkenes with highly efficient utilization of hydrogen peroxide.

In this paper, we report that *di*-iron-substituted silicotungstate (see Fig. 1) can catalyze the selective epoxidation of alkenes as well as alkanes with highly efficient utilization of hydrogen peroxide.

EXPERIMENTAL

Preparation of Polyoxometalates

The polyoxometalates $\alpha\text{-SiW}_{12}\text{O}_{40}^{4-}$, $\alpha\text{-SiW}_{11}\text{Fe(OH}_2)\text{O}_{39}^{5-}$, $\gamma\text{-SiW}_{10}\{M\text{(OH}_2)\}_2\text{O}_{38}^{6-}$ ($M =$ Fe, Mn), and $\alpha\text{-SiW}_9\{\text{Fe(OH}_2)\}_3\text{O}_{37}^{7-}$ were synthesized as tetrabutylammonium salts, as reported previously (15, 18). Tetrabutylammonium salt of $\gamma\text{-SiW}_{10}\{\text{Cu(OH}_2)\}_2\text{O}_{38}^{8-}$ was prepared in the same way as that of $\gamma\text{-SiW}_{10}\{\text{Mn(OH}_2)\}_2\text{O}_{38}^{6-}$. The characterization data were as follows. Elemental. anal.: Found (calcd) for $[(\text{C}_4\text{H}_9)_4\text{N}]_4\text{H}_4[\gamma\text{-SiW}_{10}\{\text{Cu(OH}_2)\}_2\text{O}_{38}]$: C, 20.68 (21.28); H, 3.90 (4.24); N, 1.62 (1.55). Infrared

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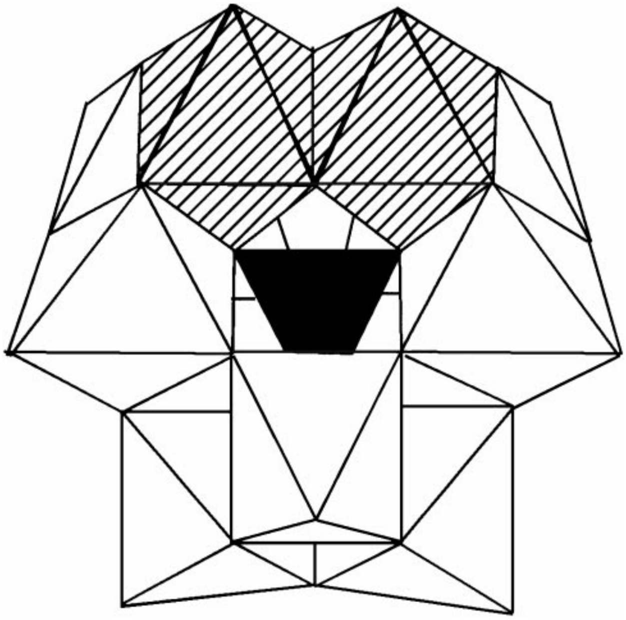

FIG. 1. Polyhedral representation of γ-SiW$_{10}$\{Fe(OH$_2$)\}$_2$O$_{38}^{6-}$. Iron ions are represented by hatched octahedra. WO$_6$ octahedra occupy the white octahedra and an SiO$_4$ group is shown as the internal black tetrahedron.

spectrum (cm^{-1}): 999 (m), 959 (s), 899 (s), 875 (s), 777 (s, br), and 553 (m). UV–visible spectrum in acetonitrile at 296 K: $\lambda = 270$ nm (ε 22800 M^{-1} cm^{-1}), 340 nm (ε 2790 M^{-1} cm^{-1}), 720 nm (ε 35 M^{-1} cm^{-1}), and 870 nm (ε 25 M^{-1} cm^{-1}).

Titration of Hydrogen Peroxide

The titration of hydrogen peroxide was carried out according to Ref. (19). First 1–2 g of the reaction solution was accurately weighed and quickly dissolved in 200 ml water. The solution was stirred with a magnetic stir bar at 296 K. Titration data were obtained with HM-30 pH meter (TOA Electrochemical Measuring Instruments). The potential was monitored as a solution of Ce(NH$_4$)$_4$(SO$_4$)$_4 \cdot 2$H$_2$O in water (0.1 M) was added with a buret into the solution at 0.1-ml intervals.

Catalytic Reaction

Homogeneous oxidation reactions were carried out in a glass vessel by mixing of 1.0 mmol of substrate, 0.2 mmol of 30% hydrogen peroxide, and 8 μmol polyoxometalate with acetonitrile (6 ml) under Ar. The reaction solution was periodically sampled and analyzed by GC on TC-WAX and FFAP capillary columns. For the calculation of the efficiency of hydrogen peroxide utilization, epoxides, alcohols, and ketones were counted as requiring one, one, and two oxidizing equivalents, respectively. The gas phase analysis was carried out by TCD GC with Porapak Q and Molecular Sieve 5A columns.

RESULTS AND DISCUSSION

The oxidation of cyclooctene with hydrogen peroxide was carried out in the presence of γ-SiW$_{10}$\{Fe(OH$_2$)\}$_2$O$_{38}^{6-}$ for 24 h at 305 K. The time course is shown in Fig. 2. Cyclooctene oxide is the major product and no induction period was observed for the formation. The selectivity to cyclooctene oxide was 96% after 24 h. Only small amounts of 2-cycloocten-1-ol and 2-cycloocten-1-one were observed. Neither acids nor carbon oxides were observed. After 24 h, hydrogen peroxide was completely consumed and the reaction stopped. It is remarkable that the efficiency of hydrogen peroxide utilization to products was almost 100%.

The efficiency on TBA-**I** was higher than those reported for iron complexes in oxidations of cyclohexene and cyclooctene with hydrogen peroxide; in cyclohexene oxidation, Fe(PA)$_2$ (PA is picolinic acid) (efficiency, 59%) (20), Fe(cyclam)(CF$_3$SO$_3$)$_2$ (cyclam is 1,4,8,11-tetraazacycloteetradecane) (42%) (21), FeCl$_3$ (11%) (22), and Fe$_3$O (OAc)$_6$(H$_2$O)$_3$ (4.2%) (23); in cyclooctene oxidation, Fe$_2$O (L)$_4$(H$_2$O)$_2$(ClO$_4$)$_4$ (L is (-)4,5 pinene bipyridine) (36%) (24) and [Fe$_4^{\mathrm{III}}$(H$_2$O)$_2$(PW$_9$O$_{34}$)$_2$]$^{6-}$ (0.32%) (25). The Gif system shows high efficiency and conversion for alkane oxidations, but is inactive for alkene epoxidations (5, 20, 21). To date, almost 100% efficiency in the epoxidation of cyclooctene with hydrogen peroxide has also been achieved for the Mn(TDCPP)Cl/Im system (H$_2$TDCPP is 5,10,15,20-tetrakis-2′,4′,6′-terimethylphenyl)porphirin) (11), TS-1, and Ti-beta (12–14). These catalysts show a high efficiency of hydrogen peroxide utilization for alkene oxidations, but a lower efficiency for alkane oxidations. In contrast with the iron, manganese, or titanium complexes as described

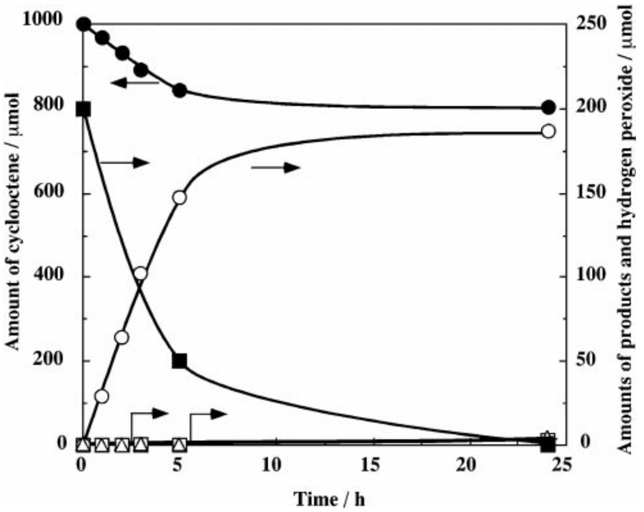

FIG. 2. Time course of oxidation of cyclooctene with hydrogen peroxide catalyzed by γ-SiW$_{10}$\{Fe(OH$_2$)\}$_2$O$_{38}^{6-}$ in acetonitrile at 305 K: (●) cyclooctene; (○) cyclooctene oxide; (□) 2-cycloocten-1-ol; (△) 2-cycloocten-1-one; (■) hydrogen peroxide.

TABLE 1

Oxidation of Alkenes Catalyzed by γ-SiW$_{10}$\{Fe(OH$_2$)\}$_2$O$_{38}^{6-}$ at 305 K

Substrate	Amount (μmol)		Conversion (%)		Product	Selectivity (%)	Efficiency for H_2O_2 utilization (%)[a]
	Substrate	H_2O_2	Substrate	H_2O_2			
Cyclooctene	1000	200	19	100	Cyclooctene oxide	96	99
					2-Cycloocten-1-ol	2	
					2-Cycloocten-1-one	2	
	1000	500	32	100	Cyclooctene oxide	97	66
					2-Cycloocten-1-ol	1	
					2-Cycloocten-1-one	2	
	1000	1000	40	97	Cyclooctene oxide	98	41
					2-Cycloocten-1-ol	1	
					2-Cycloocten-1-one	1	
	1000	1500	40	98	Cyclooctene oxide	96	27
					2-Cycloocten-1-ol	2	
					2-Cycloocten-1-one	2	
2-Octene	1000	200	17	100	2,3-Octene oxide	89	92
					2-Octen-4-ol	6	
					2-Octen-4-one	5	
1-Octene	1000	200	10	100	1,2-Octene oxide	85	53
					1-Octen-3-ol	8	
					1-Octen-3-one	7	
Cyclohexene	1000	200	16	100	Cyclohexene oxide	48	99
					2-Cyclohexen-1-ol	26	
					2-Cyclohexen-1-one	26	
	1000[b]	1000[b]	26[b]	100[b]	Cyclohexene oxide	9[b]	43[b]
					2-Cyclohexen-1-ol	18[b]	
					2-Cyclohexen-1-one	13[b]	
					1,2-Cyclohexanediol	60[b]	
Styrene	1000	200	9	100	Styrene oxide	76	40
					Benzaldehyde	24	
trans-Stilbene	1000[c]	200[c]	4[c]	100[c]	*trans*-Stilbene oxide	66[c]	27[c]
					Benzaldehyde	34[c]	
	500[b]	500[b]	18[b]	100[b]	*trans*-Stilbene oxide	66[b]	24[b]
					Benzaldehyde	34[b]	

Note. Catalyst, 8 μmol; acetonitrile, 6 ml; reaction time, 24–96 h.

[a] ([epoxide] + [alcohol] + 2[ketone] + [aldehyde])/$[H_2O_2]_c \times 100$ (%), where $[H_2O_2]_c$ is the concentration of H_2O_2 consumed.

[b] Cited from Ref. (15).

[c] Acetonitrile, 9 ml.

above, γ-SiW$_{10}$\{Fe(OH$_2$)\}$_2$O$_{38}^{6-}$ showed a high efficiency of hydrogen peroxide utilization for both oxidations of alkenes and alkanes.

Results of oxidation reactions of 2-octene, 1-octene, and cyclohexene catalyzed by γ-SiW$_{10}$\{Fe(OH$_2$)\}$_2$O$_{38}^{6-}$ are summarized in Table 1. Not only cyclooctene but also 2-octene and cyclohexene were catalytically oxidized with $\geq$92% efficiency of hydrogen peroxide utilization. The conversion and efficiency decreased for the oxidation of 1-octene with the electron deficient double bond. The epoxidation and oxidative cleavage was observed for styrene; the oxidation of styrene with hydrogen peroxide gave styrene oxide and benzaldehyde with selectivities of 76 and 24%, respectively. The efficiency for oxidation of cyclooctene and cyclohexene decreased to 27–66% with increases in the molar cycloalkenes to hydrogen peroxide ratios from 0.2 to 0.5–1.5 as shown in Table 1 while 12-tungstophosphoric acid combined with cetylpyridinium chloride shows ca. 60% efficiency for epoxidation of cyclooctene with the molar cyclooctene to hydrogen peroxide ratio of 1.5 (26, 27).

Table 2 shows the results of cyclooctene oxidation catalyzed by *di*-transition-metal-substituted and *mono*-, *di*-, and *tri*-iron-substituted silicotungstates. Cyclooctene oxide was the major product for each reaction. γ-SiW$_{10}$Mn$_2$O$_{38}^{6-}$ and γ-SiW$_{10}$\{Cu(OH$_2$)\}$_2$O$_{38}^{8-}$ silicotungstates were much less active and less efficient for the utilization of hydrogen peroxide than γ-SiW$_{10}$\{Fe(OH$_2$)\}$_2$O$_{38}^{6-}$, showing that iron is an effective element. The conversions of iron substituted silicotungstates decreased in the order of γ-SiW$_{10}$\{Fe(OH$_2$)\}$_2$O$_{38}^{6-}$ $>$ α-SiW$_9$\{Fe(OH$_2$)\}$_3$O$_{37}^{7-}$ $\gg$ α-SiW$_{11}$Fe(OH$_2$)O$_{39}^{5-}$ $\approx$ α-SiW$_{12}$O$_{40}^{4-}$ and the efficiency of hydrogen peroxide utilization decreased in the same order. Thus, the activity and efficiency for the utilization of hydrogen peroxide greatly depended on both kinds of transition

TABLE 2

Oxidation of Cyclooctene with Hydrogen Peroxide Catalyzed by *di*-Transition-Metal- and Iron-Substituted Silicotungstates at 305 K

Catalysts	Conversion (%)[a]	Selectivity (%)			H_2O_2 consumed (μmol)	Efficiency for H_2O_2 utilization (%)[a]
		Cyclooctene oxide	2-Cycloocten-1-ol	2-Cycloocten-1-one		
γ-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$	19	96	2	2	200	99
γ-$SiW_{10}\{Cu(OH_2)\}_2O_{38}^{8-}$	3	96	2	2	200	13
γ-$SiW_{10}\{Mn(OH_2)\}_2O_{38}^{6-}$	0	—	—	—	200	0
α-$SiW_{12}O_{40}^{4-}$	1	100	0	0	26	42
α-$SiW_{11}Fe(OH_2)O_{39}^{5-}$	1	100	0	0	28	25
α-$SiW_9\{Fe(OH_2)\}_3O_{37}^{7-}$	10	100	0	0	200	51

Note. Catalyst, 8 μmol; acetonitrile, 6 ml; substrate, 1 mmol; H_2O_2, 0.2 mmol; reaction time, 24 h.

[a] See Table 1.

metals and structures of iron centers, and *di*-iron-substituted γ-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$ showed the highest efficiency of hydrogen peroxide utilization and conversion among various silicotungstates.

We previously reported that nonradical processes prevail to a major degree and high-valent iron species, e.g., oxoiron, are not the major iron oxidant species (15). The following facts are consistent with this idea. (i) The oxidations of octenes in Table 1 showed low selectivity with allylic attack. (ii) No induction period was observed for the formation of cyclooctene oxide, 2-cyclooctene-1-one, and 2-cycloocten-1-ol (Fig. 2). (iii) The oxidation of *trans*-stilbene gave *trans*-stilbene oxide and benzaldehyde with selectivities of 66 and 34%, respectively (Table 1).

In conclusion, *di*-iron-substituted silicotungstate has been shown to catalyze the selective epoxidation of alkenes at 305 K with a very high efficiency of hydrogen peroxide utilization.

ACKNOWLEDGMENT

This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

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