Efficient sulfoxidation with hydrogen peroxide catalyzed by a divanadium-substituted phosphotungstate

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A B S T R A C T

A divanadium-substituted phosphotungstate $[\gamma\text{-PW}_{10}\text{O}_{38}\text{V}_2(\mu\text{-OH})_2]^{3-}$ (**I**) could act as an efficient homogeneous catalyst for selective oxidation of sulfides with 30% aqueous H_2O_2. By using **I** at 0.01–0.1 mol%, various kinds of sulfides including aryl, alkyl, and vinyl ones could be converted into the corresponding sulfoxides in excellent yields with one equivalent of H_2O_2 with respect to sulfides. The negative Hammett ρ value (-0.83) for competitive oxidation of *p*-substituted thioanisoles and the low X_{SO} (X_{SO} = (nucleophilic oxidation)/(total oxidation)) value (<0.01) for the **I**-catalyzed oxidation of thianthrene 5-oxide (SSO) revealed that **I** produces a strong electrophilic oxidant.

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1. Introduction

Developments of highly efficient catalytic systems for oxidation of sulfides to sulfoxides and sulfones have attracted much attention because they are important as intermediates for synthesis of natural products and 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 conventional methods using stoichiometric oxidants [5], catalytic oxidation with H_2O_2 is much more desirable because H_2O_2 is easily available and environmentally benign, and only water is formed as a by-product. Although many H_2O_2-based sulfoxidation systems with homogeneous and heterogeneous organocatalysts, acid catalysts, enzymes, and metal catalysts including polyoxometalates (POMs) have been reported [6–16], most systems have disadvantages; use of excess H_2O_2 (∼8 equivalents) with respect to sulfides and/or narrow applicability to a limited number of sulfides. As far as we know, there are only a few reports on catalytic sulfoxidation (e.g., Ti-, V-, W-, and Fe-based catalytic systems [7,8,10,11,16]), which shows a wide substrate scope with one equivalent of H_2O_2.

POMs are early transition-metal (V, Nb, Ta, Mo, W, etc.) oxygen cluster anions with discrete and versatile structures [17–23]. These inorganic compounds have attracted much attention in structural chemistry, biological chemistry, catalysis, molecular magnetism, and advanced material science [17–23]. Oxidation catalysis by POMs has received much attention because their chemical properties can finely be tuned by choosing constituent elements and counter cations, and they are thermally and oxidatively stable in comparison with organometallic complexes, organocatalysts, and enzymes. To date, various kinds of POMs have been developed for the H_2O_2- and O_2-based green oxidations [19–23].

We have recently reported highly efficient H_2O_2-based oxidations catalyzed by a divanadium-substituted phosphotungstate $[\gamma\text{-PW}_{10}\text{O}_{38}\text{V}_2(\mu\text{-OH})_2]^{3-}$ (**I**, Fig. 1) [24–26]. Compound **I** acts as an active homogeneous catalyst for (i) hydroxylation of alkanes, (ii) epoxidation of alkenes including electron-deficient ones, and (iii) oxidative bromination of alkenes, alkynes, and aromatics with Br^- as a bromo source (Fig. 2). In this paper, we report the **I**-catalyzed oxidation of sulfides with H_2O_2, which has never been reported previously. In the presence of **I**, various kinds of sulfides including aryl, alkyl, and vinyl ones can selectively be converted into the corresponding sulfoxides with one equivalent of H_2O_2. In addition, electronic nature of the active oxygen species formed on **I** is investigated.

2. Experimental

Inorganic salts, solvents, substrates, and 30% aqueous H_2O_2 were obtained from Tokyo Kasei, Wako, Kanto, or Aldrich (reagent grade). Solvents and substrates were purified prior to the use [27]. POMs including **I** were synthesized according to previously reported procedures [16,26,28].

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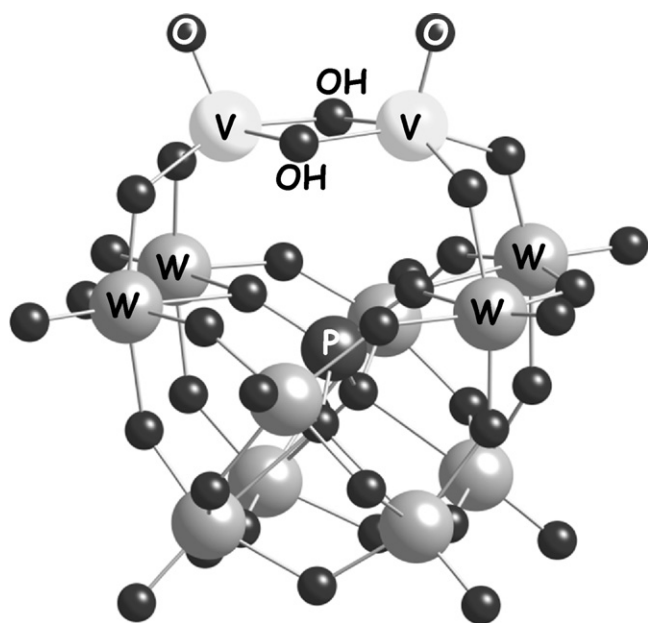*E-mail address:* tmizuno@mail.ecc.u-tokyo.ac.jp (N. Mizuno).

Fig. 1. Molecular structure of **I**.

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 comparison of their GC retention times, mass spectra, and NMR spectra with those of the authentic samples. A typical procedure for the catalytic oxidation was as follows: $TBA_4[\gamma\text{-}HPV_2W_{10}O_{40}]$ (TBA = $[(n\text{-}C_4H_9)_4N]^+$, 1 μmol), 70% aqueous perchloric acid (1 μmol), **1a** (1 mmol), and CH_3CN/t-BuOH (1.5/1.5 mL) were charged in a reaction vessel. The reaction was initiated by addition of 30% aqueous H_2O_2 (1 mmol), and the reaction solution was periodically analyzed. Before the GC analysis, the remaining H_2O_2 was decomposed at 273 K by addition of $Ru(OH)_x/Al_2O_3$ [29].

Thianthrene 5-oxide (SSO) and the corresponding oxygenated products (i.e., *cis*-thianthrene 5,10-dioxide (*cis*-SOSO), *trans*-thianthrene 5,10-dioxide (*trans*-SOSO), thianthrene 5,5-dioxide (SSO_2), and thianthrene 5,5,10-trioxide ($SOSO_2$)), were synthesized according to previously reported procedures [30,31]. The oxidation products were quantitatively analyzed by HPLC with a UV detector: CAPCELL PAK MG C18-reverse phase column (5 μm × ⌀3 mm × 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. The X_{SO} value was calculated according to the following equation [32], X_{SO} = (nucleophilic oxidation)/(total oxidation) = ($SSO_2 + SOSO_2$)/($SSO_2 + SOSO + 2SOSO_2$).

3. Results and discussion

First, effects of solvents, oxidants, and catalysts on oxidation of thioanisole (**1a**) were investigated (Table 1). In the presence of **I**, the sulfoxidation of **1a** in CH_3CN/t-BuOH (1/1, v/v) efficiently proceeded to give the corresponding sulfoxide (**2a**) in 78% yield under the stoichiometric conditions using an equimolar amount of H_2O_2 with respect to **1a** (**1a**:H_2O_2:**I** = 1000:1000:1) (Table 1, entry 1). The yield and selectivity to **2a** for oxidation of **1a** under argon were almost the same as those of oxidation under air, showing that possibility of participation of molecular oxygen in air is excluded (Table 1, entries 1 and 2). Compound **I** was much more active than $[\gamma\text{-}SiW_{10}O_{38}V_2(\mu\text{-}OH)_2]^{4-}$, showing catalytic activities of divanadium-substituted POMs are dependent on kinds of the heteroatoms in a similar way to those of hydroxylation of alkanes, epoxidation of alkenes, and oxidative bromination with H_2O_2 (Table 1, entries 1 and 11) [24–26]. Mono- and tri-vanadium-substituted phosphotungstates, $[\alpha\text{-}PVW_{11}O_{40}]^{4-}$ and $[\alpha\text{-}H_2PV_3W_9O_{40}]^{4-}$, showed lower catalytic activities (Table 1, entries 12 and 13), suggesting that the active sites are not the V—O—W and V=O sites but the bis-μ-hydroxo site of {OV—(μ-OH)$_2$—VO} in **I**. On the basis of the kinetic, spectroscopic, and computational results, it has been revealed that the bis-μ-hydroxo site can cooperatively activate H_2O_2 to form the strong elec-
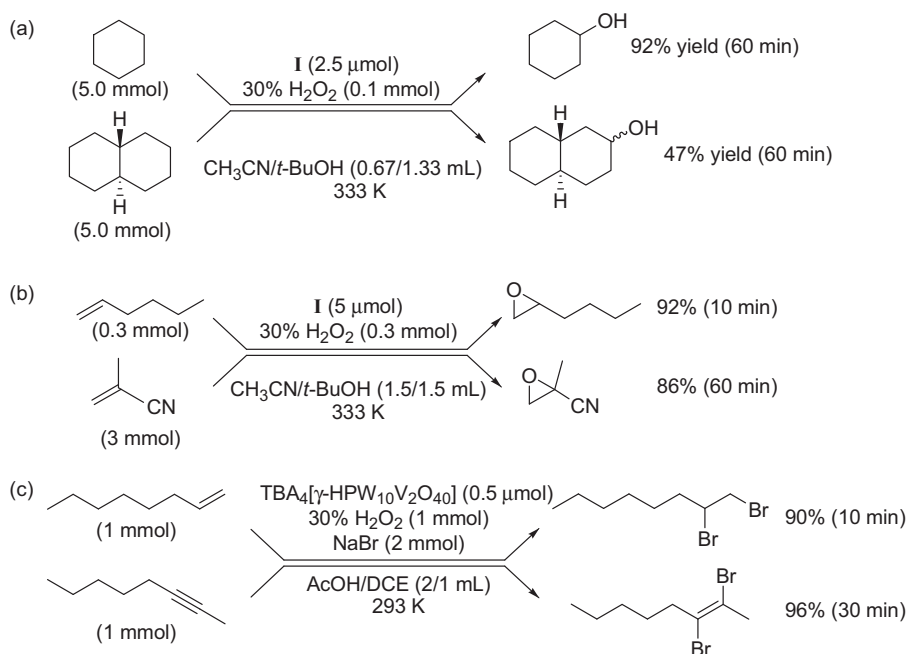

Fig. 2. Selective oxidation with H_2O_2 catalyzed by **I**. (a) Hydroxylation of alkanes [24], (b) epoxidation of alkenes [26], and (c) oxidative bromination of alkenes and alkynes [25].