Oxidative functional group transformations with hydrogen peroxide catalyzed by a divanadium-substituted phosphotungstate

Noritaka Mizuno*, Keigo Kamata, Kazuya Yamaguchi

Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

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ABSTRACT

A divanadium-substituted phosphotungstate $TBA_4[\gamma\text{-}PW_{10}O_{38}V_2(\mu\text{-}OH)(\mu\text{-}O)]$ (**I**, TBA = tetra-n-butylammonium) reacts with one equivalent H^+ to form a bis-μ-hydroxo species $[\gamma\text{-}PW_{10}O_{38}V_2(\mu\text{-}OH)_2]^{3-}$ (**I′**) in organic media. The strong electrophilic oxidants such as $[\gamma\text{-}PW_{10}O_{38}V_2(\mu\text{-}OH)(\mu\text{-}OOH)]^{3-}$ (**II**) and $[\gamma\text{-}PW_{10}O_{38}V_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2)]^{3-}$ (**III**) are formed by the reaction of the bis-μ-hydroxo species with H_2O_2. In the presence of **I** and H^+, H_2O_2-based oxidations such as (i) epoxidation of alkenes (17 examples including electron-deficient ones), (ii) hydroxylation of alkanes (11 examples), and (iii) oxidative bromination of alkenes, alkynes, and aromatics with Br^- as a bromo source (12 examples including chlorination) chemo-, diastereo-, and regioselectively proceed to give the corresponding oxidized products in moderate to high yields with high efficiencies of H_2O_2 utilization.

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1. Introduction

Oxidations of organic substrates are very important reactions, and the choice of oxidants determines practicability and efficiency of the systems. H_2O_2 is regarded as one of the "greenest" oxidants because of its high content of active oxygen species (47 wt%), high atom efficiency, and co-production of only water. The key for development of efficient H_2O_2-based oxidation systems is the design of catalysts that can effectively activate H_2O_2 and transferring of the active oxygen species to various substrates with high efficiencies and selectivities. In order to develop green oxidation systems with H_2O_2, our research group has continued to design and synthesize "molecular catalysts" based on polyoxometalates (POMs) [1].

POMs are thermally and oxidatively stable metal–oxygen anionic clusters of early transition metals and stimulated many current research activities in broad fields of science because their properties can finely be tuned by choosing constituent elements and counter cations [1–8]. Particularly, the interests in the catalysis of metal-substituted POMs, which can easily be synthesized by introduction of metal cations into the vacant site(s) of lacunary POMs as "structural motifs", have been growing. The rich diversity of lacunary POMs (ranging from monovacant to hexavacant) can lead to design various metal-substituted POMs with "controlled active sites" at the molecular level [1–8].

Very recently, we found that various H_2O_2-based oxidations effectively and selectively proceeds in the presence of a divanadium-substituted phosphotungstate $TBA_4[\gamma\text{-}PW_{10}O_{38}V_2(\mu\text{-}OH)(\mu\text{-}O)]$ (**I**, TBA = tetra-n-butylammonium) [9–11]. In this paper, we carefully examine and discuss the activation of H_2O_2 with **I** (in the presence of H^+) by means of various characterizations such as cold-spray ionization mass spectrometry (CSI-MS) and NMR spectroscopy. In addition, we extend the scope of the **I**-catalyzed H_2O_2-based oxidations such as (i) epoxidation of alkenes including electron-deficient ones, (ii) hydroxylation of alkanes, and (iii) oxidative bromination of alkenes, alkynes, and aromatics with Br^- as a bromo source (including chlorination).

2. Experimental

Inorganic salts (precursors of POMs, catalysts, and bromo and chloro sources), solvents, substrates, and 30% aq. H_2O_2 were obtained from Tokyo Kasei, Wako, Kanto, or Aldrich (reagent grade). Solvents and substrates were purified prior to the use [12]. Compound **I** was synthesized according to the previously reported procedures (see Section 3.1) [9].

The catalytic oxidations were carried out with a glass tube reactor containing a magnetic stir bar. Compound **I**, solvent, substrate, and acid (70% aq. $HClO_4$ for epoxidation and hydroxylation, AcOH for halogenation) were charged in the reactor (bromo or chloro source was also added for halogenation). The reaction was initiated by addition of 30% aq. H_2O_2. Detailed reaction conditions were given in the footnotes of Tables and Figures. The reaction progress was periodically monitored by GC or NMR. The products were confirmed by comparison of their GC–MS and NMR (^{1}H and ^{13}C) spectra with those of authentic data.

* Corresponding author. Tel.: +81 3 5841 7272; fax: +81 3 5841 7220.
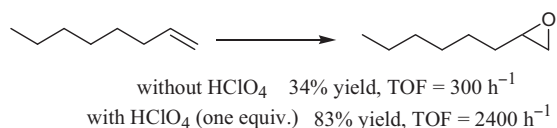*E-mail address:* tmizuno@mail.ecc.u-tokyo.ac.jp (N. Mizuno).

without HClO$_4$ 34% yield, TOF = 300 h^{-1}
with HClO$_4$ (one equiv.)   83% yield, TOF = 2400 h^{-1}

Fig. 1. Epoxidation of 1-octene. *Reaction conditions*: **I** (5 μmol), 1-octene (0.1 mmol), 30% aq. H$_2$O$_2$ (0.1 mmol), CH$_3$CN/*t*-BuOH (1.5/1.5 mL), 60 °C, 10 min.
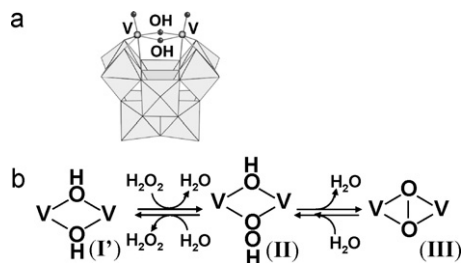

Fig. 2. (a) Structure of a bis-μ-hydroxo species **I′** and (b) activation of H$_2$O$_2$ with **I′** to form strong electrophilic oxidants such as **II** and **III**. The {WO$_6$} moieties occupy the octahedra, and the {PO$_4$} group is shown as the central tetrahedron.

3. Results and discussion

3.1. Activation of H$_2$O$_2$ with a bis-μ-hydroxo species

Compound **I** was synthesized by cation-exchange reaction of the cesium salt of a deprotonated divanadium-substituted phosphotungstate Cs$_5$[γ-PW$_{10}$O$_{38}$V$_2$(μ-O)$_2$] [13] with TBABr in an acidic medium [9]. The divanadium species in **I** was bridged with one hydroxo and one oxo ligands ({V$_2$(μ-OH)(μ-O)}). Compound **I** showed catalytic activity for epoxidation of terminal alkenes, e.g., 1-octene, with H$_2$O$_2$ (Fig. 1). In contrast, no reaction proceeded in the presence of commonly utilized vanadium compounds such as V$_2$O$_5$, NaVO$_3$, VOSO$_4$, VO(acac)$_2$, and VO(O-*t*-Bu)$_3$ under the present conditions. Surprisingly, the rate of the **I**-catalyzed epoxidation increased by a factor of 8 in the presence of only one equivalent HClO$_4$ (H$^+$) with respect to **I** (Fig. 1). The **I**-catalyzed epoxidation was carried out with different amounts of HClO$_4$ (0–1.5 equivalents with respect to **I**). The yields and the reaction rates linearly increased with an increase in the amounts of HClO$_4$ up to 1 equivalent and then did not much change. In addition, no epoxidation with HClO$_4$ proceeded in the absence of **I** (blank test).

The ^{31}P NMR spectrum (in CD$_3$CN) showed a single line at −13.8 ppm, showing that the polyanion exists as a single species in the solution. The ^{51}V NMR spectrum of **I** with HClO$_4$ (one equivalent) gave a single line at −578 ppm, showing that the two vanadium species are equivalent. The ^{1}H NMR spectrum gave a broad line at 7.0 ppm (two H$^+$ per one anion) assignable to protons of the bis-μ-hydroxo groups [14,15]. These results show that protonation of the oxo species in **I** takes place to form a bis-μ-hydroxo species [γ-PW$_{10}$O$_{38}$V$_2$(μ-OH)$_2$]$^{3-}$ (**I′**, Fig. 2(a)). Taking the above-mentioned results into account, the formation of the bis-μ-hydroxo species is very important to activate H$_2$O$_2$ effectively (Fig. 1), and the role of HClO$_4$ is a proton source to generate the active **I′** species from **I**.

Next, the reaction of **I′** with H$_2$O$_2$ was investigated. The CSI-MS (cation mode) spectrum of **I′** in 1,2-dichloroethane showed two set of signals (Fig. 3(a)). The set of signals **A** (centred at *m/z* = 3583) had an isotopic distribution that agrees with the calculated pattern of a bis-μ-hydroxo species {TBA$_4$[PW$_{10}$O$_{38}$V$_2$(μ-OH)$_2$]}$^+$ (Fig. 3(b)). The set of signals **A′** (centred at *m/z* = 3565 (3583 − 18)) was due to the fragment of **I′** (possibly {TBA$_4$[PW$_{10}$O$_{38}$V$_2$(μ-O)]}$^+$) [16]. Upon addition of H$_2$O$_2$ (430 equivalents with respect to **I**) to the solution, a new set of signals (**B**) centred at *m/z* = 3599 (3583 + 16)
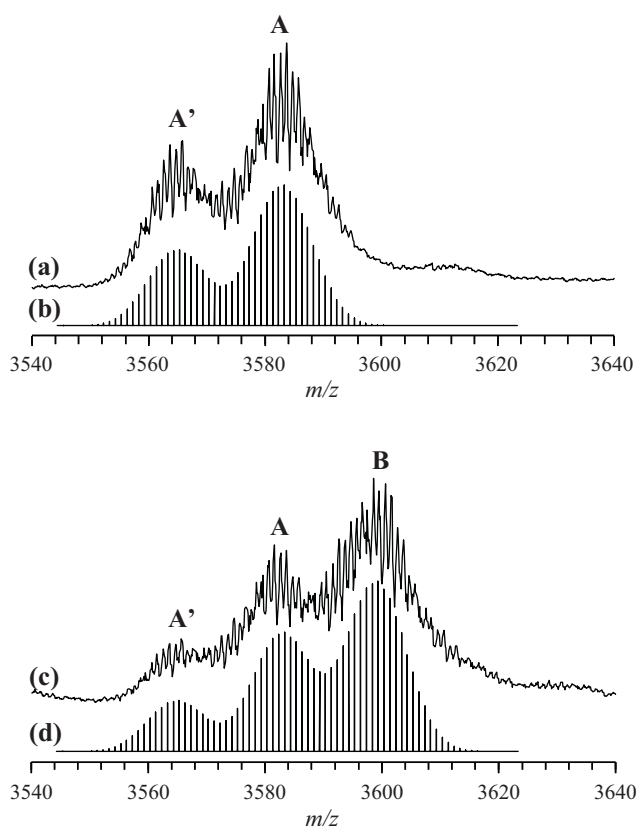

Fig. 3. CSI-MS (cation mode) of (a) **I′** and (c) **I′** treated with H$_2$O$_2$: **I′** (0.56 mM), 1,2-dichloroethane, 95% H$_2$O$_2$ (430 equivalents with respect to **I′**), −20 °C, 5 min. The lines in (b) are the pattern calculated for a mixture of {TBA$_4$[PW$_{10}$O$_{38}$V$_2$(μ-O)]}$^+$ (35%) and {TBA$_4$[PW$_{10}$O$_{38}$V$_2$(μ-OH)$_2$]}$^+$ (65%). The lines in (d) are the pattern calculated for a mixture of {TBA$_4$[PW$_{10}$O$_{38}$V$_2$(μ-O)]}$^+$ (35%), {TBA$_4$[PW$_{10}$O$_{38}$V$_2$(μ-OH)$_2$]}$^+$ (40%), and {TBA$_4$[PW$_{10}$O$_{38}$V$_2$(μ-OH)(μ-OOH)]}$^+$ (**II**, 25%).

appeared (Fig. 3(c)). The set of signals is likely assignable to the calculated pattern of a hydroperoxo species {TBA$_4$[PW$_{10}$O$_{38}$V$_2$(μ-OH)(μ-OOH)]}$^+$ (Fig. 3(d)). In addition, in the ^{1}H NMR spectrum of **I′** treated with H$_2$O$_2$ (in 1,2-dichloroethane-*d$_4$*), protons assignable to hydroperoxo (at 9.49 ppm) and hydroxo (at 5.31 ppm) species were observed [14,15]. These CSI-MS and NMR data strongly suggest the formation of a hydroperoxo species [γ-PW$_{10}$O$_{38}$V$_2$(μ-OH)(μ-OOH)]$^{3-}$ (**II**) by the reaction of the bis-μ-hydroxo core in **I′** with H$_2$O$_2$.

In the ^{51}V NMR spectrum of **I′** treated with H$_2$O$_2$ (in CD$_3$CN/*t*-BuOH), three signals were observed (Fig. 4), and these species are in equilibrium. Signals at −582 and −561 ppm were assignable to the bis-μ-hydroxo (**I′**) and the hydroperoxo species (**II**) [9–11], respectively. In addition to these signals, a signal at −630 ppm was observed (**III**). The concentration ratio of [**II**]/[**I′**] in equilibrium was proportional to [H$_2$O$_2$]/[H$_2$O] (Fig. 5(a)), supporting the reversible formation of **II**. The ratio of [**III**]/[**I′**] was proportional to [H$_2$O$_2$]/[H$_2$O]^2 (Fig. 5(b)). Therefore, it is likely that **III** is the μ-η^2:η^2-peroxo species [γ-PW$_{10}$O$_{38}$V$_2$(μ-η^2:η^2-O$_2$)]$^{3-}$ formed by the successive dehydration of **II** [14,15].

On the basis of the above-mentioned experimental results, we summarize a possible path for the formation of electrophilic oxidants **II** and **III** by the reaction of **I** (in the presence of H$^+$) with H$_2$O$_2$ (Fig. 2(b)). Upon addition of organic substrates, e.g., 1-octene, to a CH$_3$CN/*t*-BuOH (v/v = 1/1) solution containing **I′**, **II**, and **III**, the ^{51}V NMR signal of **II** was weakened and that of **III** almost disappeared, suggesting that **III** is the (main) active species for the oxidation. We hereafter mention the applicability of the **I**/H$^+$/H$_2$O$_2$ system to various H$_2$O$_2$-based oxidations.
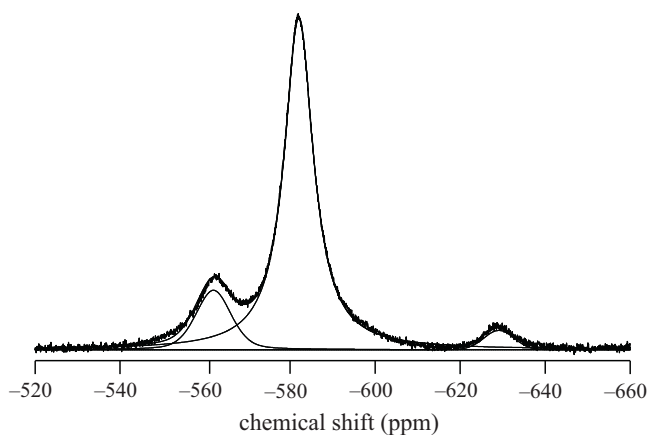
Fig. 4. ^{51}V NMR spectrum of a bis-μ-hydroxo species $[\gamma\text{-}PW_{10}O_{38}V_2(\mu\text{-}OH)_2]^{3-}$ treated with H_2O_2: **I** (3.3 mM), $HClO_4$ (3.3 mM), CD_3CN/t-BuOH (1/2 mL), H_2O_2 (72 mM), H_2O (106 mM).

3.2. Epoxidation of alkenes

The development of efficient catalysts for the H_2O_2-based epoxidation of alkenes is one of the most important challenging subjects. We found that epoxidation chemo-, diastereo-, and regioselectively proceeds, giving the corresponding epoxides in high yields with high efficiencies of H_2O_2 utilization in the presence of **I**. The scope of the **I**-catalyzed epoxidation is summarized in Table 1. Epoxidation of common terminal (including propylene) as well as cyclic alkenes efficiently proceeded to give the corresponding epoxides in high yields within only 10 min using one equivalent H_2O_2. As

Table 1
Epoxidation of various alkenes.[a]

Substrate	Product	Time (min)	Yield (%)
(propylene)	(epoxide)	10[b]	90
n-C$_4$H$_9$—	n-C$_4$H$_9$—	10	90
n-C$_5$H$_{11}$—	n-C$_5$H$_{11}$—	10	88
(cyclohexene)		5	74
(cyclooctene)		10	95
(3-methylcyclohexene)		10	87[c]
(trans-1,4-hexadiene)		10	81[d]
(d-limonene)		10	85[d]
AcO—	AcO—	60	84
Cl—	Cl—	60	73
(diallyl ether epoxide)		60	87
n-C$_4$H$_9$—O—	n-C$_4$H$_9$—O—	60	68
Ph—O—	Ph—O—	60	70
		60	74
		60	94[e]
HO—	HO—	60	94[e]
NC—	NC—	60	86[e]

[a] *Reaction conditions*: **I** (5 µmol), $HClO_4$ (5 µmol), substrate (0.3 mmol), 30% aq. H_2O_2 (0.3 mmol), CH_3CN/t-BuOH (1.5/1.5 mL), 60 °C.
[b] Propylene (6 atm).
[c] *Trans/cis* = 94/6.
[d] [Terminal epoxide]/[Total epoxides] ≥ 0.99.
[e] Substrate (3 mmol).

Fig. 5. Plots of (a) $[\mathbf{II}]/[\mathbf{I'}]$ against $[H_2O_2]/[H_2O]$ and (b) $[\mathbf{III}]/[\mathbf{I'}]$ against $[H_2O_2]/[H_2O]^2$. The concentrations of **I'**, **II**, and **III** were estimated by ^{51}V NMR.

mentioned in Fig. 1, the turnover frequency (TOF) for the **I**-catalyzed epoxidation of 1-octene reached up to 2400 h^{-1}, and the value was the largest among those reported for the metal-catalyzed H_2O_2-based epoxidations of terminal alkenes ($\sim$700 h^{-1}) [17–20]. For the epoxidation of *cis*-2-octene, the configuration around the double bond was completely retained in the corresponding epoxide, showing that the present epoxidation proceeds via a non-radicalic way. The high *trans* diastereoselectivity (*trans/cis* = 94/6) for the epoxidation of 3-methyl-1-cyclohexene was observed. In the case of non-conjugated dienes such as *trans*-1,4-hexadiene and *d*-limonene, the more accessible terminal double bonds (not more reactive electron-rich internal ones) were epoxidized with a completely regioselective manner. These unprecedented diastereo- and regioselectivities are likely due to the steric hindrance of the active oxygen species formed on the rigid polyanion framework.

Next, we turn our attention to epoxidation of electron-deficient alkenes with acetate, chloro, ether, carbonyl, and cyano groups at the allylic positions. Orbital energies of π(C=C) HOMO of these alkenes (ranging from -10.15 to -10.95 eV) are significantly lower than those of common alkenes (ca. -9 eV). Therefore, nucleophilic oxidants, e.g., OOH^- generated from H_2O_2 under strong alkaline conditions, rather than electrophilic oxidants are generally useful for these alkenes [21–25]. However, many functional groups are not intact because of the strong alkaline conditions and the strong nucleophilic nature of oxidants. Thus, the applicability of nucleophilic oxidants is very limited. In the presence of **I**, alkenes with various electron-withdrawing functional groups at the allylic positions, e.g., acetate, chloro, ether, carbonyl, and cyano groups, selectively oxidized to the corresponding epoxides in moderate to high yields (Table 1). These results suggest that the electrophilic oxidants formed on **I** are strong enough to oxidize such electron-deficient alkenes. In particular, it is notable that the epoxidation of methacrylonitrile chemoselectively proceeded to give the corresponding epoxynitrile without formation of the corresponding epoxyamide. On the other hand, in the epoxidation with OOH^-, the formation of epoxyamide is intrinsically inevitable [21–25].

3.3. Hydroxylation of alkanes

Selective oxygenation of alkanes under mild conditions remains to be a major challenge in industrial as well as synthetic chemistry [26–29]. We found that **I** can act as an efficient homogeneous catalyst for H_2O_2-based hydroxylation of various alkanes. The results are summarized in Table 2. Oxidation of cyclic alkanes such as cyclohexane, cyclooctane, cyclododecane, adamantane, and norbornane proceeded selectively ($\geq98\%$ selectivity), giving the corresponding secondary alcohols without significant formation of the corresponding ketones and C–C bond cleaved products. Previously, we reported that secondary alcohols hardly react with the bis-μ-hydroxo in $[\gamma\text{-SiW}_{10}O_{38}V_2(\mu\text{-OH})_2]^{4-}$ because of the steric crowding between secondary alcohols and the polyanion framework [30]. Therefore, the present high selectivity to secondary alcohols for cyclic alkanes would cause the suppression of successive alcohols oxidations. Acyclic alkanes such as propane, butane, 2-methylpropane, and *n*-hexane were also oxidized to the corresponding alcohols as major products.

The regioselectivity for the hydroxylation of substituted cycloalkanes such as 1,2-dimethylcyclohexane and *trans*-decalin with both secondary and tertiary C–H bonds was next examined. For both substrates, the stereospecific hydroxylations took place (Table 2): The oxidation of 1,2-dimethylcyclohexane and *trans*-decalin gave *trans*-3,4-dimethylcyclohexanol and *trans*-2-decalinol in 86% and 93% selectivities, respectively. In contrast, the mixtures of various alcohols and the corresponding ketones are obtained in the previously reported iron- and osmium-based systems [31–33]. Such high regioselectivities of **I** to the only one secondary alcohols even in the presence of the more reactive electron-rich tertiary C–H bonds have never been reported so far. This is also due to the steric hindrance of the active oxygen species formed on the rigid polyanion framework.

3.4. Oxidative bromination of alkanes, alkynes, and aromatics

Bromination of organic substrates is one of the most important transformations. Br_2 has still widely been utilized for bromination even at present despite their disadvantages. An alternative environmental friendly and economical approach is oxidative bromination using inorganic bromide (Br^-) salts as bromo sources and oxidants (H_2O_2 or O_2 is the oxidant of choice from the standpoint of green chemistry) [34]. As mentioned in Section 3.1, strong electrophilic oxidants are formed by the reaction of **I′** with H_2O_2, would effi-

Table 2
Hydroxylation of various alkanes.[a]

Substrate	Product	Time (min)	Yield (%)
(cyclohexane)	(cyclohexanol with OH)	60	92
(cyclooctane)	(cyclooctanol with OH)	60	84
(cyclododecane)	(cyclododecanol with OH)	60	79
(adamantane)	Adamantanols	120	98[b]
(norbornane)	(norbornanol with OH)	120	80
(methylcyclohexane)	Dimethylcyclohexanols	60	59[c]
(trans-decalin)	(trans-2-decalinol with OH)	60	51
(propane)	(2-propanol with OH)	300	17[d]
(butane)	(2-butanol with OH)	300	21[e]
(2-methylpropane)	(tert-butanol with OH)	300	29[f]
(n-hexane)	Hexanols	240	52[g]

[a] *Reaction conditions*: **I** (1.3 mM), $HClO_4$ (1.3 mM), substrate (4.7 M for cyclohexane, 0.3 M for adamantine, 7.5 M for *n*-hexane, 2.5 M for others), 30% aq. H_2O_2 (50 mM), CH_3CN/*t*-BuOH (0.67/1.33 mL), 60 °C (69 °C for *n*-hexane).
[b] 1-ol:2-ol:1,3-diol = 82:15:3.
[c] 3,4-Dimethyl:1,2-dimethyl:2,3-dimethyl = 86:10:4.
[d] Propane (6 atm). Acetone (17% yield).
[e] Butane (2.2 atm). 2-Butanone (3% yield).
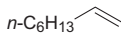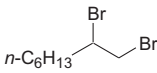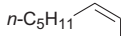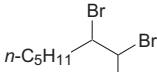[f] 2-Methlpropane (2.2 atm).
[g] 2-ol:3-ol:1-ol = 70:27:3. 2-Hexanone (4% yield).
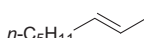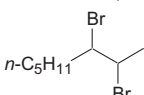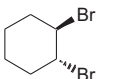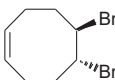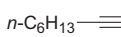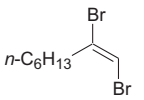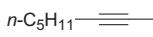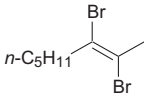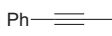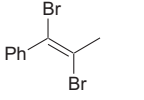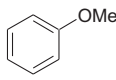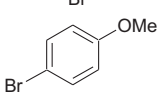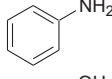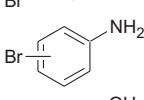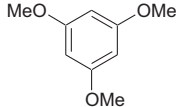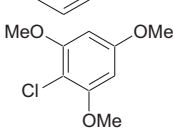
ciently oxidize Br^- to Br^+ and/or Br_2 species (active species for bromination).

As we expected, **I** showed the high catalytic performance for the H_2O_2-based oxidative bromination of various alkenes, alkynes, and aromatics under ambient conditions (Table 3). When the bromination of 1-octene was carried out with **I** using stoichiometric amounts of H_2O_2 (one equivalent) and NaBr (two equivalents), 90% yield of 1,2-dibromooctane was obtained within only 10 min. In this case, TOF reached up to 10,800 h^{-1} and much larger than those of previously reported H_2O_2-based oxidative bromination systems ($\sim$315 h^{-1}) [35–38]. The bromination of *cis*- and *trans*-2-octenes diastereoselectively proceeded to afford *threo*- and *erythro*-2,3-bromooctanes, respectively. Cyclohexene also diastereoselectively gave *trans*-1,2-dibromocyclohexane. For 1,5-cyclooctadiene, the corresponding *trans*-dibromoalkene was selectively obtained as a major product.

Notably, the **I**-catalyzed bromination of terminal as well as internal alkynes exclusively gave the corresponding *E*-dibromoalkenes without formation of *Z*-isomer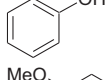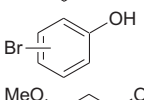s, tetrabromoalkane, ketones, and bromoketones. As above-mentioned, the strong electrophilic oxidants formed on **I** likely oxidize Br^- species. The reaction of an alkyne with the oxidized bromide species (Br^+ and/or Br_2 species) gave a cyclic bromonium cation intermediate on which unoxidized Br^- readily reacts from the reverse side

Table 3
Bromination of various alkenes, alkynes, and aromatics with NaBr.[a]

Substrate	Product	Time (min)	Yield (%)
n-C$_6$H$_{13}$ (alkene)	n-C$_6$H$_{13}$ CHBr–CH$_2$Br	10	90
n-C$_5$H$_{11}$ (cis alkene)	n-C$_5$H$_{11}$ CHBr–CHBr	10	76[b]
n-C$_5$H$_{11}$ (trans alkene)	n-C$_5$H$_{11}$ CHBr–CHBr	10	87[c]
cyclohexene	trans-1,2-dibromocyclohexane	10	82
cyclooctadiene	dibromocyclooctene	10	84
n-C$_6$H$_{13}$—≡ (alkyne)	n-C$_6$H$_{13}$ C(Br)=CHBr	60	92
n-C$_5$H$_{11}$—≡—CH$_3$ (alkyne)	n-C$_5$H$_{11}$ C(Br)=C(Br)CH$_3$	30	96
Ph—≡—CH$_3$ (alkyne)	Ph C(Br)=C(Br)CH$_3$	30	94
anisole (OMe)	4-bromoanisole (Br, OMe)	30	96
aniline (NH$_2$)	bromoaniline (Br, NH$_2$)	10	81[d]
phenol (OH)	bromophenol (Br, OH)	10	50[e]
1,3,5-trimethoxybenzene (MeO, OMe, OMe)	chloro-trimethoxybenzene (MeO, OMe, Cl, OMe)	120	88[f]

[a] *Reaction conditions*: **I** (0.5 μmol), substrate (1 mmol), 30% aq. H$_2$O$_2$ (1 mmol), NaBr (2 mmol for alkenes and alkynes, 1 mmol for aromatics), AcOH/1,2-dichloroethane (2/1 mL), 20 °C.
[b] *Threo* isomer.
[c] *Erythro* isomer.
[d] *Para*:*ortho* = 82:18.
[e] *Para*:*ortho* = 59:41.
[f] *Reaction conditions*: **I** (0.5 μmol), substrate (1 mmol), 30% aq. H$_2$O$_2$ (2 mmol), LiCl (5 mmol), AcOH/1,2-dichloroethane (2/1 mL), 60 °C.

[39], resulting in the exclusive formation of the corresponding *E*-dibromoalkene. The above-mentioned diastereoselective bromination of internal alkenes also supports this mechanism.

Bromination of aromatics such as anisole, aniline, and phenol efficiently proceeded using stoichiometric amounts of H$_2$O$_2$ (one equivalent) and NaBr (one equivalent), affording the corresponding monobromobenzene derivatives. In addition, the present system was applicable to oxidative chlorination using LiCl as a chloro source, giving the corresponding monochlorobenzene in high yield.

4. Conclusions

In summary, compound **I** could act as an efficient homogeneous catalyst for H$_2$O$_2$-based epoxidation, hydroxylation, and bromination. The strong and rigid electrophilic oxidants such as **II** and **III** were formed by the reaction of **I** (in the presence of H$^+$) with H$_2$O$_2$, which would be the active species for the present oxidations (in particular **III**).

Acknowledgment

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