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Bis(μ-hydroxo) bridged di-vanadium-catalyzed selective epoxidation of alkenes with H_2O_2

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Abstract

The Keggin-type di-vanadium-substituted silicotungstate $[\gamma\text{-}1,2\text{-}H_2SiV_2W_{10}O_{40}]^{4-}$ with the $\{VO\text{-}(\mu\text{-}OH)_2\text{-}VO\}$ core catalyzes the epoxidation of various alkenes using only 1 equiv. H_2O_2 with the high epoxide yield and high efficiency of H_2O_2 utilization under very mild reaction conditions. Notably, this system shows unique stereospecificity, diastereoselectivity, and regioselectivity, which are quite different from those reported for the epoxidation systems including $[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]^{4-}$.

Keywords: Alkene; Epoxidation; Hydrogen peroxide; Polyoxometalate; Vanadium

1. Introduction

Vanadium is an important element in biology, inorganic chemistry and organic syntheses [1–7], and can heterogeneously or homogenously catalyze selective oxidation reactions of alkanes, alkenes, aromatics, alcohols, halides, etc. [1–3,6–12]. While the homogenous oxidation catalysis by mono- and di-vanadium complexes has extensively been studied, scarcely is known of the oxidation catalysis by bis(μ-hydroxo) bridged di-vanadium compounds [1,2,6,7,13,14]. In addition, even mono-vanadium complexes could not efficiently catalyze the epoxidation of alkenes with a green oxidant of H_2O_2 because of the contribution of the radical mechanism; for example, the oxidation of cyclohexene with H_2O_2 catalyzed by vanadium-based catalysts proceeded mainly at the allylic position to give the corresponding enol and enone (allylic oxidation) [8–12] and the efficiency of H_2O_2 utilization is intrinsically low. Therefore, vanadium-catalyzed H_2O_2-based epoxidation of alkenes with high selectivity to the epoxide and high efficiency of H_2O_2 utilization is previously unknown while it is well known that other transition metals such as tungsten, manganese, and iron show relatively high activity, selectivity, and efficiency of H_2O_2 utilization [15].

Here, we report that the $[\gamma\text{-}1,2\text{-}H_2SiV_2W_{10}O_{40}]^{4-}$ (**I**) with the $\{VO\text{-}(\mu\text{-}OH)_2\text{-}VO\}$ core can efficiently catalyze epoxidation of alkenes using only 1 equiv. H_2O_2 with the high epoxide yield and high efficiency of H_2O_2 utilization [16]. Notably, this system shows unique stereospecificity, diastereoselectivity, and regioselectivity, which are quite different from those reported for the epoxidation systems [16].

2. Results and discussion

The scope of the present epoxidation by tetra-*n*-butylammonium salt of **I** (TBA-**I**) with regard to various kinds of mono-alkenes using 1 equiv. H_2O_2 (except for gaseous alkenes such as propene and 1-butene) was examined. The results are summarized in Table 1. Under the present reaction conditions, neither allylic oxidation nor hydrolysis of epoxides proceeded in all cases. The epoxidation did not proceed at all in the absence of catalyst (entry 8). Mono- and tri-vanadium substituted compounds and fully occupied silicotungstate were completely inactive under the present conditions (entries 5–7). By using TBA-**I**, non-activated aliphatic terminal alkenes including propene could be transformed to the corresponding epoxide with high selectivity and efficiency of H_2O_2 utilization (entries 1–4, and 11). A larger-scale reaction (50-fold scaled up) for 1-octene showed the same results as those for the small-scale experiments in Table 1 (99% selectivity to 1,2-epoxyoctane,

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Table 1
Epoxidation of various alkenes with H_2O_2[a]

Entry	Catalyst	Alkene	Yield (%)	Product (selectivity (%))	H_2O_2 efficiency[b] (%)
1[c]	TBA-**I**	Propene	87	1,2-Epoxypropane (99)	87
2[c]	TBA-**I**	1-Butene	91	1,2-Epoxybutane (99)	91
3	TBA-**I**	1-Hexene	92	1,2-Epoxyhexane (99)	92
4	TBA-**I**	1-Octene	93	1,2-Epoxyoctane (99)	93
5[d]	$[\alpha\text{-SiVW}_{11}O_{40}]^{5-}$	1-Octene	<1	–	–
6[d]	$[\alpha\text{-1,2,3-SiV}_3W_9O_{40}]^{7-}$	1-Octene	<1	–	–
7[d]	$[\gamma\text{-SiW}_{12}O_{40}]^{4-}$	1-Octene	<1	–	–
8	None	1-Octene	<1	–	–
9	TBA-**I**	*cis*-2-Octene	90	*cis*-2,3-Epoxyoctane (99, only *cis*)	90
10	TBA-**I**	2-Methyl-1-heptene	88	1,2-Epoxy-2-methylheptane (98)	90
11	TBA-**I**	1-Decene	93	1,2-Epoxydecane (99)	93
12	TBA-**I**	Styrene	88	Styrene oxide (99)	88
13	TBA-**I**	Cyclohexene	90	1,2-Epoxycyclohexane (99)	92
14	TBA-**I**	Cyclooctene	93	1,2-Epoxycyclooctane (99)	93

[a] Reaction conditions: alkene (33.3 mM), catalyst (1.67 mM), H_2O_2 (30% aq., 33.3 mM), CH_3CN/*t*-BuOH (1.5/1.5 mL), 293 K, 24 h. Yields and selectivities were determined by gas chromatography or ^1H NMR using an internal standard technique and were based on alkenes.

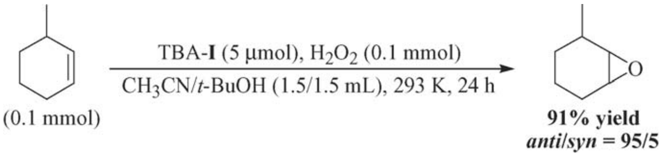
[b] H_2O_2 efficiency (%) = [products (mol)/consumed H_2O_2 (mol)] × 100.

[c] Propene (6 atm), 1-butene (3 atm).

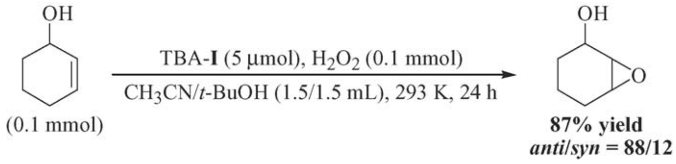
[d] Tetra-*n*-butylammonium salts were used.

93% GC yield, and 86% isolated yield). The reaction rate increased with increase in the reaction temperature, and the TOF reached up to 38 h^{-1} at 313 K, keeping the selectivity to 1,2-epoxyoctane as high as >99%, while the efficiency of H_2O_2 utilization was a little decreased from 93% (293 K) to 85% (313 K). The catalytic epoxidation of cyclic alkenes such as cyclohexene and cyclooctene also efficiently proceeded to afford the corresponding epoxides in high yields (entries 13 and 14). The interesting point is that styrene (both styrene and styrene oxide are unstable under acidic conditions) was highly selectively epoxidized to styrene oxide without any by-products (entry 12).

For the competitive epoxidation of *cis*- and *trans*-2-octenes (100 μmol each, the other conditions were the same as those in Table 1), the initial rates for the epoxidation of *cis*- and *trans*-2-octene were 0.32 and 0.001 mM min^{-1}, respectively. The ratio of the formation rate of *cis*-2,3-epoxyoctane to that of the *trans* isomer was >300 and the value is much larger than those (1.3–11.5) reported for the other stereospecific epoxidation systems [17]. In this case, the configuration around the C=C moieties was completely retained in the corresponding epoxides. The epoxidation of 3-substituted cyclohexenes such as 3-methyl-1-cyclohexene and 2-cyclohexen-1-ol showed unusual diastereoselectivities; the epoxidation was highly diastereoselective and gave the corresponding epoxides with oxirane ring *trans* to the substituents (*anti* configuration) [Eqs. (1) and (2)].



(1)



(2)

Further, it is noted that more accessible, but less nucleophilic double bonds in non-conjugated dienes such as *trans*-1,4-hexadiene, *R*-(+)-limonene, 7-methyl-1,6-octadiene, and 1-methyl-1,4-cyclohexadiene were highly regioselectively epoxidized. The results for the epoxidation of dienes with H_2O_2 catalyzed by TBA-**I** are shown in Table 2. For the *trans*-1,4-hexadiene epoxidation (entry 1), the [terminal epoxide]/[total epoxide] ratio was >0.99 and much higher than those reported for the epoxidation with NaOCl or PhIO; Mn(TTPPP)(OAc)/NaOCl (0.35) [18], Mn(T(2′,6′-G1APh)P)Cl/PhIO (0.20) [19], $Mo(CO)_6$/CHP (0.14) [20], Mn(TPP)(OAc)/NaOCl (0.03) [18], and Mn(T(3′,5′-G2Ph)P)Cl/PhIO (0.03) [21]. In addition, for the (*R*)-(+)-limonene epoxidation (entry 2), the [8,9-epoxide]/[total epoxide] ratio was 0.99 and the value was much higher than those reported for the epoxidation with H_2O_2 by $PhCN/KHCO_3$ (0.37) [22], and Ti-beta zeolite (0.55) [23]. The comparison with sterically hindered porphyrin systems with NaOCl or PhIO shows that the regioselectivity for TBA-**I** is higher than the values reported (0.62–0.75) [18,24–26]. Similarly, in the case of 7-methyl-1,6-octadiene (entry 3), the [terminal epoxide]/[total epoxide] was 0.93 and the value was much higher than those for the H_2O_2-based epoxidation systems of Al_2O_3/H_2O_2 (<0.01) [27], $CF_3CH_2OH/Na_2HPO_4/H_2O_2$ (<0.01) [28], and $(CF_3)_2CO/C_2F_5OH/NaHPO_4/H_2O_2$ (<0.01) [29].

Next, the regioselectivity for the epoxidation of dienes by TBA-**I** is compared with those by various tungstate