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Selective oxidations of allylic alcohols with H_2O_2 on a series of lanthanide decatungstate modified with 1-hexadecylpyridinium cation [$\{C_5H_5N(CH_2)_{15}CH_3\}_7H_2Ln(III)W_{10}O_{36}$; cetyl-LnW10, Ln: La–Er]: kinetic features and working mechanisms

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Abstract

Selective oxidation of 1-octen-3-ol to 1,2-epoxy-3-octanol and 1-octen-3-on with H_2O_2 catalyzed by $\{C_5H_5N(CH_2)_{15}CH_3\}_7H_2Ho(III)W_{10}O_{36}$(cetyl-HoW10) in a $CHCl_3$–H_2O_2 aqueous biphasic system, adapted as a test catalytic reaction, was kinetically investigated. The rate equations for the epoxide and enon formation were successfully described by equations: $R_{epoxy} = k_{1,epoxy}[substrate][H_2O_2]^{1.6}$, and $R_{enon} = k_{1,enon}[substrate][H_2O_2]^{-0.6}$. A working mechanism in which H_2O_2 molecule acts additionally to the substrate molecule which has been activated by interaction with a peroxo-species formed on the cetyl-LnW10 catalyst was proposed; the H_2O_2 molecule promotes the epoxide formation, but suppresses the enon formation. 2-Hexen-1-ol was easily oxidized in the catalyst system, although 2-octene without a terminal OH-group was not. Moreover, the activity decreased drastically as the olefinic-group was far away from the terminal position. These results indicate that the terminal OH-group plays an important role in the activation of the substrates. The working state and the activity of catalyst were greatly influenced by the polarity of the solvent used. Especially, in the organic solvent-free system, the activity was very much promoted. Thus, cetyl-LnW10 is a suitable catalyst, from the environmental viewpoint. With the oxidations of both 1-octen-3-ol and 2-hexen-1-ol catalyzed by a series of Ln(III)W10; Ln: La–Er, the activities varied regularly according to the tendency of contraction of the Ln(III) ion. Those findings were interpreted reasonably by the mode of interaction and the working mechanism postulated, and clearly support the proposal that the $4f^n$-electrons of the Ln(III) ion participate in the catalysis. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Lanthanide decatungstate; Selective oxidation; Allylic alcohols; Working mechanism

1. Introduction

Catalyst systems, derived from H_2O_2 and the usual type of heteropoly-oxometalates ("Keggin type"), and also from H_2O_2 and oxoanions, have effectively oxidized terminal alcohols, olefins and allylic alcohols [1–11]. Various 'transition-metal-substituted polyoxometalates' based on the Keggin structure have also been well-known as excellent catalysts for the selective oxidations of various organic substrates [12–17].

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We have synthesized and characterized a series of lanthanide decatungstates [$M_7H_2LnW_{10}\cdot nH_2O$; LnW10, Ln = La–Yb] [18]. The lanthanide decatungstates modified with a 1-hexadecylpyridinium cation (cetyl-LnW10) behaved as unique catalysts for H_2O_2 oxidations of alcohols and olefins; for instance, cetyl-HoW10 in a $CHCl_3$–H_2O_2 aqueous biphasic system has effectively catalyzed secondary alcohols such as 2-octanol to 2-octanone and terminal alcohols containing a phenyl group, such as benzyl alcohol, but did not catalyze terminal alcohols such as 1-hexanol to the corresponding aldehyde [19,20]. With the epoxidation of olefins, similarly, the inner olefin, such as cyclooctene, was rather rapidly converted to epoxycyclooctane, while the terminal olefin containing a phenyl group, such as styrene, was not epoxidized. Under organic solvent-free conditions, especially cetyl-HoW10 behaved as an active catalyst for the H_2O_2 oxidations of the above-mentioned alcohols, olefins and allylic alcohols. Furthermore, the catalytic ability and stability were very high even at 90 °C in those reacting systems [19].

The catalytic activities for the H_2O_2 oxidation of benzylalcohol and cyclooctene in a $CHCl_3$–H_2O_2 aqueous biphasic system have been compared among the series of cetyl-LnW10 [Ln: La–Er]. The activity for the former tended to increase with the contraction of the Ln(III) ion in cetyl-LnW10; on the contrary, the activity for the latter tended to decrease with the ion size contraction [20]. Those findings were favorably interpreted according to a working hypothesis proposed by Mimoun and co-workers [21,22] and a peroxo-complex model previously postulated in a H_2O_2–LnW10 reacting system [23,24,30].

In the present paper, the catalytic activity and selectivity for the oxidation of allylic alcohols such as 1-octen-3-ol and 2-hexen-1-ol with H_2O_2 on the series of cetyl-LnW10 compounds are investigated kinetically to examine the stereo-selective features and additionally the effects of the OH-group in the substrates on the catalyses in detail to understand further their working states and mechanisms. In the case of 1-octen-3-ol, for instance, the selectivity for the epoxide formation greatly increased with the H_2O_2 concentration; the epoxide yield increased to 90% or more in 60% (H_2O_2) at 30 °C in a $CHCl_3$–H_2O_2 aqueous biphasic system. The ratio of the epoxide formation rate to the enon-one in 1-octen-3-ol and also the epoxide formation rate in 2-hexen-1-ol were found to vary, although slightly, along with the contraction in the Ln(III) ion size. The chemical effect of the Ln(III) ion on the catalysis will be discussed based on those findings.

2. Experimental

2.1. Materials and preparation procedures

A series of $Na_7H_2Ln(III)W_{10}O_{36}\cdot nH_2O$ (Na-Ln W10; Ln: La–Er) compounds were synthesized according to the literature [18,25]. The samples, Na-LnW10, were successfully modified with a 1-hexadecylpyridinium cation according to the literature [2,26]. Typically, to a stirred solution of those samples (ca. 1 g) in distilled water (5 ml), an aqueous solution of 1-hexadecylpyridinium chloride monohydrate (ca. 9 M amounts) was added dropwise at room temperature. After 2 h, the resulting precipitate was filtered, washed with distilled water, and dried in vacuo. The catalyst samples will be designated cetyl-LnW10.

An aqueous solution of $Na_4W_{10}O_{32}$ was prepared according to the literature [4] as follows. $Na_2WO_4\cdot 2H_2O$ (3.3 g, 10 mmol) was dissolved in distilled water (50 ml) at 80 °C, and the pH of the solution was adjusted to 2.0 by adding a $HClO_4$ solution. The sample was similarly modified with a 1-hexadecylpyridinium cation (cetyl-W10). An aqueous solution of $H_3PW_{12}O_{40}\cdot nH_2O$, obtained from Nippon New Metal Co. Ltd., was also modified with a 1-hexadecylpyridinium cation (cetyl-PW12).

2.2. Analyses and characterization

The samples, thus, prepared were identified mainly by UV–VIS, FT-IR and ICP with reference to the previous papers [18,20]. The compositions of Na, Ln, and W were analyzed by an ICP apparatus, Simadzu Model ICP-1000III. FT-IR spectra were recorded on a Perkin-Elmer Model 1760X over the frequency range of 4000–450 cm^{-1} with a resolution of 4 cm^{-1} by the normal KBr-disk method. The results of ICP-analyses for Na-LnW10 were confirmed to coincide well with the results previously reported [18,20]. The FT-IR spectra of Na-LnW10 and the characteristic bands

also corresponded well to those mentioned previously [18,20].

A peroxo-complex was suggested to be formed in a LnW10/H_2O_2 reacting system, the structure of which has been postulated by in situ FT-IR, FT-Raman, and ^{183}W NMR spectrometries, [20,23,24] and its catalytic behavior has also been studied kinetically as referred in Fig. 10(B) [29,30].

2.3. Catalytic reactions and procedures

The organic reagents (special grade), which were purchased from Kanto Chemical Co. Ltd., E. Merk and Tokyo Kasei, were used without further treatment. H_2O_2 aqueous solution produced by Tokai Denka Ind. Ltd., was used. The oxidation reactions were carried out [19,20,26] as follows. In a three-necked round-bottom flask (100 ml), H_2O_2 (18–60%, 10 ml; 100 mmol), a substrate (8 mmol), a solvent (0–20 ml) and pentadecane (0.123 g; 0.58 mmol) as an internal standard were introduced. After ca. 30 min of holding the mixture at the reaction temperatures (0–70 °C) under N_2 atmosphere, the reaction was started by the addition of a catalyst (0.05–0.2 g; 0.01–0.04 mmol). A part of the reacting solution was sampled at an interval and was added to $CHCl_3$ to extract the reactant and products for analysis. The product yield was determined by GC (0.25 mm × 30 m DB-Wax capillary column) using the internal standard method. When *t*-butyl alcohol and acetonitrile were used as the solvent, a constant amount of the standard substance (0.123 g; 0.58 mmol) was previously added to $CHCl_3$ (10 ml) for the extraction.

3. Results

On cetyl-HoW10 as a test catalyst under an organic solvent-free condition, 2-octen-1-ol was oxidized ca. five to six times more rapidly than was 1-octen-3-ol, in which the former was converted to 2,3-epoxy-1-octanol without the oxidation of the terminal OH-group, while the latter gave 1,2-epoxy-3-octanol and 1-octen-3-on in a ratio of ca. 3:1, as compared in Table 4 of [19]. The activity for the epoxidation of cyclooctene was too low, ca. 1/20 or 1/30 of that for 2-octen-1-ol. Thus, from those comparisons, the OH-group has been suggested to play quite an important role in the activation step of the catalytic epoxidation of allylic alcohols.

3.1. Epoxidation of an allylic alcohol having an olefinic-group at the terminal, 1-octen-3-ol, with H_2O_2

3.1.1. H_2O_2 concentration dependence of the oxidation rate: kinetic analysis

The oxidation of 1-octen-3-ol on cetyl-HoW10 has been carried out at 30 °C in the $CHCl_3$ (20 ml)–H_2O_2 aqueous biphasic system under different concentrations of H_2O_2, 18–60%. The substrate disappeared gradually with time, and then 1,2-epoxy-3-octanol and 1-octen-3-on formed in a constant ratio of ca. 2:1, as illustrated, e.g. 30% H_2O_2 in Fig. 1(a). The first-order analysis was successfully applied to the time course of the substrate as shown in Fig. 1(b). From the inclination of the linear line, we can determine exactly the apparent rate constant, $k_{1,\mathrm{obs}}$. The turnover frequency (TOF) for the epoxide and enon formations, per hours and per molar-catalyst, could then be estimated based on the values of the formation ratio and $k_{1,\mathrm{obs}}$, respectively. The data similarly collected for 18–60% H_2O_2 were also favorably analyzed, and the rate constants and the TOF values obtained are summarized in Table 1. The $\mathrm{TOF_{epoxy}}$ values increase greatly with increasing H_2O_2 concentration. On the contrary, the $\mathrm{TOF_{enon}}$ tends to decrease, although the data seem to be scattered. In order to examine the H_2O_2 concentration dependence of the TOF values, ln(TOF) was plotted against ln(H_2O_2-concenration, %) in Fig. 2. From the slopes of the curves, we can evaluate the reaction orders of the formation processes of 1,2-epoxy-3-ol and 1-octen-3-on from 1-octen-3-ol. In fact, the activity for the former product increases depending upon the order of ca. 1.6 of the H_2O_2-concenration. On the other hand, that for the latter decreases depending upon the order of ca. −0.6, although the $\mathrm{TOF_{total}}$ increased according to the order of ca. 1.0. As a result, the reaction rate equations for the selective oxidations of 1-octen-3-ol to 1,2-epoxy-3-octanol and 1-octen-3-on with H_2O_2 are derived as Eqs. (1) and (2), respectively.

$$R_{\mathrm{epoxy}} = k_{1,\mathrm{obs}}[\mathrm{substrate}]^{1.0}[\mathrm{H_2O_2}]^{1.6} \quad (1)$$

$$R_{\mathrm{enon}} = k_{1,\mathrm{obs}}[\mathrm{substrate}]^{1.0}[\mathrm{H_2O_2}]^{-0.6} \quad (2)$$

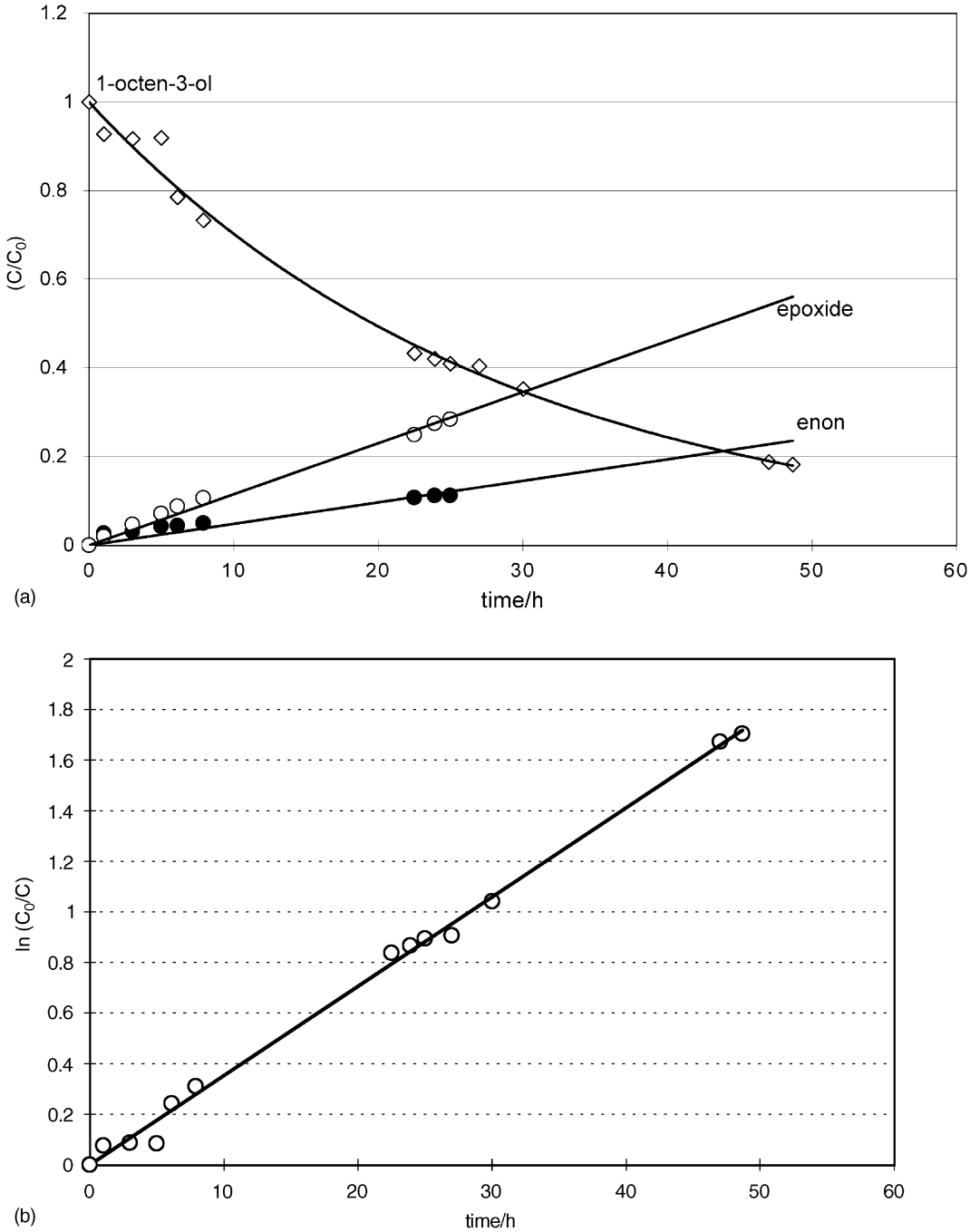

Fig. 1. (a) Kinetic data for the selective oxidation of 1-octen-3-ol to 1,2-epoxy-3-octanol and 1-octen-3-on on cetyl-HoW10 in the $CHCl_3$ (20 ml)–H_2O_2 (30%) aqueous biphasic system at 30 °C: substrate 8.0 mmol, catalyst 0.04 mmol. (b) Application of the first-order equation to the kinetic data: plots of $\ln(C_0/C)$ vs. time.

Table 1
The H_2O_2 concentration dependence of the first-order rate constant, $k_{1,obs}$ TOF_{epoxy} and TOF_{enon} for the H_2O_2 oxidation of 1-octen-3-ol in $CHCl_3$ solvent (20 ml) at 30 °C

H_2O_2 (%)	$k_{1,obs}$ (h^{-1})	k_{epoxy} (h^{-1})	k_{enon} (h^{-1})	TOF_{total} (h^{-1})	TOF_{epoxy} (h^{-1})	TOF_{enon} (h^{-1})
60	0.0672	0.0541	0.0068	13.8	12.2	1.5
54	0.0546	0.0408	0.0084	10.3	9.1	1.3
48	0.0461	0.0332	0.009	8.2	6. 8	1.5
42	0.0424	0.0252	0.0097	8.1	6.2	2.0
36	0.0403	0.0208	0.0081	7.3	5.4	1.8
30	0.0353	0.0183	0.0105	5.6	3.7	1.9
24	0.0278	0.0132	0.0084	5.4	3.4	2.0
18	0.0259	0.0056	0.0128	4.5	1.4	3.1

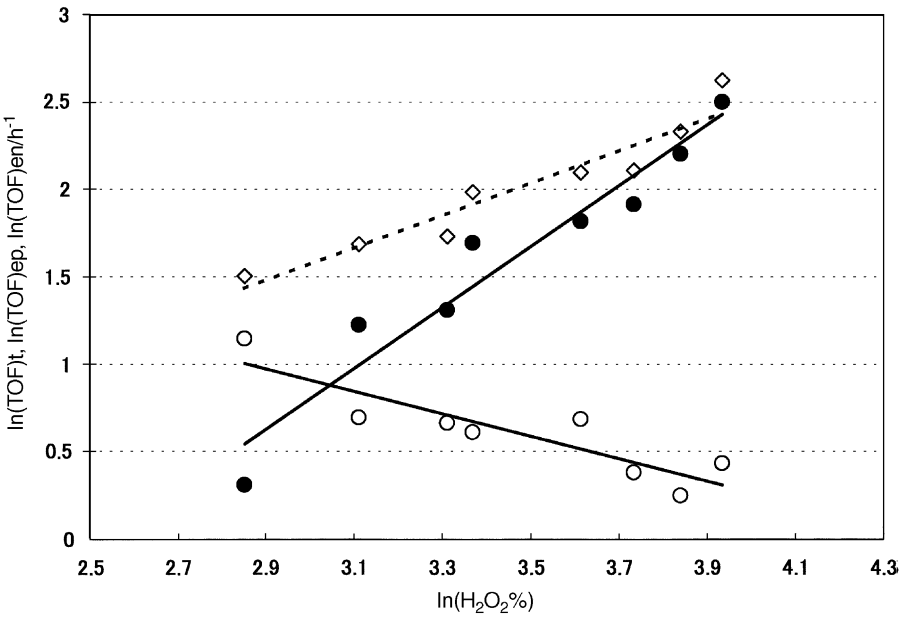

Fig. 2. The H_2O_2 concentration dependencces of the total oxidation rate (TOF_{total}) of 1-octen-3-ol and the formation rates of TOF_{epoxy} and TOF_{enon}. Plots of ln(TOF) vs. ln(H_2O_2 concentration, %): (◇) TOF_{total}; (●) TOF_{epoxy}; and (○) TOF_{enon}. Substrate 8.0 mmol, catalyst 0.04 mmol, H_2O_2 (18–60%, 10 ml) 100 mmol.

Table 2
Temperature dependence of H_2O_2 oxidation of 1-octen-3-ol on cetyl-LnW10[a]

Temperature (°C)	$1/T$ ($\times 10^{-3}$) (K^{-1})	TOF_{total} (h^{-1})	TOF_{epoxy} (h^{-1})	TOF_{enon} (h^{-1})
30	3.30	26.2	20	6.2
40	3.195	45.5	31	14.5
50	3.096	134	87	47
60	3.003	244	142	102
70	2.916	320	165	155

[a] Substrate 8.0 mmol, catalyst 0.04 mmol, in $CHCl_3$ solvent (3.0 ml) at 30–70 °C.

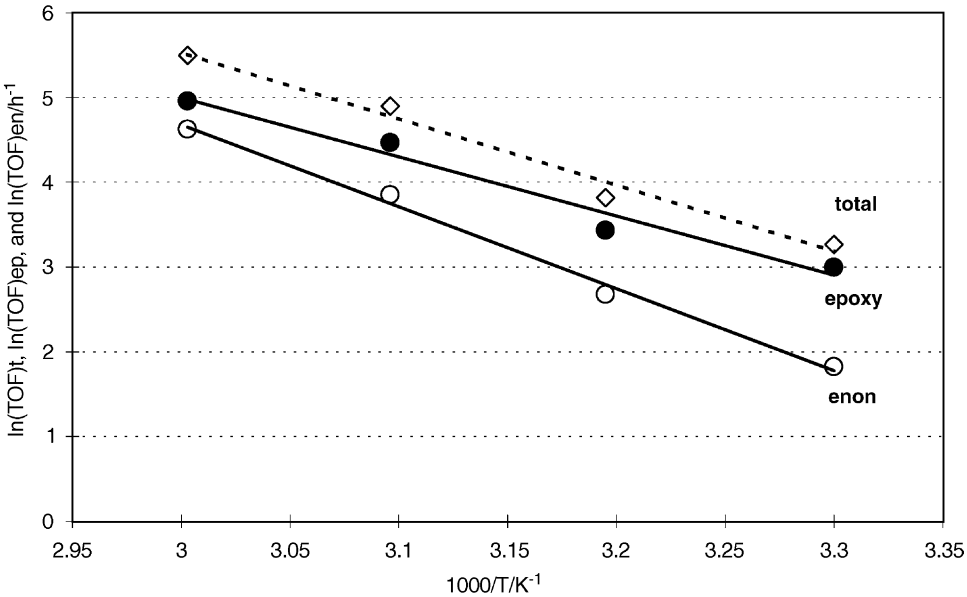

Fig. 3. The temperature dependences of the selective oxidation rates of 1-octen-3-ol on cetyl-HoW10 in the $CHCl_3$ (3 ml)–H_2O_2 (30%) aqueous biphasic system at 30–70 °C: Arrhenius plots for TOF_{total} (◇); TOF_{epoxy} (●); and TOF_{enon} (○).

3.1.2. Temperature dependences of the oxidation rates: Arrhenius parameters

The oxidation of 1-octen-3-ol on cetyl-HoW10 has been carried out in the temperature range of 30–70 °C in the $CHCl_3$ (3.0 ml)–H_2O_2 (30%) aqueous biphasic system. The data collected were analyzed well by the first-order kinetics, according to the procedure described earlier. The results are summarized in Table 2, and the Arrhenius plots for the TOF values show good linear lines as illustrated in Fig. 3, in which the point at the highest temperature (70 °C) was rejected because it deviated somewhat below the straight lines. The Arrhenius parameters evaluated from the linear lines are given in Table 3. It is noted that the activation energy (80 kJ mol^{-1}) for the enon formation is ca. 30% higher than that (58 kJ mol^{-1}) for the epoxide formation. Thus, we can see that the ratio of the epoxide to the enon greatly increases with decreasing temperature; the epoxide formation becomes more favorable at lower temperatures.

Table 3
Arrhenius parameters for the selective oxidation of 1-octen-3-ol to epoxide and enon formation with H_2O_2 on cetyl-LnW10 in $CHCl_3$ solvent (3.0 ml) at 30–60 °C

Reaction	E_a (kJ mol^{-1})	ln(TOF_0) (h^{-1})
Epoxide formation	58	25.9
Enon formation	80	33.7

3.1.3. Catalytic activities on a series of cetyl-LnW10 (Ln: La–Er) compounds during the H_2O_2 oxidations of 1-octen-3-ol in the $CHCl_3$–H_2O_2 aqueous biphasic system

The kinetic data were similarly well analyzed on catalysts other than cetyl-HoW10 in the $CHCl_3$–H_2O_2 aqueous biphasic system at 30 °C. TOF_{epoxy} and TOF_{enon} for the H_2O_2 oxidation of 1-octen-3-ol in the series of Ln(III)W10 (Ln: La–Er) were successfully evaluated. Those values were plotted as a function of the ionic sizes of Ln(III) in Fig. 4, in which TOF_{epoxy} seems to retain on a flat line; curve A, but TOF_{enon} tends to increase slightly with the contraction in the Ln(III) ionic size; curve B, although the data points are rather diverse from each other. Thus, the ratio of TOF_{epoxy}/TOF_{enon} clearly decreases between 2.0 and 3.0 with the contraction; curve C, the values of which were magnified by 10 in Fig. 4. Thus, the Ln(III) ionic size, and thus, the $4f^n$-electron, might be suggested

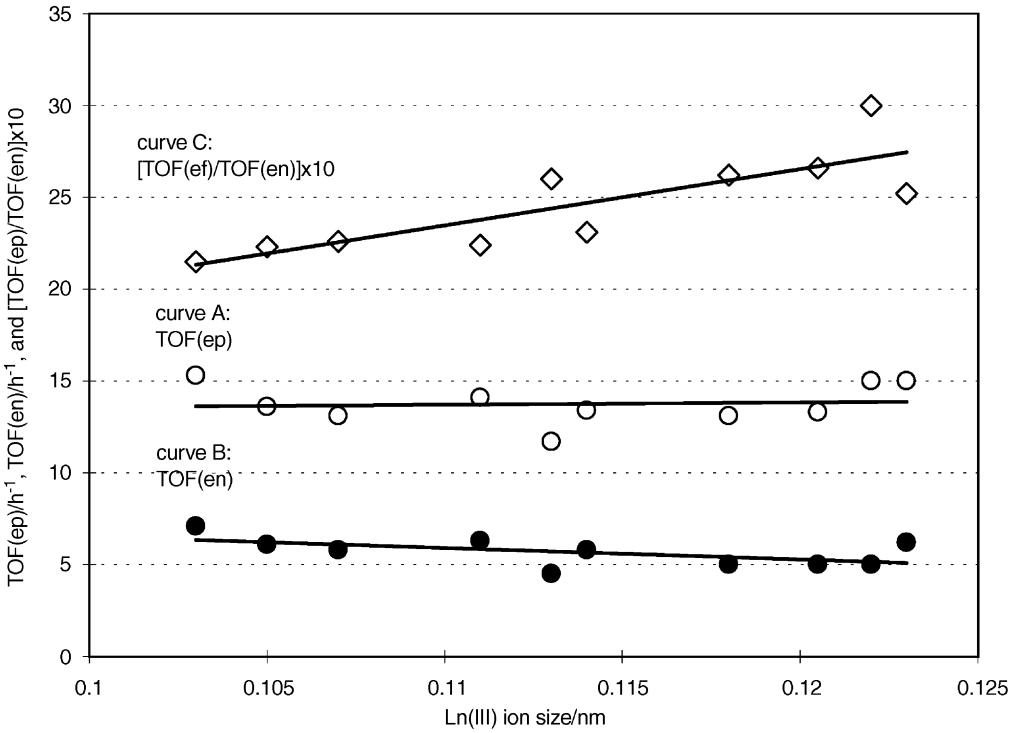

Fig. 4. The comparisons of the catalytic activities and selectivities for the H_2O_2 oxidations of 1-octen-3-ol on the catalyst series of cetyl-Ln(III)W10 in the $CHCl_3$ (10 ml)–H_2O_2 (30%) aqueous biphasic system at 30 °C. Plots of TOF_{epoxy}, TOF_{enon} and the ratio of [TOF_{epoxy}/TOF_{enon}] magnified by 10 as a function of the ionic radii of Ln(III). Substrate 8.0 mmol, H_2O_2 (30%, 10 ml) 100 mmol, catalyst 0.04 mmol.

to affect the enon formation greatly rather than the epoxide formation.

3.2. Epoxidation of allylic alcohols having the OH-group in the terminal with H_2O_2

3.2.1. Activation of the olefinic-group located in a different position

We are interested in how the activity of cetyl-LnW10 for the epoxidation differs with the olefinic-groups located in different positions. Hence, the epoxidation of 2-, 3- and 4-hexen-1-ol were investigated using cetyl-HoW10 as a test catalyst in the $CHCl_3$–H_2O_2 aqueous biphasic system under the following conditions; substrate 8.00 mmol, catalyst 0.04 mmol, H_2O_2 (30%) 10 ml (100 mmol), $CHCl_3$ 10 ml, at 30 °C. The changes in the concentration of the substrates and the corresponding epoxides formed with time were measured at intervals. For comparison, the oxidations of *cis*-5-octen-1-ol and 2-octene were measured similarly. The epoxides initially formed tended to be converted further to undetectable products, especially in the oxidation of 3- and 4-hexen-1-ol. However, in any case, the time course of the substrates was successfully analyzed by first-order kinetics, as shown in Fig. 5. The apparent first-order rate constants ($k_{1,obs}$) were exactly determined from the slope of the curves, and then the turnover frequency (TOF, h^{-1}) was also evaluated, as summarized in Table 4. The TOF values for those substrates are compared clearly in Fig. 6. When the olefinic-group is far from the terminal OH-group (2 → 3 → 4), the TOF values decrease almost in proportion to an exponential function. The potentiality of the cetyl-LnW10 catalyst for the epoxidation of the substrates without the OH-group, e.g. 2-octene, is very poor. The TOF for *cis*-5-octen-1-ol is, in fact, one order of magnitude higher than that for 2-octene, although the olefinic-group is too far from

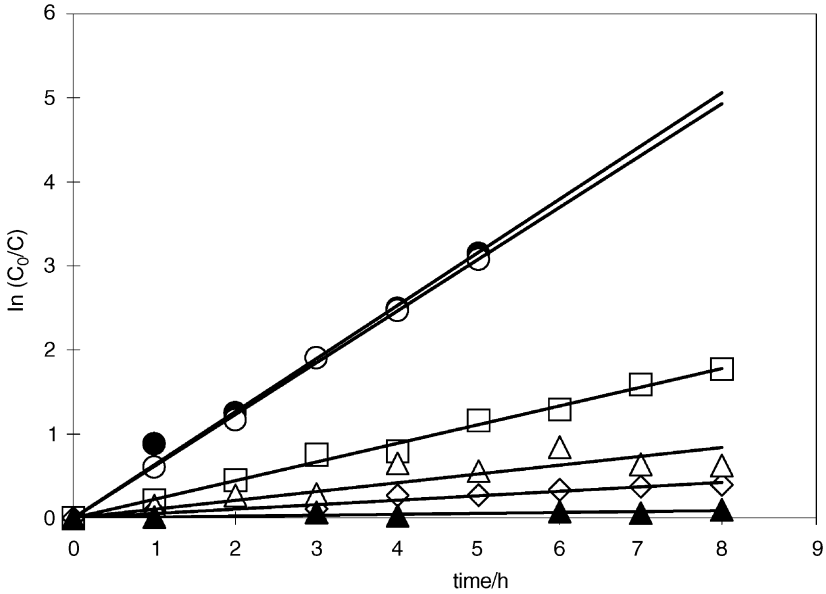

Fig. 5. The first-order analysis for the kinetic data for the epoxidations of the series of hexene-1-ol on cetyl-HoW10 in the $CHCl_3$–H_2O_2 aqueous biphasic system at 30 °C: (●, ○) *trans*- and *cis*-2-hexene-1-ol; (□, ◇) *cis*-3- and 4-hexene-1-ol; (△, ▲) *cis*-5-octene-1-ol and 2-octene, respectively. Substrates 8.0 mmol, catalyst 0.04 mmol, H_2O_2 (30%, 10 ml) 100 mmol, $CHCl_3$ 10 ml.

the terminal OH-group. Thus, these results suggest clearly that the terminal OH-group plays an important role in inducing the substrates effectively into an activated state for the epoxidation.

3.2.2. Epoxidations of trans- and cis-2-hexen-1-ol in various organic solvent–H_2O_2 aqueous biphasic systems

The catalytic behavior of cetyl-HoW10 for the epoxidation of *trans*- and *cis*-2-hexen-1-ol with H_2O_2 was examined in the biphasic media; aqueous H_2O_2–organic solvents having different polarities such as C_6H_6, $CHCl_3$, *t*-BuOH, and CH_3CN [28]. In any case, the data collected in the course of the reactions were also analyzed successfully according to first-order kinetics. The rate constant ($k_{1,obs}$) and the corresponding TOF values, thus, obtained are summarized in Table 5. The TOF values are illustrated in Fig. 7.

Table 4
Epoxidation rates of various hexen-1-ol with H_2O_2 on cetyl-HoW10 in $CHCl_3$ at 30 °C

Substrate	$k_{1,obs}$ (h^{-1})	TOF (h^{-1})
Trans-2-hexen-1-ol	0.632	91
Cis-2-hexen-1-ol	0.616	89
Cis-3-hexen-1-ol	0.222	32
Cis-4-hexen-1-ol	0.052	7.5
Cis-5-octen-1-ol	0.105	15
2-Octene	0.011	1.6

Table 5
Epoxidation rates of 2-hexene-1-ol with H_2O_2 in various solvents on cetyl-HoW10 at 30 °C

Solvent	Substrate	$k_{1,obs}$ (h^{-1})	TOF (h^{-1})
C_6H_6	*Trans*-2-hexen-1-ol	1.22	176
	Cis-2-hexen-1-ol	1.28	185
$CHCl_3$	*Trans*-2-hexen-1-ol	0.632	91
	Cis-2-hexen-1-ol	0.616	89
t-BuOH	*Trans*-2-hexen-1-ol	1.59	229
	Cis-2-hexen-1-ol	1.36	196
CH_3CN	*Trans*-2-hexen-1-ol	1.76	254
	Cis-2-hexen-1-ol	1.47	212
In-organic solvent-free	*Trans*-2-hexen-1-ol	7.29[a]	729
	Cis-2-hexen-1-ol	7.10[a]	710

[a] $k_{0,obs}$ (mmol h^{-1}).

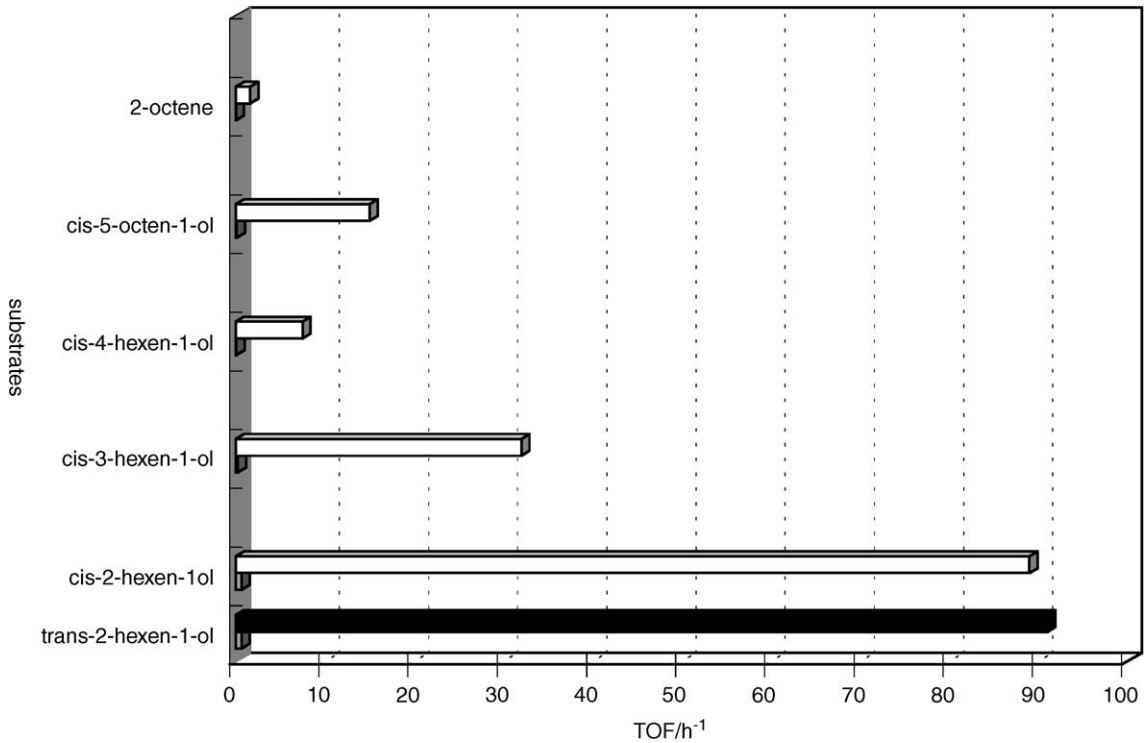

Fig. 6. The TOF evaluated from the first-order rate constants ($k_{1,obs}$) for the epoxidations of the series of hexene-1-ol with H_2O_2 on cetyl-HoW10 in Fig. 5.

In CH_3CN solvent having a high polarity ($\varepsilon = 37.5$), the reaction was thought to be carried out apparently in a monophasic state such that the substrate and catalyst dissolve mutually in a mixed solvent of aqueous H_2O_2 and CH_3CN. However, in benzene ($\varepsilon = 2.3$), the reaction certainly took place in the organic solvent–aqueous H_2O_2 biphasic system, in which both the substrate and catalyst dissolve homogeneously in the organic phase. In the solvents having a medium polarity such as $CHCl_3$ ($\varepsilon = 4.8$) and *t*-BuOH ($\varepsilon = 12.5$), the reaction can be regarded apparently as proceeding in a biphasic system, although the substrate and catalyst may be distributed partially in both phases. The concentrations of the substrate and catalyst could not be evaluated exactly in these situations. Thus, the activity and selectivity would vary not only with the polarity, but also with the extent of the distribution of both the substrate and catalyst into the reacting region (layer), although the TOF values tend to decrease with the decrease in the polarity of the solvent. However, attention should be paid to the fact that the activities for the *trans*-isomer tends to be higher than that for the *cis*-isomer in the solvents having higher polarity; that is, in the CH_3CN–H_2O_2 aqueous system, the activity for the *trans*-isomer was greater (ca. 20%) than that for the *cis*-isomer, although in the benzene–H_2O_2 aqueous biphasic system, on the contrary, the former activity was less (ca. 5%) than the latter. Those points will be discussed in detail in the following sections.

3.2.3. *Temperature dependences of the epoxidation of trans- and cis-2-hexen-1-ol in CH_3CN solvent and organic solvent-free systems*

In the CH_3CN solvent–H_2O_2 aqueous system, the epoxidations of *trans*- and *cis*-2-hexen-1-ol took place in a unified phase, while in the organic solvent-free system the reaction occurred in the biphasic media; aqueous H_2O_2–substrate dissolved the catalyst directly, in a temperature range of 0–30 °C. The amount of the catalyst used was reduced to one-fourth, because the activity was too high to be measured without

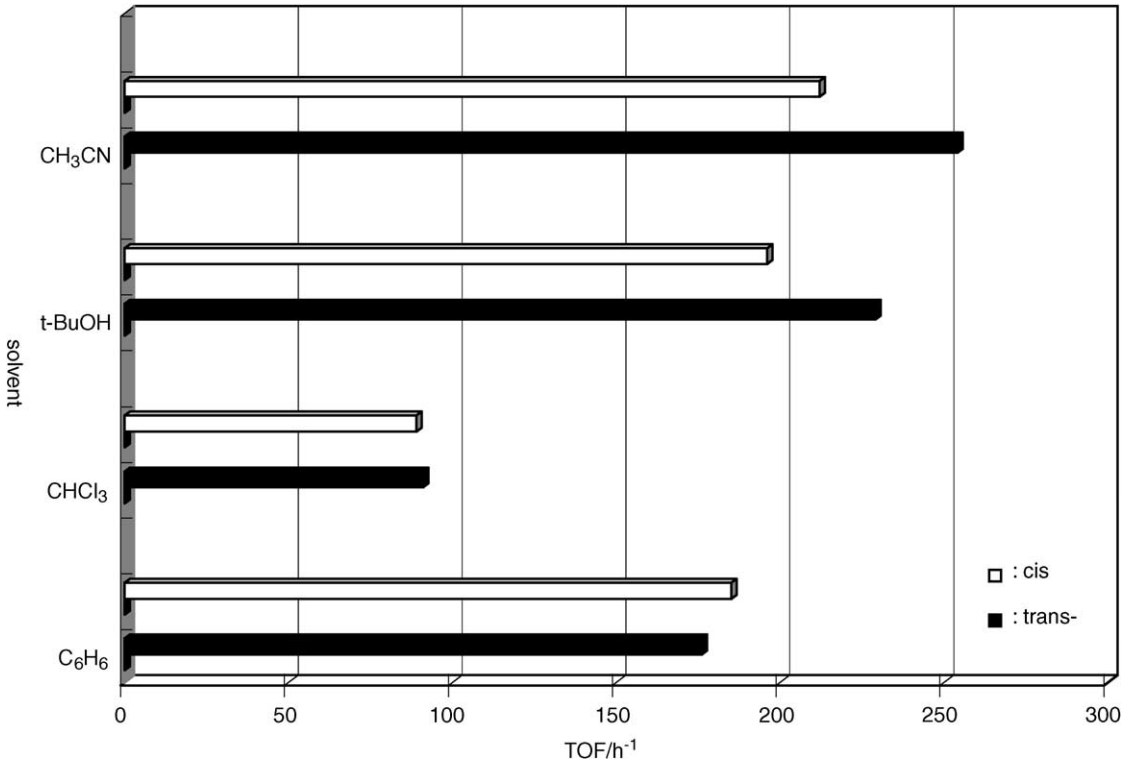

Fig. 7. Effects of the solvents on the TOF for the epoxidation of *trans*- and *cis*-2-hexene-1-ol with H_2O_2 on cetyl-HoW10 at 30 °C: (■) and (□) *trans*- and *cis*-2-hexene-1-ol, respectively. Substrate 8.0 mmol, catalyst 0.04 mmol, H_2O_2 (30%, 10 ml) 100 mmol, solvents 10 ml.

saturation. Thus, the reaction conditions were selected as follows: substrate 8 mmol, catalyst 0.01 mmol, H_2O_2 (30%) 100 mmol. The amount of catalyst used was low compared with that of the substrate, and also the reaction temperature was rather low. In fact, the data collected for both the substrate and product in the course of the reaction were quantitatively analyzed by zero-order kinetics at least up to ca. 60–70% conversion. TOF (h^{-1}) values, as estimated from the zero-order rate constant ($k_{0,obs}$ (mmol h^{-1})) per 0.01 mmol of the catalyst, are added in Table 6.

The TOF values in the organic solvent-free system appear to be about three- and nine-times higher than those in the CH_3CN system at 30 and 0 °C, respectively, in Table 6. The *trans*-isomer is also preferentially epoxidized rather than the *cis*-isomer. The Arrhenius plots of TOF for both *trans*- and *cis*-2-hexen-1-ol in CH_3CN solvent and in the organic solvent-free system show good linear lines as illustrated in Fig. 8. The Arrhenius parameters estimated from the plots are summarized in Table 7. It should be noted that the activation energies are about 20–25 kJ mol^{-1} lower in the organic solvent-free state than in the

Table 6
Temperature dependences of epoxidation rates of 2-hexen-1-ol with H_2O_2 on cetyl-HoW10 in CH_3CN and in organic solvent-free at 0–30 °C

Temperature (°C)	Substrate	TOF (h^{-1})	
		In CH_3CN	In solvent-free
30	*Trans*-2-hexen-1-ol	254	729
	Cis-2-hexen-1-ol	212	710
20	*Trans*-2-hexen-1-ol	97.7	428
	Cis-2-hexen-1-ol	75	347
10	*Trans*-2-hexen-1-ol	33.7	159
	Cis-2-hexen-1-ol	22.7	145
0	*Trans*-2-hexen-1-ol	10.1	93
	Cis-2-hexen-1-ol	9.1	75

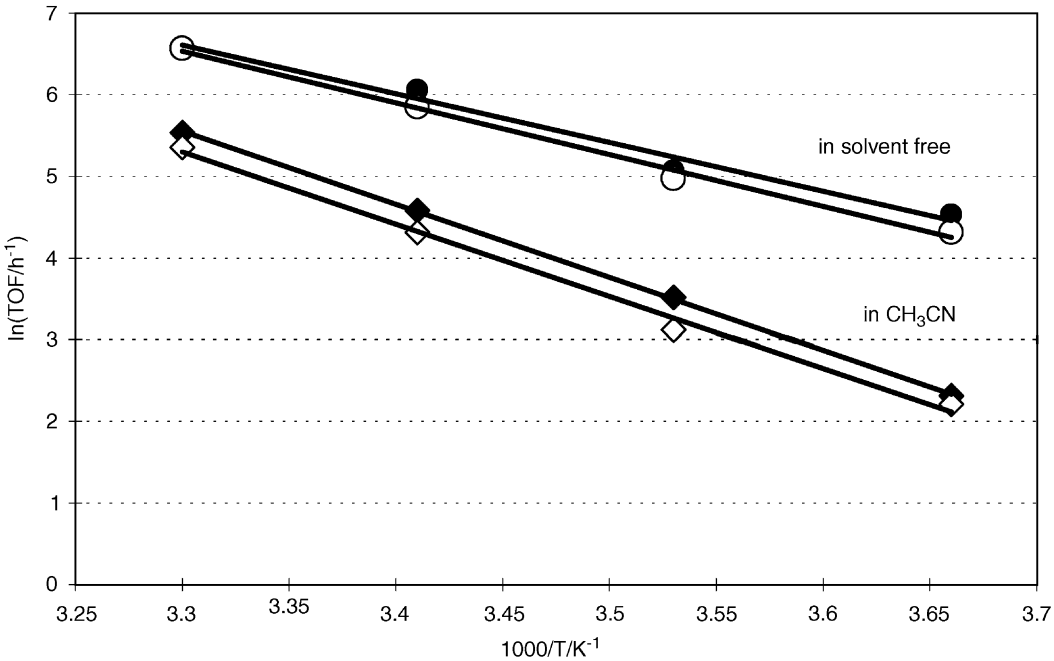

Fig. 8. Arrhenius plots for the epoxidation rates (TOF, h^{-1}) of *trans*- and *cis*-2-hexene-1-ol with H_2O_2 on cetyl-HoW10 in the CH_3CN and in the organic solvent-free systems in the temperature range of 0–30 °C: (●) and (○) *trans*- and *cis*-2-hexene-1-ol in organic solvent-free; (◆) and (◇) *trans*- and *cis*-2-hexene-1-ol in CH_3CN, respectively. Substrate 8.0 mmol, H_2O_2 (30%, 10 ml) 100 mmol, catalyst 0.04 mmol in CH_3CN (10 ml) and 0.01 mmol in the solvent-free.

Table 7
Arrhenius parameters for epoxidation rates of *trans*- and *cis*-2-hexen-1-ol with H_2O_2 on cetyl-HoW10 in CH_3CN and solvent-free states at 0–30°C

Solvent	Substrate	Arrhenius parameters	
		ln(TOF) (h^{-1})	E_a (kJ mol^{-1})
In CH_3CN	*Trans*-2-hexen-1-ol	34.5	73.5
	Cis-2-hexen-1-ol	35.1	74.4
In solvent-free	*Trans*-2-hexen-1-ol	26.3	49.6
	Cis-2-hexen-1-ol	27.4	52.6

CH_3CN solvent, as will be discussed in the following sections.

3.2.4. *Catalytic activities of the series of cetyl-LnW10 (Ln: La–Er) compounds for H_2O_2 oxidations of trans- and cis-2-hexen-1-ol in an organic solvent-free state*

The reaction rates for H_2O_2 oxidation of *trans*- and *cis*-2-hexen-1-ol were measured for the series of cetyl-LnW10 catalysts [Ln: Na–Er] under the organic solvent-free condition as follows; substrates 8.00 mmol, catalyst 0.04 mmol, H_2O_2 (30%) 10 ml (100 mmol) at 0 °C. The data gathered in the course of the reactions were also analyzed successfully according to zero-order kinetics. TOF values for *trans*- and *cis*-2-hexen-1-ol were evaluated similarly from the changes in the substrates with time, and the mean TOF values are illustrated in Fig. 9 for comparison. On cetyl-W10 (decatungstate, without the lanthanide ion) measured as a reference, however, the substrates were not stoichiometrically converted to the epoxides even in an early stage, indicating that the epoxide formed is converted further to unknown compounds. The activities of the cetyl-PW12 catalyst were too low to measure the concentration change in the substrates with time under the same conditions, although the TOF value estimated only roughly was given for comparison.

We should pay attention to the fact that the allylic alcohols are efficiently oxidized on the cetyl-LnW10 catalyst to the corresponding epoxides without further degradation up to 60–70% conversion at 0 °C in the

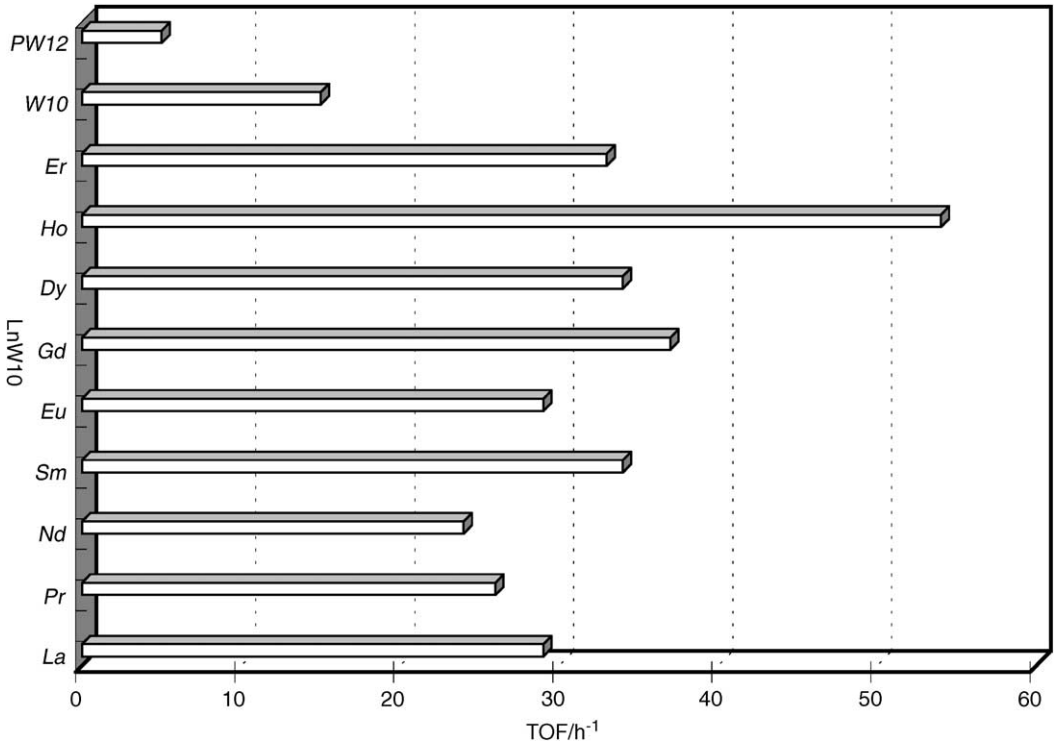

Fig. 9. The mean values of the TOF for the epoxidation of *trans*- and *cis*-2-hexene-1-ol with H_2O_2 on the series of cetyl-Ln(III)W10 and on the reference catalysts (cetyl-W10 and PW12) in the organic solvent-free system at 0 °C. Substrate 8.0 mmol, H_2O_2 (30%, 10 ml) 100 mmol, catalyst 0.04 mmol.

organic solvent-free system. Furthermore, it should be noted that the activity tends to be higher on the catalysts having heavy lanthanide elements than those having light and/or medium weight elements. From the comparison of those data, the working states on cetyl-Ln(III)W10 should be greatly differentiated from the catalysts without lanthanide elements (cetyl-W10 and PW12), clearly suggesting some physicochemical contributions of the Ln(III) ion centered in the catalysis.

4. Discussion

4.1. Catalytic interactions and mechanistic aspects for the H_2O_2 oxidation of allylic alcohols on cetyl-LnW10

The catalytic activities for the epoxidation of cyclooctene and the oxidative dehydrogenation of benzyl alcohol on the series of cetyl-LnW10; Ln: La–Yb compounds have been investigated in the $CHCl_3$–H_2O_2 aqueous biphasic system at 60 °C. The activity for the former reaction tended to decrease with the contraction of the Ln(III) ion in the cetyl-LnW10 catalysts; on the contrary, that for the latter tended to increase inversely [20]. Those results were favorably interpreted according to a mechanistic model in the oxidation step by Mimoun and co-workers [21,22] and the peroxo-complex model postulated, [23,24] in which the active species has been regarded as a mononuclear peroxo-tungstate coordinated by a bulky Ln-containing polyoxotungsutate group as a kind of ligand, as illustrated in Fig. 10(B). That is, the epoxidation of the olefin was considered to be initiated by a nucleophilic attack of the olefin-group on the W(VI) ion, and the oxidative dehydrogenation of the alcohol to occur due to an electronic interaction of the peroxo-species with the hydrogen atoms of the OH- and CH_2-groups [20].

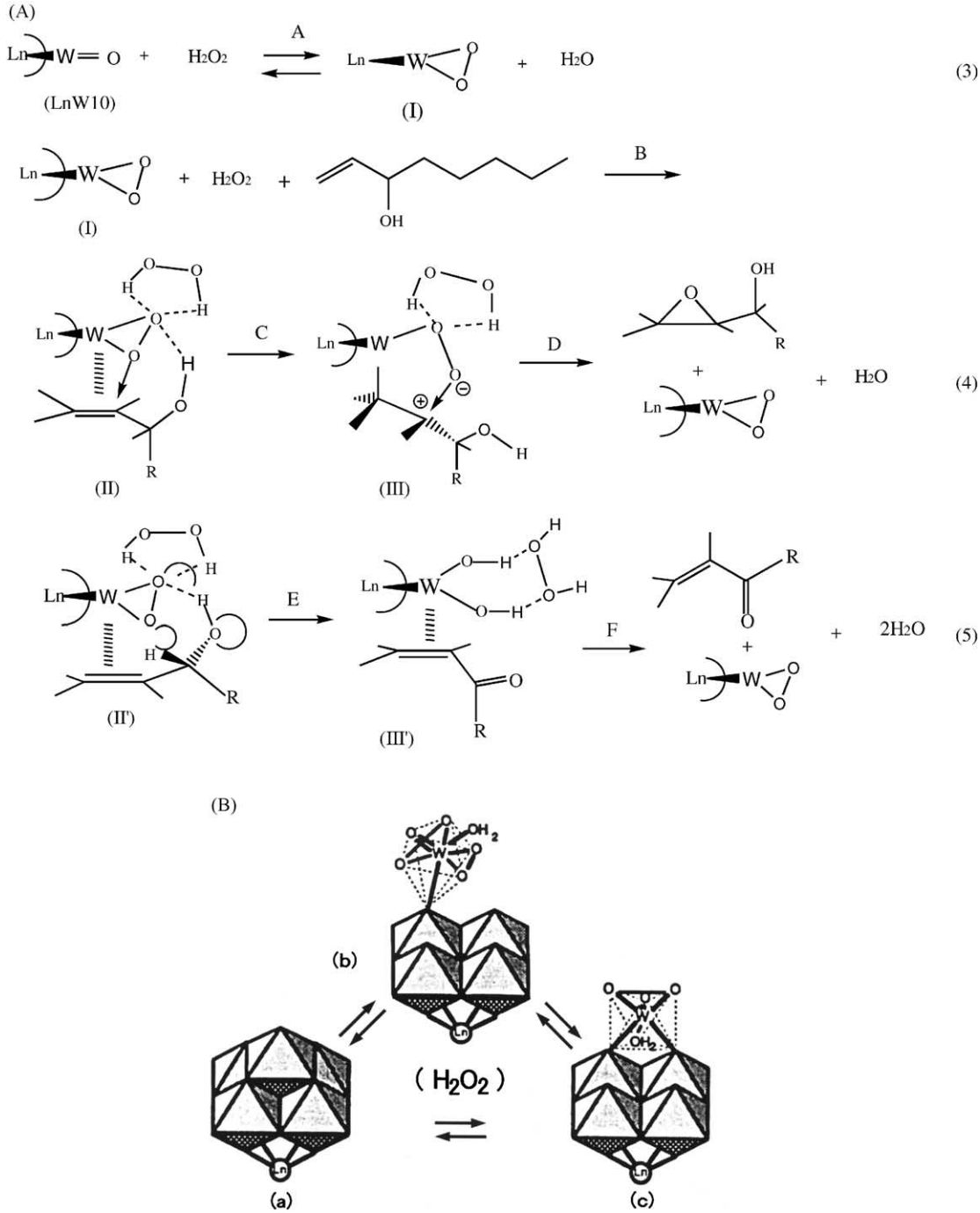

Fig. 10. (A) Schematic representation of a deduced working mechanism for the selective oxidations of allylic alcohols on cetyl-Ln(III)W10: the epoxide and enon formations correspond to Eqs. (4) and (5), respectively. (B) The structure model and catalytic cycle of species (I) in Eq. (3), as formed in Ce-, Nd-, and SmW10/H_2O_2 reacting systems, which have been postulated by in situ FT-IR, FT-Raman, and ^{183}W NMR spectrometries [20,23,24] and also by a kinetical analysis [29,30].

In the H_2O_2 oxidation of allylic alcohols on the catalyst system, thus, both the interactive modes could be expected to act cooperatively. In fact, the reaction rates, R_{epoxy}, were promoted according to 1.6 of the order of the H_2O_2 concentration, and on the contrary, R_{enon} was suppressed according to 0.6 of the order, as summarized in the rate Eqs. (1) and (2), respectively. In the H_2O_2–LnW10 reacting system, a peroxo-complex has been confirmed to be formed at first as schematically expressed by Eq. (3) in Fig. 10(A) [23,24]. In the H_2O_2–LnW10–allylic alcohol reacting system, thus, such a peroxo-species would interact simultaneously with an allylic alcohol and the additional H_2O_2 molecules, as illustrated as species (II) and (II′) in Eqs. (4) and (5), respectively, in Fig. 10(A). This means that the additional H_2O_2 molecules act to activate positively the substrate molecule for the epoxide formation (step C) at 1.6 of the order and, on the contrary, negatively toward the enon formation (step E) with −0.6 of the order. Furthermore, the steps D and F will be followed easily to derive the formations of the epoxide and enon, respectively. Therefore, the deduced working mechanism could be explained as follows: (1) the negative charge on the oxygen ion in the peroxo-species may tend to be considerably low accompanied by interaction with an additional H_2O_2 molecule, (2) the interaction of the oxygen ion with the OH-group in the substrate might become weak and at the same time the interaction between W(VI) and the olefin group might become strong, and thus, (3) the formation of species (III) from species (II), step C, will be favored. On the contrary, step E will be rather prohibited, as illustrated in Eqs. (4) and (5) in Fig. 10(A).

4.2. Catalytic features and working states of cetyl-Ln(III)W10 on the H_2O_2 oxidation of allylic alcohols

The effects of the solvent on the chemo-selectivity for the epoxidation of 2-hexene-1-ol as shown in Table 5 and Fig. 7 are greatly suggestive for considering the catalytic features and the working states of cetyl-Ln(III)W10. Such chemo-selectivity would be caused by a size effect of the substrates: The highly hydrophobic long chains of the hexadecyl-group in the catalyst may be shrunk tightly in a polar solvent such as CH_3CN. In such a situation, the *cis*-isomer may have more difficulty compared to the *trans*-isomer in gaining access to the catalyst core (LnW10) site through the narrow interspace surrounded by the long chains of the hexadecyl-group, because the cross-section in the former is regarded to be slightly larger than that in the latter. On the other hand, the *cis*-isomer is oxidized easily rather than the *trans*-isomer in a non-polar solvent system such as C_6H_6. In such, a non-polar solvent, the hydrophobic long chain of the hexadecyl-group may be loosely extended toward the surrounding media so that both the *trans*- and *cis*-isomers are evenly close to an active center of the catalyst. Similar trends in the activities have been reported by Prat et al. who have observed the reactions in buffered water–alcohol mixtures around pH 4.5 at 20 °C with a 1.5 M amount of hydrogen peroxide (30%), a 0.01 M amount of tungstic acid, and a 0.02–0.03 M amount of sodium acetate or trimethylamine *N*-oxide [27] and by Neumann et al. who have investigated the epoxidation of a series of hexen-1-ol (1 mmol) compounds with 30% hydrogen peroxide (2 mmol) on 'sandwich' type transition-metal substituted polyoxometalates, e.g. $[WZnMn_2(II)(ZnW_9O_{34})_2]^{12-}$ (0.001 mmol) in a biphasic media at 25 °C [14]. Thus, this might suggest that an activated interaction mode for the epoxidation of the *cis*-isomer is energetically more advantageous than that of the *trans*-isomer in the catalyses. In their catalyst systems, in other words, the activation is suggested to take place usually in a working state which is rather free from steric hindrance.

The activity for the oxidation of 2-octanol to 2-octanone decreased with a decrease in the polarity of the organic solvents used, as previously reported [19]. The order of the activity is almost the same as that for the present epoxidation of 2-hexene-1-ol except for the C_6H_6 solvent, in which the activity was rather higher than in the case of the $CHCl_3$ solvent. Thus, the working state of the catalyst may also be considered to be similar to those for 2-octanol oxidation described in detail in the previous paper [19], i.e. in the H_2O_2–cetyl-LnW10 catalyst system, the neighborhood of the active site is greatly hydrophilic, and the catalyst core is surrounded by long hydrophobic hexadecyl chains.

In this situation, the distributed state of the solvent molecules necessarily depends greatly upon their polarities. Substrate molecules have to access the active site by going through the hydrophobic region at first and then the hydrophilic region, containing the solvent

molecules, for the activation. The great differences in the activity of the organic solvents used (Table 5 and Fig. 7), thus, should be caused by the varieties of those working states, besides the differences in the apparent concentrations of the catalyst and substrate as indicated in the previous section. In fact, the activities in the present catalyst systems were varied greatly from solvent to solvent and also from substrate to substrate.

Additionally, the TOF for hexen-1-ol decreased drastically when the position of the olefinic-group was far from the terminal OH-group, and further, the TOF for *cis*-5-octen-1-ol was ca. 10 times higher than that for 2-octene without the OH-group (Table 4 and Fig. 6). Thus, it should be emphasized again that the terminal OH-group plays an important role in the activation of the olefinic-group on the present catalyst systems.

It should also be noted that the TOF for the epoxidation of 2-hexen-1-ol is substantially promoted in the organic solvent-free state, e.g. ca. three to nine times higher than in the CH_3CN solvent at 30–0 °C as compared in Table 6. Under the organic solvent-free condition, the catalyst with 1-hexadecylpyridinium is dissolved and dispersed directly in the substrate, and thus, the reaction apparently takes place in a biphasic state and in an extremely concentrated state of the substrate. Therefore, a rapid reaction rate could be realized, although H_2O_2 molecules have to be transferred from the aqueous H_2O_2 to the catalyst-containing substrate phase. Additionally, it should be mentioned that the activation energies are about 20–25 kJ mol^{-1} lower in the organic solvent-free state than in the CH_3CN solvent. These differences in the activation energy (ca. 20 kJ mol^{-1}) might suggest that the approach of substrate molecules to the active site on the catalyst core is greatly interrupted by the CH_3CN solvent molecules distributed in and/or around the 1-hexadecylpyridinium chains [19].

4.3. Some chemical effects of Ln(III) ion in cetyl-LnW10 on the catalytic oxidation of allylic alcohols with H_2O_2

The activities for the epoxidation of cyclooctene and the oxidative dehydrogenation of benzylalcohol on the series of cetyl-Ln(III)W10 compounds had been measured in $CHCl_3$–H_2O_2 aqueous biphasic system, in which the former tended to decrease with the contraction of the Ln(III) ion size, and on the contrary, the latter tended to increase inversely [20]. Based on those findings, it has been proposed that an electrophilic interaction of the W(VI) ion with the olefinic-group causes the epoxide formation to progress favorably. On the other hand, a nucleophilic interaction of the peroxo-group with the H-atom in the OH-group does the same for the enon formation, as illustrated in Fig. 8 of [20]. The density, $+\delta$, on the W(VI) might become low with the contraction of the Ln(III) ion size, because the bonding interaction between Ln(III) and polyoxotungstate units is stronger, when the lanthanide is heavier (18) and upon further speculation, when the number n in the $4f^n$-electrons is greater.

The reactive interaction modes of allylic alcohols with the peroxo-complex formed on cetyl-Ln(III)W10 were postulated to be species (II) and (II′) in Eqs. (4) and (5) in Fig. 10(A). The interaction modes between the peroxo- and OH-groups also contributed greatly to the epoxide formation, as discussed earlier. Furthermore, a free H_2O_2 molecule participates additionally in the epoxide- and enon-formation steps, as shown in Eqs. (4) and (5), positively in the former and negatively in the latter. With the oxidation of 1-octen-3-ol, the rate for the enon formation increased slightly with the contraction of the Ln(III) ion size, although that for the epoxide formation retained almost constant. Thus, the ratio of TOF_{epoxy}/TOF_{enon} was found to decrease with the ion size contraction between ca. 2.0 and 3.0, as shown by curve C in Fig. 4. This trend coincides well with that of the oxidative dehydrogenation of benzylalcohol [20]. In the case of the epoxidation of 2-hexen-1-ol, the activity also tended to increase rather greatly with the Ln(III) ion contraction, in contrast to the case of the epoxidation of cyclooctene [20]. However, this tendency is understood by a postulation in which, upon the epoxidation of 2-hexen-1-ol, the activation could be controlled preferentially by the interaction between the peroxo- and OH-groups rather than the interaction between the W(VI) ion and the olefin group, the strength of which also varied with the Ln(III) ion contraction. Finally, it should be emphersized that Ln(III) in cetyl-Ln(III)W10, and further the $4f^n$-electron, clearly participated directly or indirectly in the catalytic oxidation of allylic alcohols, by comparing the TOF values with those on cetyl-W10 and PW12 in Fig. 9.

4.4. Utilization of H_2O_2–cetyl-LnW10 catalyst systems for selective oxidation of hydrocarbons

In aqueous H_2O_2–Ce(IV)-, Nd(III)-, and Sm(III) W10 reaction systems, the H_2O_2 decomposition was greatly suppressed with the use of an increased amount of H_2O_2 except for Ce(IV)W10 [29]. In fact, alcohols and olefins (20 mmol) on cetyl-HoW10 (0.02 mmol) were quantitatively catalyzed to the corresponding aldehydes and epoxides with H_2O_2 (30%, 30 mmol) in the organic solvent-free state even at 90 °C, as referred to Table 4 of [19].

The activities of cetyl-HoW10 for 2-, 3-, and 4-hexene-1-ol shown in Fig. 6 seem to be comparable with those of Prat et al. [27]. The TOF for 2-hexene-1-ol was roughly estimated to be only ca. 25 h^{-1} at 20 °C based on their reaction conditions. It decreases drastically when the olefinic-group is kept away from the terminal OH-group (2 → 3 → 4); this is very similar to the present data, as described in Section 4.2. In the oxidation of 3- and 4-hexen-1-ol, the formation of by-products similarly could not be avoided. With respect to the epoxidation of hexen-1-ol, the present catalyst especially in the organic solvent-free state (TOF ca. 400 h^{-1} at 20 °C in Table 6) is clarified to be much more active than their catalyst system.

In the catalyst systems of Neumann et al. [14] as previously described, about 70–80% conversions resulted in the oxidation of *trans*- and *cis*-2-hexen-1-ol after 18 h. TOF values are estimated to be roughly 40–45 h^{-1} based on the reaction conditions. The TOF values also greatly increased on $Na_{11}[WZnRu_2(ZnW_9O_{34})_2]$ in an aqueous phase; 192 and 174 h^{-1} for *cis*- and *trans*-2-hexen-1-ol at 25 °C, respectively (Table 4 in [14]). The TOF for *cis*-3-hexen-1-ol was certainly lowered to one-fifth of that for *cis*-2-hexen-1-ol.

The cetyl-HoW10 catalyst was elucidated to be twice as active or more than those catalysts by Neumann et al. from comparison of those TOF values, and thus, should be fully utilized for H_2O_2 oxidation of hydrocarbons, as tentatively stated in the preceding papers [19,20]. Especially, it must be emphasized that the present catalyst systems are quite stable and effectively workable under mild conditions (at 0 °C) and in the organic solvent-free state, as required recently from the environmental viewpoint.

5. Conclusions

Selective oxidation of allylic alcohols such as 1-octen-3-ol and 2-hexen-1-ol which have an olefinic-group and an OH-group at the terminal, respectively, with H_2O_2 on cetyl-LnW10 was kinetically investigated under various working conditions: (1) the reaction rate equation for 1-octen-3-ol has been expressed by the first-order of the substrate in the organic solvent–H_2O_2 aqueous biphasic systems, and also the rates for the epoxide- and the enon-formation depended upon 1.6 and −0.6 of the order of the H_2O_2 concentration, respectively, as summarized in Eqs. (1) and (2). The mechanistic aspects of the selective oxidation are summarized in Eqs. (4) and (5) of Fig. 10(A); (2) the activity for a series of hexene-1-ol compounds decreases drastically when the olefinic-group is far from the terminal OH-group, and 2-octene without the OH-group, as a reference, is not really epoxidized, suggesting that the terminal OH-group plays an important role in inducing the substrates effectively into an activated state for the epoxidation; (3) in organic solvent–aqueous H_2O_2 biphasic systems, the working states and abilities of the cetyl-LnW10 catalysts are strongly regulated by the polarity of the solvent used; (4) in the organic solvent-free system, the activity is extremely accelerated, thus, cetyl-LnW10 must be utilized as a catalyst, from the environmental viewpoint; (5) with the epoxidation of 2-hexen-1-ol, the activity tends to increase in correlation with the contraction of the Ln(III) ion centered in cetyl-Ln(III)W10. With the oxidation of 1-octen-3-ol, the activity ratio of the epoxide- to enon-formation, TOF_{epoxy}/TOF_{enon}, tends to decrease with the contraction of the Ln(III) ion. These findings were understood favorably based on the interactive modes and the working mechanism postulated in Fig. 10, suggesting also that the $4f^n$-electron of the Ln(III) ion participates directly or indirectly in the catalyses.

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