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Bio-inorganic approach to hydrocarbon oxidation

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Abstract

Oxidation reactions mimicking the biological oxidative processes are summarized. A dioxygen molecule can be activated by way of reductive activation within a coordination sphere of transition metal complexes, and the resulting electrophilic oxo species, which can also be generated by treatment with an oxo transfer reagent (so-called ''shunt path''), exhibit oxidizing ability just like an oxene species. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Monooxygenase; Reductive activation of dioxygen; Epoxidation; Hydroxylation

1. Introduction

A number of catalytic oxidation reactions with molecular oxygen have been developed for the industrial production of oxygenates, because dioxygen is the cheapest oxidant in the chemical industry. However, in spite of the extensive efforts to find effective catalyst systems, epoxidation of olefin (except ethylene), hydroxylation of aromatics and selective conversion of lower alkane still have not been realized by the oxidation with molecular oxygen. All these reactions are exothermic, down-hill reactions (in the sense of thermodynamics) and, in the biological systems, a group of enzymes, monooxygenases, catalyze these reactions quite selectively under the mild conditions. In the past decade, there have been considerable investigations focusing on the function of monooxygenase and the reaction mechanism of typical enzymes such as cytochrome P-450 has been well-elucidated. By mimicking the active sites and reactions of monooxygenase, novel oxidations with molecular oxygen in the presence of reducing agents have been developed. In the present review, strategy of these biomimetic oxidations and recent advances in the field are briefly summarized with emphasis on the catalytic reactions.

2. Reaction and mechanism of monooxygenase

Enzymes which activate dioxygen to oxidize organic substrates into oxygenates are classified into two groups according to the mode of oxygen incorporation (Scheme 1). Dioxygenase incorporates two oxygen atoms of a dioxygen molecule into the sub-

Dioxygenase

$$S + O_2 \longrightarrow SO$$

Monooxygenase

$$S + O_2 + 2H^+ + 2e^- \longrightarrow SO + H_2O$$

Scheme 1.

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strate, whereas monooxygenase transfers only one oxygen atom. The latter usually requires NAD(P)H as a cofactor and the other oxygen atom in dioxygen is converted to water.

As summarized in Table 1, most reactions catalyzed by monooxygenases are remarkable, since the reactions include epoxidation of C–C unsaturated bond and hydroxylation of aromatic ring or C–H bond in saturated hydrocarbon which are hardly achieved by the conventional catalytic systems. Dioxygenase also catalyzes marvelous reactions including regio- and stereo-selective oxidations as well as the reaction giving very unstable product such as prostaglandin. Although the reactions are highly specific, they are rather effortless in terms of activation energy.

Iron and copper are most frequently found in the active center of oxygenases, among which the reaction mechanism of cytochrome P-450 has been most extensively investigated. Cytochrome P-450 is a family of ubiquitous heme-monooxygenase whose active site consists of protoheme-iron-thiolate chromsphere (Fig. 1). Some of the cytochrome P-450 catalyze specific regio- and/or stereoselective oxidations in physiologically important biosyntheses of steroids and fatty acids and another group of cytochrome P-450 are known to be non-specific and show high catalytic activities for a variety of oxidations, e.g. epoxidation of olefin, hydroxylation of aromatic or saturated hydrocarbon, oxidative cleavage of heteroatomic portion of a substrate, oxo-transfer reaction of a molecule containing a hetero atom etc.

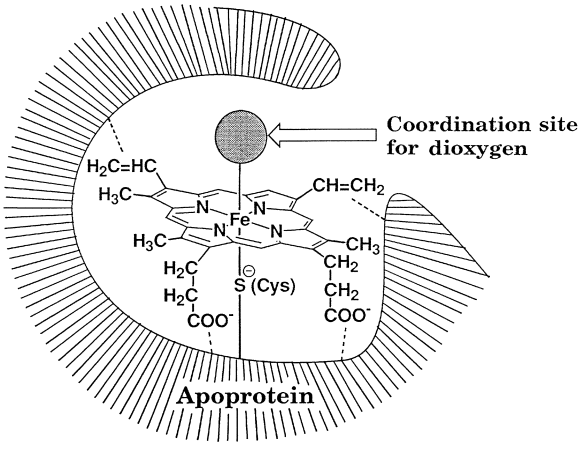


Fig. 1. Proposed structure of the active site of P-450.

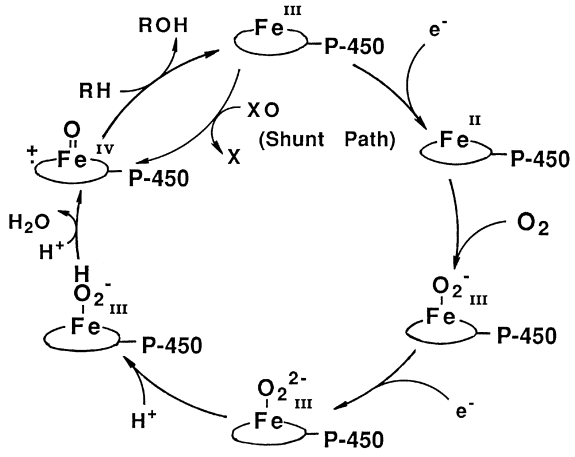


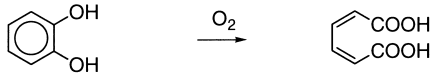
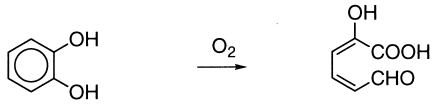
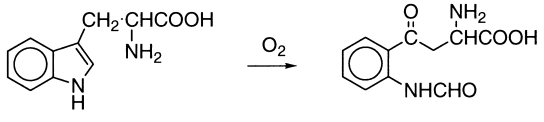
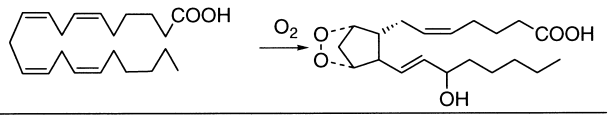
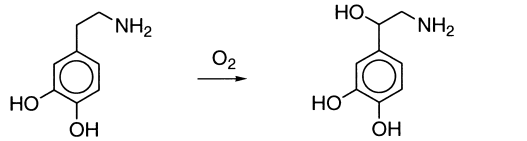
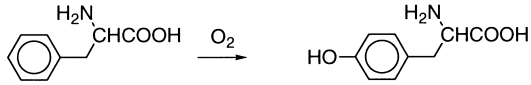
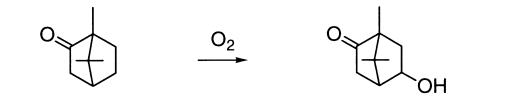
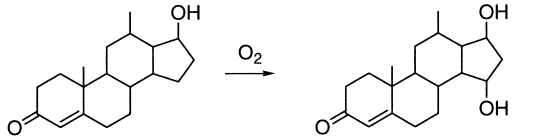
Fig. 2. Postulated reaction mechanism for hydrocarbon oxidation with P-450.

The reaction mechanism of cytochrome P-450 has been established not only by the biological studies but also by the synthetic works on metalloporphyrin relevant to the possible intermediates in the catalytic cycle. The most probable mechanism is proposed by Groves et al. as shown in Fig. 2 [1,2]. The active species for the reaction is assumed to be a high valent iron oxo species **6** resulting from the heterolytic O–O bond cleavage of the coordinated dioxygen molecule. The synthetic models for **6** [3] as well as intermediates **3** [4], **4** [5] and **5** [6] have been prepared, isolated and characterized.

The most important aspect of the reaction scheme is the reductive activation of dioxygen with two electrons and protons from NADPH associated with effective electron and proton transfer systems. Thus, the active species with the strong oxidizing ability, **6**, can be generated exothermically with the elimination of a water molecule. The formed high valent iron oxo species is active enough to induce electrophilic addition to unsaturated C–C bonds and direct oxidation of saturated hydrocarbons.

Cytochrome P-450 can catalyze not only aerobic oxidations in the presence of NADPH but also anaerobic oxidations by oxidants such as iodosylbenzene, alkylhydroperoxide, hydrogen peroxide or peracid and the latter type of reaction is called "shunt path" [1]. Since the concept of the shunt path was postulated for the olefin epoxidation in 1979 for the first time, a number of similar systems have been examined. Not

Table 1. Examples of dioxygenases and monooxygenases.

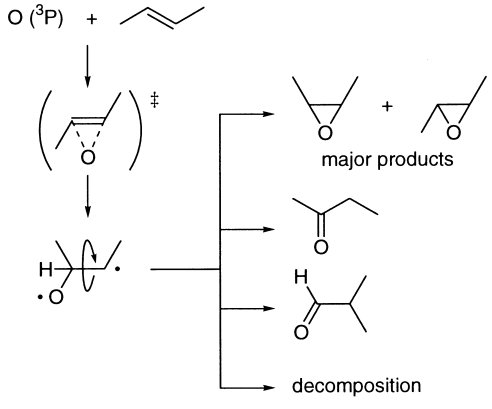
enzyme	reaction
Dioxygenases	
Pyrocatecase Nonheme Fe Pseudomonas arvilla c-1 M. W. 60,000 (α, β)	
Metapyrocatecase 4 Fe Pseudomonas arvilla M. W. 140,000 (α4)	
Triptophane 2,3-dioxygenase heme Fe Pseudomonas acidorans M. W. 121,000 (α4)	
Prostaglandin synthetase heme Fe M. W. 130,000 (α2)	
Monooxygenases	
Dopamine β-hydroxylase 4-7 Cu M. W. 290,000 (α2,β2)	 + ascorbic acid + dehydroascorbic acid
Phenylalanine hydroxylase nonheme Fe	 + NADPH + H^+ + $NADP^+$ + H_2O
Camphor methylene hydroxylase (P450cam) heme Fe Pseudomonas ptida M. W. 45,000	 + NADPH + H^+ + $NADP^+$ + H_2O
Cytochrome P450meg heme Fe Bacillus megaterium M. W. 52,000	 + NADPH + H^+ + $NADP^+$ + H_2O
Methane monooxygenase 2 Fe Methylococcus capsulatus M. W. 210,000 (α2,β2,γ2)	CH_4 + NADH + H^+ $\xrightarrow{O_2}$ CH_3OH + NAD^+ + H_2O

only iron porphyrin complexes but also many other transition metal systems turn out to be active for the cytochrome P-450-type reactions by the action of various kinds of oxidants with a high oxygenation chemical potential. Synthetic applications have been widely reported on the basis of the shunt path concept with oxidants as well as the reductive activation of dioxygen.

3. Reactivities of active species of oxygen

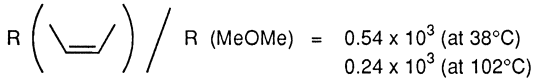
We have already understood that remarkable reaction of monooxygenase mainly comes from the powerful oxidizing ability of the active oxygen species, high valent oxo-iron species produced by the reductive activation of dioxygen by NAD(P)H.

Before introduction of synthetic applications of the biomimetic systems, the reactivity of typical active oxygen species is briefly summarized. The reaction of atomic oxygen at the ground state, O (^{3}P, oxene), generated photochemically was examined more than 30 years ago (Scheme 2) [7]. The first step of the reaction of oxene with olefin is electrophilic addition to form a triplet biradical intermediate, which is rapidly converted to epoxide if the hot molecule is quenched effectively by collision. Some amounts of byproducts such as ketone and aldehyde are formed as results of migration of hydrogen atom and methyl group, respectively. The oxene species also adds to conjugated carbon–carbon unsaturated bond but the intermediate of the reaction easily polymerizes to give resinous product. If such polymerization does not occur, main product may be phenol resulting from the NIH shift. It may be concluded that if active oxygen species like oxene is formed in the presence of olefinic or aromatic hydrocarbon and undesired polymerization is suppressed, epoxidation of olefin or hydroxylation of aromatics is easily realized even in the absence of any catalyst.

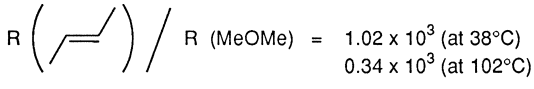


Scheme 2.

The oxene species can abstract a hydrogen atom from hydrocarbon but this abstraction is relatively slow at room temperature. The rate of the addition of oxene to *cis*- or *trans*-2-butene was 10^3 times faster than the abstraction of hydrogen atom from dimethyl ether as revealed by the competitive reaction (Eqs. (1) and (2); *R* stands for rates.) [8].

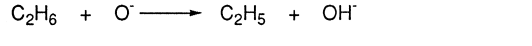


(1)

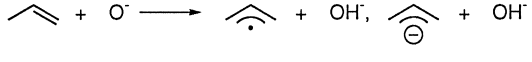


(2)

On the other hand, oxygen atom having a negative charge, O^-, never shows electrophilic reactivity towards hydrocarbon. The reaction of O^- was studied both in gas phase [9] and on a solid surface [10] and it always abstracts hydrogen or proton as shown in Eqs. (3)–(5). Once this type of abstraction occurs at the early stage of the oxidation of unsaturated hydrocarbon, we can never expect olefin epoxidation and probably aromatics hydroxylation. On the basis of these facts, we can understand the reason why such oxygenations are never realized on the conventional solid oxidation catalysts with molecular oxygen. The dissociative adsorption of dioxygen on the solid catalysts

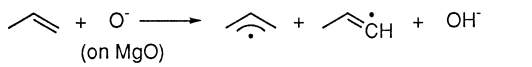


(3)



(4)

C$_3$H$_6$, i-C$_4$H$_8$ radical / anion = 95 / 5
1-C$_4$H$_8$, 2-C$_4$H$_8$ radical / anion = 60 / 40



(5)

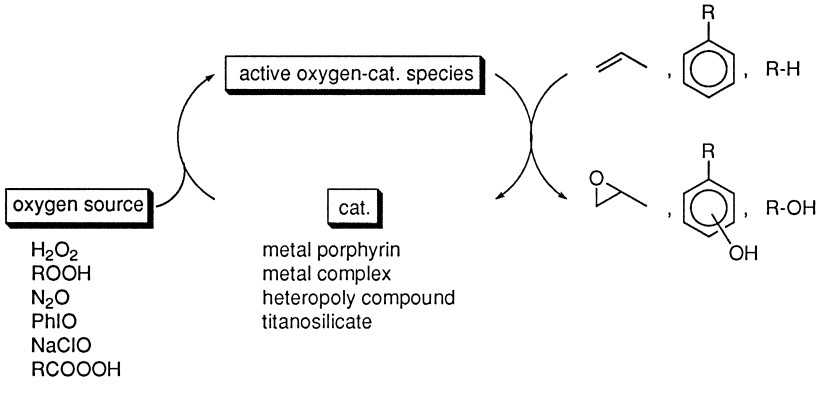
essentially accompanies electron transfer from catalyst to dioxygen to compensate large dissociation energy of dioxygen. The main active oxygen species on the transition metal or metal oxide catalysts are known to be O^-, O^{2-} and rarely O_2^-. Since even O_2^- is reported to work as a nucleophile [11], it may be impossible to expect that these nucleophiles add to unsaturated carbon–carbon bond to form epoxide or phenol. Thus, the olefin epoxidation and aromatics hydroxylation require special oxidants such as N_2O, H_2O_2, O_3, NaClO, PhIO, peroxide and peracid to generate neutral electrophilic oxygen atom without additional energy (or reducing agents to make such oxygen atom exothermically by leaving a water molecule).

4. Oxygen transfer reaction

A huge number of catalyst systems for olefin epoxidation have been reported so far on the basis of the shunt path concept of cytochrome P-450 (Scheme 3). It was found that many transition metal porphyrins such as manganese [12], chromium [13], ruthenium [14] and osmium complexes [15] are effective for olefin epoxidation. A variety of oxygen sources such as H_2O_2, O_3, NaClO, PhIO, N_2O, peracid, and hydroperoxide are used for the reaction. Electrocatalysis to activate dioxygen reductively is also successfully employed [16].

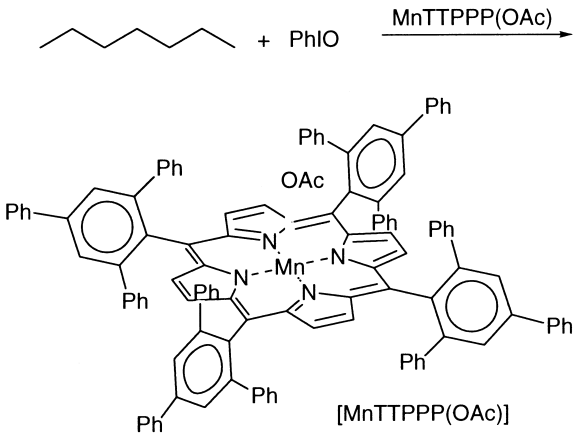
Because of the oxidative degradation of the metalloporphyrin skeleton under the reaction conditions, the catalytic activities of these systems are limited. In order to overcome this disadvantage, much efforts have been paid to prepare robust porphyrins. Introduction of electro-negative groups on the pyrrole ring of the porphyrin increases the lifetime of the catalytic species and also enhances the oxidizing capability by increasing the electrophilicity of active iron-oxo species. Thus, maximum turnover number more than 200,000 was reported for the epoxidation of α-methylstyrene with 5,10,15,20-tetrakis (2′,6′-difluorophenyl)porphyrin [17]. Perfluorinated porphyrin iron complex was found to show high and stable catalytic activity [18]. It has been also clarified that porphyrin is not always necessary for the reaction. Various kinds of organic and even inorganic matrices can be utilized to support active transition metal cations. Inorganic matrices such as microporous materials, layered materials and heteropoly compounds are more stable with respect to the oxidative conditions as well as higher temperature. Titanosilicate was successfully utilized for the propylene epoxidation and aromatics oxidation with hydrogen peroxide [19]. Heteropoly compounds combined with phase transfer catalysts are also employed for a series of oxidation with hydrogen peroxide [20].

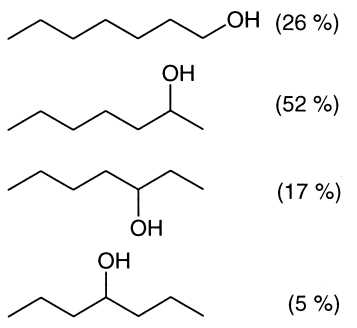
The most serious disadvantage of the reaction modeling the shunt path oxidation is quantitative consumption of expensive oxidants. Hydrogen peroxide and hypochloride are relatively cheap but consumption of them still strongly limits the application of the reaction to the production of bulk chemicals. Therefore, oxygen transfer reaction based on the shunt path should be directed towards the regio- or



Scheme 3.

stereoselective synthesis of more expensive fine chemicals.



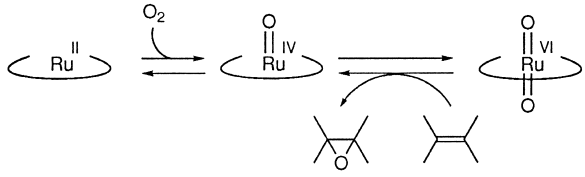


(6)

Regioselective hydroxylation of *n*-alkane was attempted using both hindered porphyrin complexes and microporous materials. Highly hindered porphyrin, 5,10,15,20-tetrakis(2′,4′,6′-triphenylphenyl)-porphyrin Mn complex [21] is rather effective than iron phthalocyanine prepared in the cavity of Y-Zeolite [22] for the terminal oxidation of *n*-alkane (Eq. (6)). Although a considerable amount of 1-ol is formed, regioselectivity is insufficient and the main product is still 2-ols.

Asymmetric epoxidation of prochiral olefin using chiral porphyrin complexes was attempted soon after the establishment of the shunt path concept (Fig. 3). Groves et al. prepared the chiral porphyrin complex [23], and Mansuy et al. reported the "basket-handle" iron porphyrin complex bearing the L-phenylalanine residues [24] and the enantioselective epoxidation of styrenes was achieved with 48% excess of (R)-epoxides (styrene). The enatioexcess of epoxide was improved by Naruta et al. apparently through the π–π interaction between chiral ligand and substrates [25].

More highly stereoselective epoxidation have been developed by chiral manganese Schiff base complexes by Jacobsen [26] and Katsuki (Eq. (7)) [27]. Olefins bearing various functional groups such as ether, ester, amide, nitro, nitrile and acetylene groups can be epoxidized successfully, and conjugated mono-, di-, tri-, and even tetra-substituted olefins are converted to the epoxides in up to 99% ee.



Scheme 4.

Formation of P-450-like active species from dioxygen without using any oxidant was examined by several groups. It was reported that ruthenium(II) porphyrin complex is oxidized by molecular oxygen to di-oxo ruthenium(VI) complex, which oxidizes tetramethylethylene to the epoxide at room temperature accompanied by the formation of the starting ruthenium(II) complex (Scheme 4) [14]. This means that ruthenium porphyrin complex can catalyze epoxidation of olefin with molecular oxygen. Unfortunately, turnover frequency of the system is too much low and no effective aerobic epoxidation without oxidants or reducing agents have been reported until now.

Similar challenges using transition metal cations supported in more robust matrices were also made. Selective oxidations of propane to acetone and 2-propanol and isobutane to *tert*-butanol with molecular oxygen were reported for azido(tetraphenylporphyrinato)complexes of Cr(III), Mn(III) and Fe(III) at

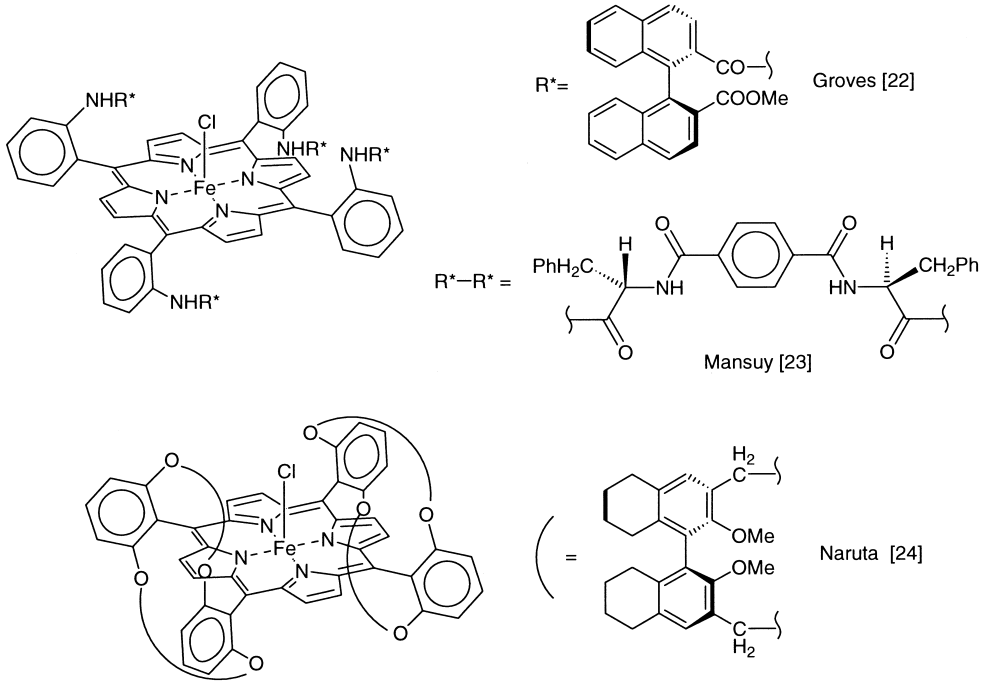
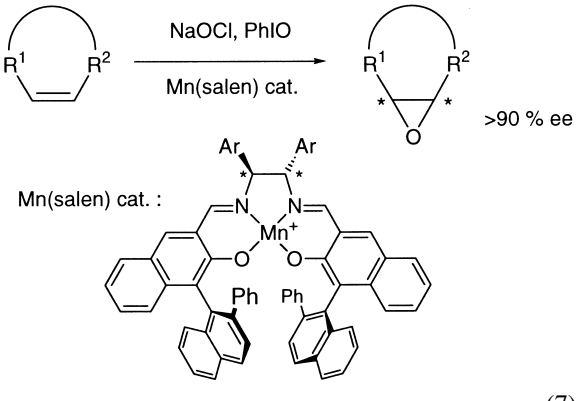


Fig. 3. Chiral porphyrin complexes used for the asymmetric epoxidation of prochiral olefin.

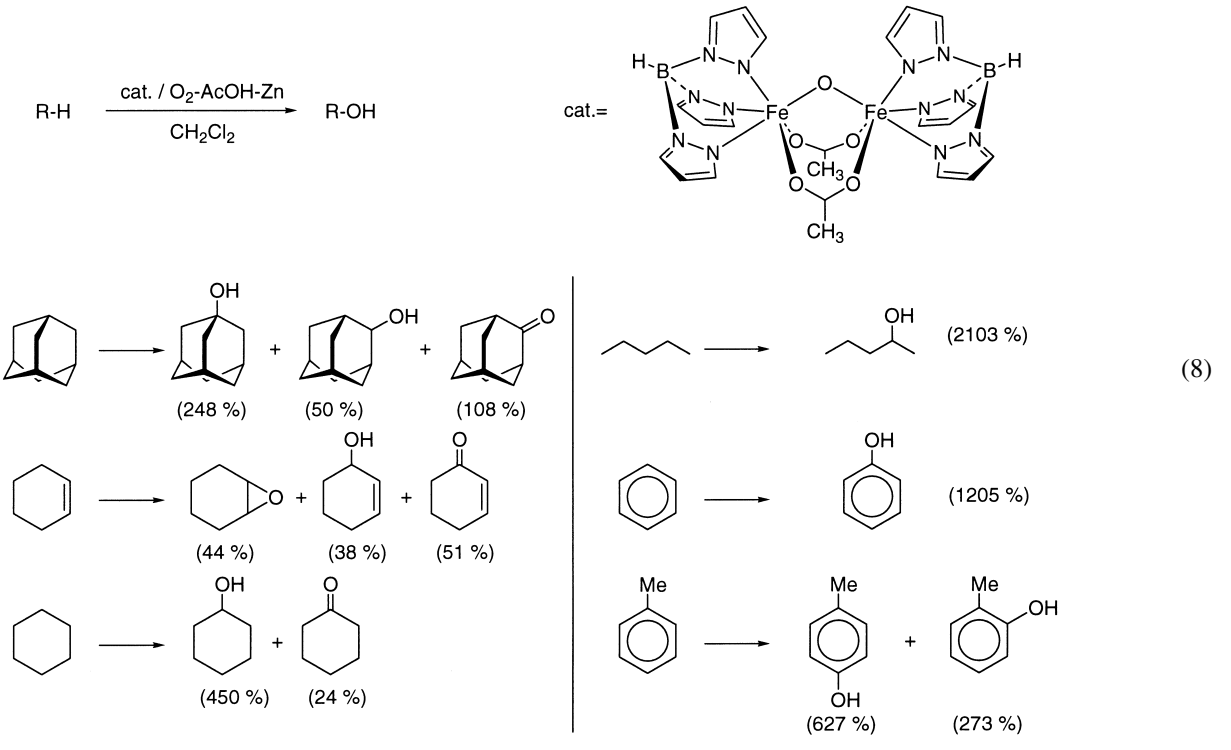
100°C–150°C and 80°C, respectively [28]. Aerobic oxidation of methane to methanol was also claimed using iron(III) supported on sodalite matrix at 420°C [29]. The heterogeneous catalysis by isolated transition metal cation in the solid matrices may be expected to develop a new field of future catalytic oxidation.



(7)

5. Aerobic oxidation with reducing agents

As described earlier, monooxygenase may be recognized as the effective catalyst system to promote epoxidation of olefin and hydroxylation of saturated hydrocarbon and aromatics by activating dioxygen to oxene-like active species with the assistance of protons and electrons from the strong reducing agent NAD(P)H. By following the concept, activation of dioxygen by artificial reducing agents may be expected to establish new effective oxidation systems with molecular oxygen. The effective aerobic oxidation of saturated C–H bond and unsaturated C–C bond with iron complex catalyst in the presence of reducing agent has been known for a long time as Udenfriend reaction [30]. Ascorbic acid is successfully employed as a reducing agent to activate molecular oxygen. Barton et al. developed an aerobic oxidation using zinc powder as a reducing agent in the



(8)

acidic conditions [31]. Saturated hydrocarbon is oxidized to the corresponding alcohol or ketone by aerobic oxidation at ambient temperature and the reaction system composed of iron complex/pyridine/acetic acid/zinc powder is called Gif system. We have also demonstrated an aerobic oxidation with zinc powder by mimicking the active site of methanemonooxygenase (MMO) and the system can oxidize not only saturated hydrocarbon but also olefin and aromatics at room temperature forming alcohol, epoxide and phenol (Eq. (8)) [32].

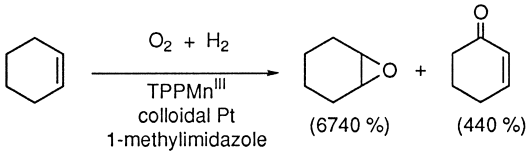
Although these reactions have contributed to the establishment of the concept of biomimetic oxidation, consumption of NAD(P)H, ascorbic acid or zinc powder may not be recommended for the practical synthesis. Thus employment of cheaper reducing agents such as hydrogen, carbon monoxide and aldehyde were challenged and a group of new reductive oxidations have been developed in the last decade. The reaction mechanism differs depending on the system but it is clear that oxene species can be generated easily by using a reducing agent as demonstrated by the comparison of energy to form it (Table 2). Dissociation of dioxygen requires a huge energy but it is decreased remarkably by using reducing agents and oxidizing ability of dioxygen is enhanced kinetically in the presence of them.

Table 2
Thermochemistry of O_2-activation

O_2-activation	ΔH (kcal/mol)
$O_2 \rightarrow 2O$	119
$O_2+2H^+ +2e^- \rightarrow O+H_2O$	−730
$O_2+H_2 \rightarrow O+H_2O$	1.4
$O_2+CO \rightarrow O+CO_2$	−8
$O_2+CH_3CHO \rightarrow O+CH_3COOH$	−10

Aerobic epoxidation of olefin with molecular hydrogen was first demonstrated by Tabushi et al. using Mn tetraphenylporphyrin complex (Eqs. (9) and (10)) [33]. Geraniol and related olefins were epoxidized by molecular oxygen selectively. Regios-

electivity of the epoxidation suggested that active species of oxygen is electrophilic just like cytochrome P-450. The reaction was examined as the model of monooxygenase but a serious defect of the reaction from the standpoint of synthetic chemistry is noted, that is, too much hydrogen is wasted independently from the epoxidation. More effective



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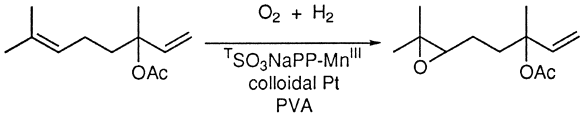
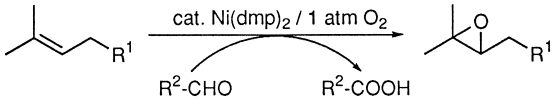
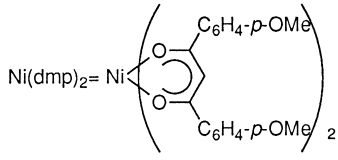


(10)

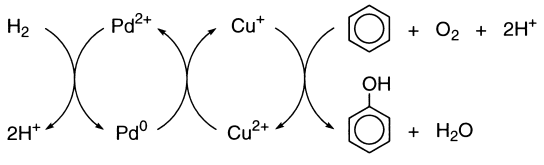


(11)



epoxidation was developed by Yamada et al. using acetaldehyde as a reductant (Eq. (11)) [34]. The system is applicable to most kinds of olefin and may offer a useful aerobic epoxidation method for organic synthesis. Murahashi et al. have also developed useful organic synthesis by using acetaldehyde as a reducing agent [35].

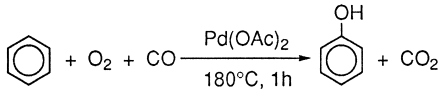
Hydroxylation of aromatic hydrocarbon to phenols was also studied by Sasaki et al. employing $Cu(I)/O_2/H_2SO_4$ (Scheme 5) [36]. The system converts Cu(I)



Scheme 5.

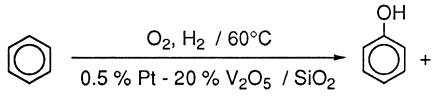
into Cu(II) stoichiometrically but the reaction proceeds catalytically when Cu(II) is reduced to Cu(I) by molecular hydrogen in the presence of a palladium cocatalyst [37].

The aerobic oxidation of benzene to phenol is also possible by using carbon monoxide as the reducing agent. Fujiwara et al. reported a palladium-catalyzed hydroxylation of benzene with molecular oxygen and carbon monoxide at elevated temperature (Eq. (12)) [38]. Although the catalyst system appears to be far from enzyme,



(12)

^{18}O tracer experiments reveal that one atom of dioxygen is incorporated into phenol and the other to carbon dioxide just like the reaction of monooxygenase. The most effective hydroxylation of aromatic hydrocarbons with molecular oxygen and hydrogen was recently developed by Miyake et al. (Eq. (13)) [39]. Benzene is selectively oxidized to phenol on the noble metal catalyst with vanadium pentoxide supported on silica gel, in particular, $Pt–V_2O_5/SiO_2$. The reaction was carried out both in liquid phase in the



(13)

Selectivity	99.7 % based on benzene 30 - 40 % based on O_2
Activity	210 g / kg-cat·hr (1 atm) 1230 g / kg-cat·hr (5kg / cm^2)
	cf. 1470 g / kg-cat·hr (1 atm; 0.5 mol % Pt- 0.5 % Pd / ZrO_2)

presence of acetic acid at 20°C–60°C and in the gas phase at elevated temperature [40]. Sufficient space time yield for industrial production of phenol was obtained in the reaction under pressure and formation of carbon oxides was almost suppressed. The only weak point of the reaction is waste of hydrogen. The efficiency of oxygen to form phenol is 30%–40% meaning that still 7–8 moles of hydrogen is consumed to form one mole of phenol. Although the reaction is the most effective one ever reported and almost satis-

fies industrial demands, a little bit improvement, especially decrease of hydrogen consumption, is requested before the commercial production. Nevertheless, the reductive activation of oxygen is expected to develop new industrial oxidations of future technology.

6. Biomimetic oxidations modeling binuclear enzymes

Apart from heme iron oxygenases such as cytochrome P-450, a number of enzymes having a binuclear active center are known. Methanemonooxygenase having a binuclear iron site and tyrosinase having a dicopper center have been extensively investigated. Binuclear sites are also found in oxygen carriers such as hemerythrin and hemocyanin. We have prepared novel binuclear μ–η^2:η^2 dioxygen copper complexes using hindered hydrotris(3,5-dialkylpyrazolyl)borates which exactly reproduce the physicochemical properties of the active centers of hemocyanin and tyrosinase (Fig. 4) [41]. This work has been extended to the formation of di-μ-oxo copper complexes by using triazacyclononane ligands by Tolman et al. [42]. Characteristic reactivity of coordinated dioxygen was observed in both complexes [43,44]. Binuclear dioxygen complexes of iron have also been prepared in connection with the reaction mechanism of MMO [45–48]. Existence of μ–η^2:η^2 or di-μ-oxo cobalt complex (Fig. 4) and its high reactivity were recently reported by us [49]. New types of dioxygen activation will be developed on the basis of peculiar chemical and geometrical properties of binuclear complexes. Actually, a regiospecific oxidative polymerization of phenol producing excellent engineering plastics was realized by employing binuclear copper complex catalysts (Scheme 6) [50]. Aerobic oxidation based on the catalysts having a multimetal center is also expected to develop a new field of oxidation in near future.

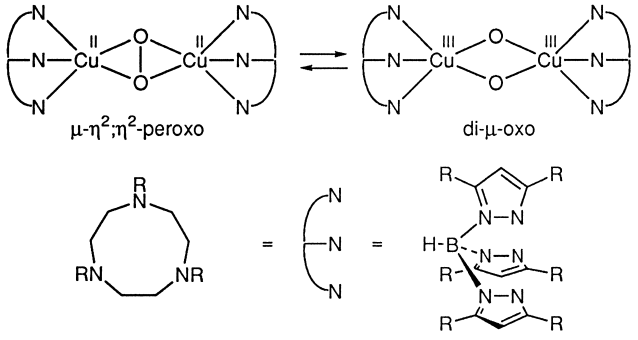
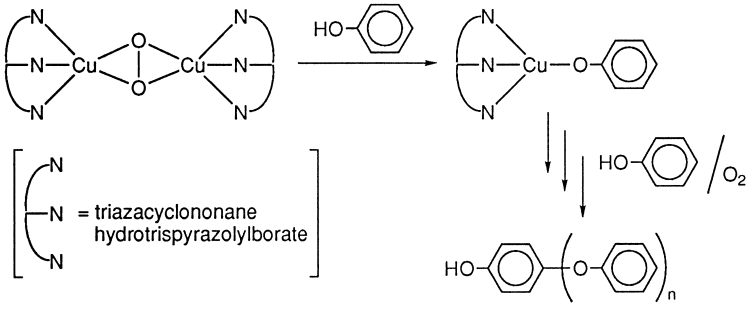


Fig. 4. Novel binuclear dioxygen copper complexes which reproduce the physicochemical properties of the active centers of hemocyanin and tyrosinase.



Scheme 6.

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