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Reactivities of active oxygen species and their roles in the catalytic oxidation of inactive hydrocarbon

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Abstract

Reactivities of active oxygen species with hydrocarbons and their roles in the catalytic oxidation are discussed. The concepts and recent developments including the activation of dioxygen molecule with reducing agents are summarized with emphasis on the catalytic oxidation of inactive hydrocarbons. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Selective oxidation; Active oxygen species; Biomimetic oxidation; Reductive oxidation; Oxene

1. Introduction

Catalytic oxidation with molecular oxygen has been investigated extensively in the last several decades as the most prospective conversion to introduce functional group into inactive hydrocarbons for the utilization of cheaper organic carbon resources. The oxidation reaction inevitably accompanies the combustion of hydrocarbon to carbon oxides and how to decrease such combustion and how to increase the selectivities to the target oxygenates are key technology for the industry. Both hydrocarbon and molecular oxygen are activated on the catalyst which usually consists of transition metal mixed oxides. However, generally speaking, catalysts play more important roles in the activation of dioxygen, and the nature of activated oxygen species influences strongly the rate and selectivity of the reaction. Recently, not only the direct activation of dioxygen with catalyst but also indirect activation, especially the activation of dioxygen in the presence of reducing agents have been investigated extensively and these new type activations of dioxygen have been widely employed in the functionalization of inert hydrocarbon [1]. The concepts and recent advances in the field are summarized and discussed with emphasis on the catalytic conversion of inactive hydrocarbon.

2. Reactivities of $O(^3P)$, O^- and O_2^-

Several kinds of active oxygen species such as O^-, O^{2-}, O_2^- etc., have been detected on the surface of oxidation catalysts mainly by spectroscopic methods. The nature of these active oxygen species found on the catalyst surface depends strongly on the counter metal cation and structural conditions. However, in spite of such specificity, it seems to be important to examine the fundamental reactivity of each species with hydrocarbon.

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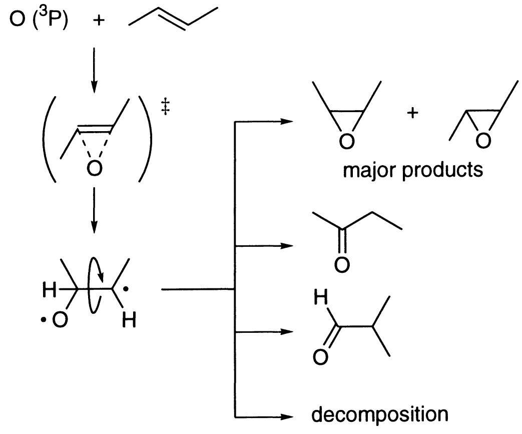
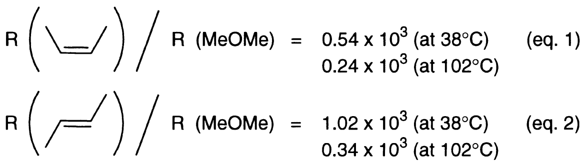


Scheme 1.

The reaction of atomic oxygen at the ground state, O (^{3}P, oxene), generated photochemically was investigated precisely more than 30 years ago by Sato and Cvetanovic [2,3] (Scheme 1). The first step of the reaction of oxene with olefin is an electrophilic addition to form a triplet biradical intermediate, which is rapidly converted to epoxide if the hot molecule formed in the reaction is quenched effectively by collision. Some amounts of byproducts such as ketone and aldehyde are formed as the results of the migration of hydrogen atom and methyl group, respectively. The oxene species also adds to conjugated carbon–carbon unsaturated bond but the reaction intermediate easily polymerizes to give resinous products. If such polymerization does not occur, main product may be phenol resulting from the NIH shift of arene oxide formed intermediately. 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 without any catalyst.

The oxene can abstract a hydrogen atom from inert hydrocarbon at room temperature but this abstraction is relatively slow compared with the addition to C–C unsaturation. 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 demonstrated by the competitive reaction in gas phase [4].

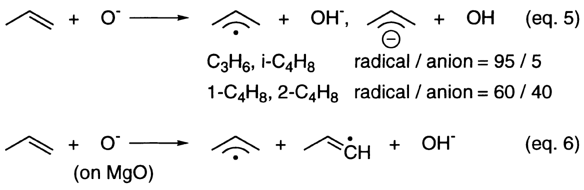


On the other hand, every oxygen species having negative charge behaves as the nucleophile. The reaction between O_2^- and RX was reported as a nucleophilic substitution (S_N-2) accompanied with an electron transfer to produce ROOR (Eq. (3)) [5–8]. The reactivity of O_2^- with hydrocarbon is not so high. It never reacts with usual olefin at room temperature and abstracts hydrogen atom or proton only from highly activated methylene or from molecules having lower pK_a values [9,10]. However, it serves as the precursor of hydroxyl radical in the protic solvent. Very reactive hydroxyl radical is produced in situ via OOH resulted from the combination between O_2^- and proton [11,12]. Nevertheless, O_2^- is rather inactive to hydrocarbon in the absence of proton source.

$$\begin{aligned} &RX + O_2^- \rightarrow RO_2\cdot + X^- \\ &RO_2\cdot + O_2^- \rightarrow RO_2^- + O_2 \qquad \text{(eq.3)} \\ &RO_2^- + RX \rightarrow ROOR + X^- \end{aligned}$$

On the contrary, it has been reported that O^- is far more active and reacts with any hydrocarbon as strong nucleophile. The reaction was studied in gas phase at first [13,14] and then on a solid surface [15,16]. It always abstracts hydrogen or proton as shown in Eqs. (4)–(6).

$$C_2H_6 + O^- \longrightarrow C_2H_5 + OH^- \qquad \text{(eq. 4)}$$



When 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 the reactivities of O(^{3}p) and O^-, we can understand the reason why such oxygenations are never realized in the conventional oxidation on the solid catalysts with molecular oxygen. The dissociative adsorption of dioxygen on the solid catalysts essentially accompanies electron transfer from catalyst to dioxygen to compensate large dissociation energy of dioxygen. Actually, main active oxygen species on the transition metal or metal oxide catalysts are O^-, O_2^- and rarely O^{2-}. Since all these species are nucleophile, it may be impossible to expect that these species add to unsaturated carbon–carbon bond to form epoxide or phenol. Thus olefin epoxidation and aromatics hydroxylation require special oxidants such as N_2O, H_2O_2, O_3, NaClO, PhIO, peroxide and peracid to transfer neutral and electrophilic oxygen atom to active site of catalyst or reducing agents such as hydrogen molecule to generate atomic oxygen species without any additional energy by the reaction with dioxygen leaving a water molecule.

This consideration has developed new type oxidations, “oxygen transfer reaction” using oxidants which can transfer atomic oxygen easily and “reductive oxidation” employing molecular oxygen with reducing agents such as H_2, CO and aldehyde.

3. Selection of metal oxide catalyst

Needless to say, the selection of metal element for the design of the oxidation catalysts depends strongly on the nature of oxygen species which reflect the character of the counter metal cation on the metal oxide catalyst. As exemplified in Fig. 1, almost all catalytic oxidations of hydrocarbon consist of two competitive steps, the dehydrogenation step and/or oxygen addition step to unsaturated carbon atom in the reactant or intermediate.

The dehydrogenation step is rather easy, because both electrophilic and nucleophilic oxygen species can abstract hydrogen. The addition step is observed only when reactant hydrocarbon or intermediate has no weaker C–H bond which is easily cleaved. In other wards, the addition step is realized only for ethylene, butadiene and π-allyl intermediates which exclusively consist of vinylic C–H bonds and C–C unsaturated bonds. In addition, it needs oxygen species having less nucleophilic character.

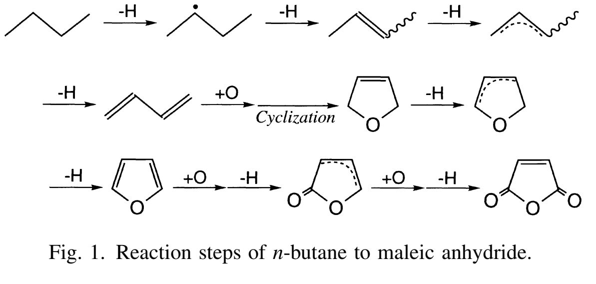
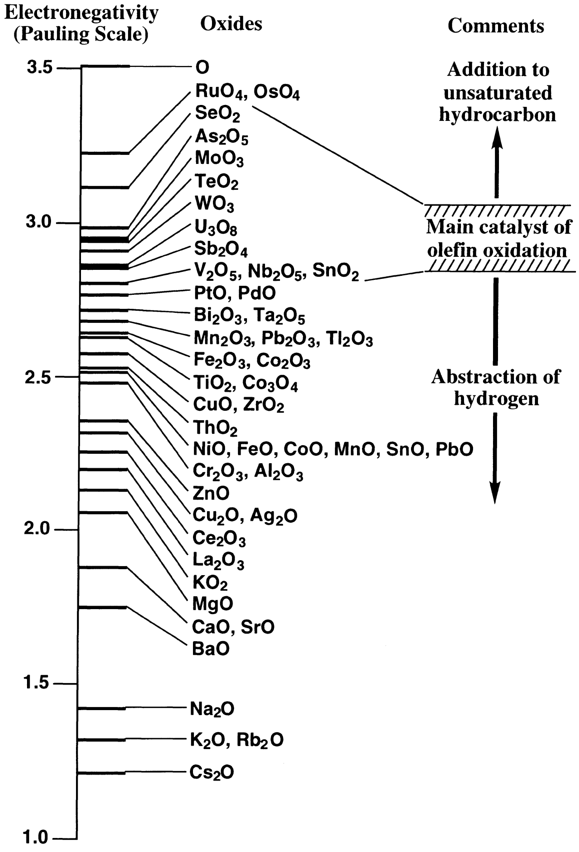


Fig. 1. Reaction steps of *n*-butane to maleic anhydride.

Table 1
Electronegativity and catalytic behavior of metal oxides



Electronegativity (Pauling Scale) **Oxides** **Comments**

3.5
O
RuO_4, OsO_4
SeO_2
As_2O_5
MoO_3
TeO_2
WO_3
3.0
U_3O_8
Sb_2O_4
V_2O_5, Nb_2O_5, SnO_2
PtO, PdO
Bi_2O_3, Ta_2O_5
Mn_2O_3, Pb_2O_3, Tl_2O_3
Fe_2O_3, Co_2O_3
2.5
TiO_2, Co_3O_4
CuO, ZrO_2
ThO_2
NiO, FeO, CoO, MnO, SnO, PbO
Cr_2O_3, Al_2O_3
ZnO
2.0
Cu_2O, Ag_2O
Ce_2O_3
La_2O_3
KO_2
MgO
CaO, SrO
BaO
1.5
Na_2O
K_2O, Rb_2O
Cs_2O
1.0

Addition to unsaturated hydrocarbon

Main catalyst of olefin oxidation

Abstraction of hydrogen

In Table 1, the average value of the electronegativity of oxide ion is estimated for each metal oxide according to the rule of electronegativity equalization presented by Sanderson [17,18–20]. Atomic oxygen, $O(^3P)$, has the highest electronegativity showing the electrophilic addition to the C–C unsaturation as mentioned above. RuO_4 and OsO_4 are well known reagents which cleave C–C unsaturated bond by electrophilic attacks. The electrophilicity of oxide ion decreases with decreasing value of electronegativity. On the basis of above consideration, we can understand easily the reason why MoO_3, Sb_2O_4,

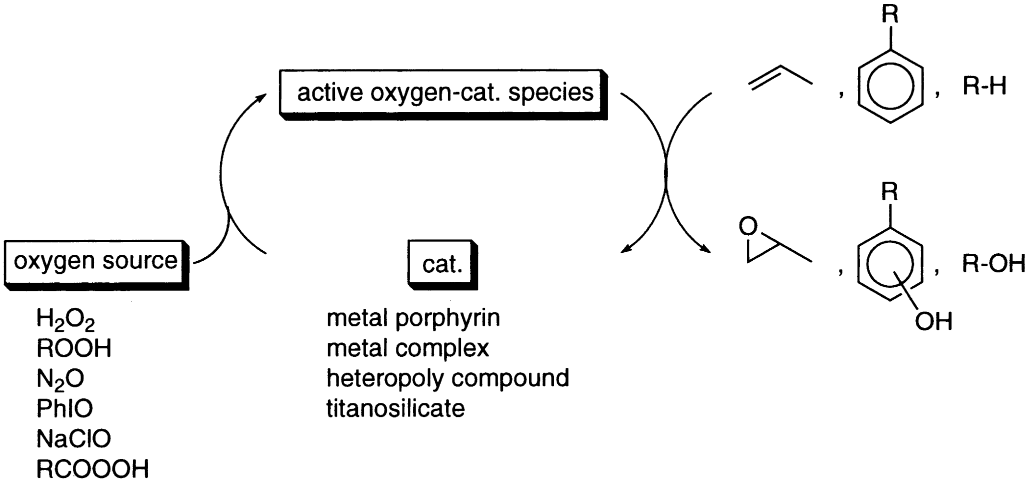
TeO_2 and V_2O_5 are essentially employed for the oxidation catalyst which converts hydrocarbon to oxygenates. On the contrary, catalytic oxidation which consists of only dehydrogenation step, i.e., oxidative coupling of methane (OCM), does not need any electrophilic oxygen species. Thus, alkali or alkali earth metal oxides with or without basic transition metal oxides are essentially employed for the OMC reaction where active oxygen having less nucleophilic character is rather injurious by forming carbon oxides. Since active oxygen is prepared on the catalyst surface by completely different ways in the oxygen transfer reactions or reductive oxidations, the design of catalyst is not restricted by the rule mentioned above. Actually, a variety of catalysts have been successfully employed for the epoxidation of olefin and hydroxylation of aromatics and paraffinic hydrocarbons in these new types of oxidation reactions.

4. Oxygen transfer reaction

Cytochrome P-450, a well known monooxygenase, is a family of ubiquitous heme-enzyme whose active site consists of protoheme–iron–thiolate chromosphere. It catalyzes a variety of aerobic oxidations, involving a reducing agent, NADPH, e.g. epoxidation of olefin, hydroxylation of aromatic or saturated hydrocarbon, oxidative cleavage of heteroatomic portion of substrate, oxo-transfer reaction of a molecule containing hetero atom etc. The reaction mechanism of cytochrome P-450 has been established not only by the biological studies but also by the synthetic works on metalloporphyrin and the most probable mechanism was proposed by Groves et al. [21,22] as shown in Fig. 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, which shows strong oxidizing ability to induce electrophilic addition to unsaturated C–C bonds and direct hydroxylation of aromatic and saturated C–H bonds just like oxene.

The most important aspect of the reaction scheme of cytochrome P-450 is the reductive activation of dioxygen with two electrons and two protons from NAD(P)H associated with effective electron and proton transfer systems. At the same time, cytochrome P-450 and its model complexes [23,24–27] can promote anaerobic oxidations by oxidants such as iodosylbenzene, alkyl and hydrogen peroxide, or peracid and the latter type reaction is called "shunt path". Not only iron porphyrin complexes but also many other transition metal cations fixed in the organic or inorganic matrices are available for the shunt path type reactions by the oxygen atom transfer from various kinds of oxidants [28,29] (Scheme 2).

Inorganic matrices such as microporous materials, layered materials and heteropoly compounds are more stable with respect to the oxidation conditions as well as higher temperature. Titanosilicate was successfully employed for the propylene epoxidation and aromatic



Scheme 2.

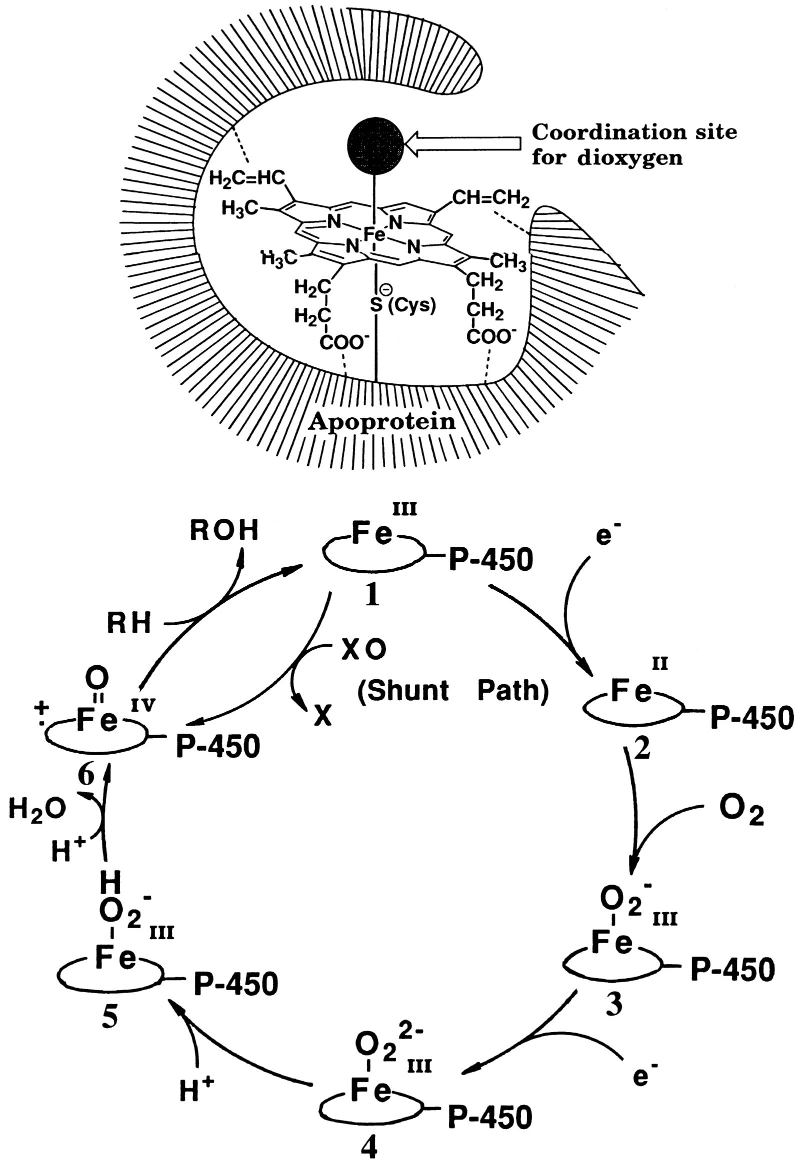
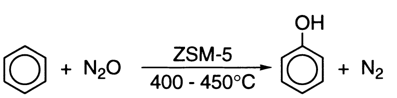


Fig. 2. Structure of active site (top) and proposed reaction mechanism for cytochrome P-450.

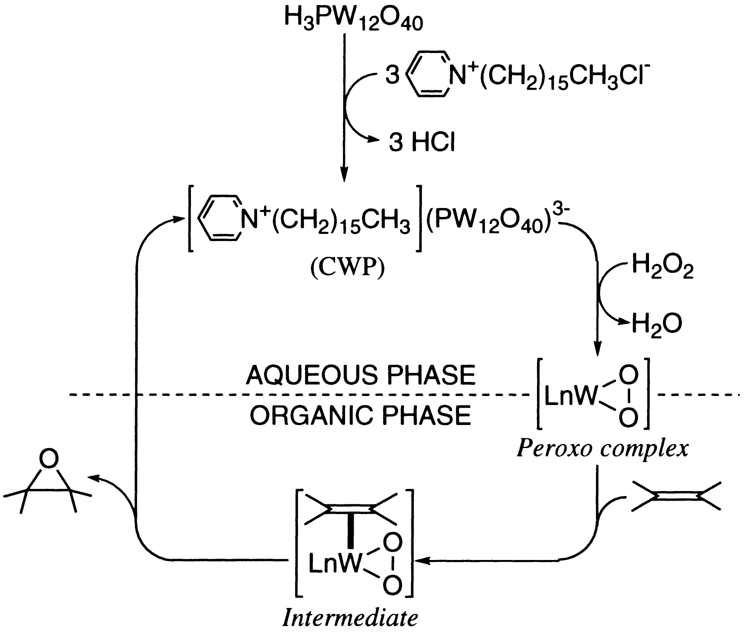
oxidation with hydrogen peroxide [30]. Heteropoly compounds combined with phase transfer catalysts are also utilized for a series of oxidation with hydrogen peroxide [31] (Scheme 3). The hydroxylation of benzene to phenol has been investigated extensively by using N_2O as the oxygen source [32,33–35]. Very high selectivity to phenol (97–98%) and fairly high space time yield (4 mol of phenol/kg-cat h^{-1}) were recently reported [36].



(eq. 7)

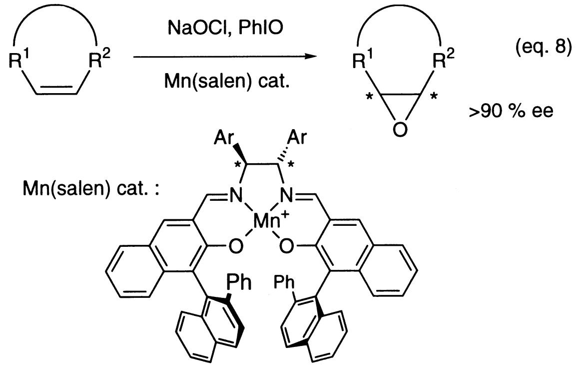
Selectivity of benzene to phenol; 97 - 98 %
Productivity; 4 mole phenol / kg-cat·hr

The most serious disadvantage of the reaction modeling the shunt path oxidation is quantitative consumption of expensive oxidants. Hydrogen peroxide and



Scheme 3.

hypochloride are relatively cheap but consumption of them still strongly limits the application of the reaction to the production of bulk chemicals. One of the most prospective application of the shunt path may be asymmetric epoxidation of prochiral olefin using chiral transition metal complex catalysts. Highly stereoselective epoxidation have been developed by chiral manganese Schiff base complexes by Jacobsen [37,38] and Katsuki (Eq. (8)) [39]. Olefins bearing various functional groups such as ether, ester, amide, nitro, nitrile and acetylene groups are epoxidized selectively and conjugated mono-, di-, tri-, and even tetra-substituted olefins can be converted to the epoxides in up to 99%.



5. Reductive oxidation

As shown in Fig. 2, the reaction mechanism of typical monooxygenase, cytochrome P-450 is 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 involving two protons and two electrons from strong reducing agent, NADPH. By following the concept, the activation of dioxygen by artificial reducing agents may be expected to develop new effective oxidation systems with molecular oxygen.

Barton et al. [40,41,42] established an aerobic oxidation using zinc powder as the reducing agent in acidic conditions. The reaction system is composed of an iron complex, pyridine, acetic acid and Zn powder is called Gif system, which can oxidize saturated hydrocarbon to alcohol or ketone by aerobic oxidation at ambient temperature. We have also demonstrated an aerobic oxidation with zinc powder by mimicking the active site of methanemonooxygenase and the system can oxidize not only saturated hydrocarbon but also olefin and aromatics to the corresponding alcohol, epoxide and phenol at room temperature (Eq. (9)) [43,44]. Although these reactions have contributed to the establishment of the concept of biomimetic oxidation, consumption of NADPH or Zn powder may not be recommended for the practical synthesis.

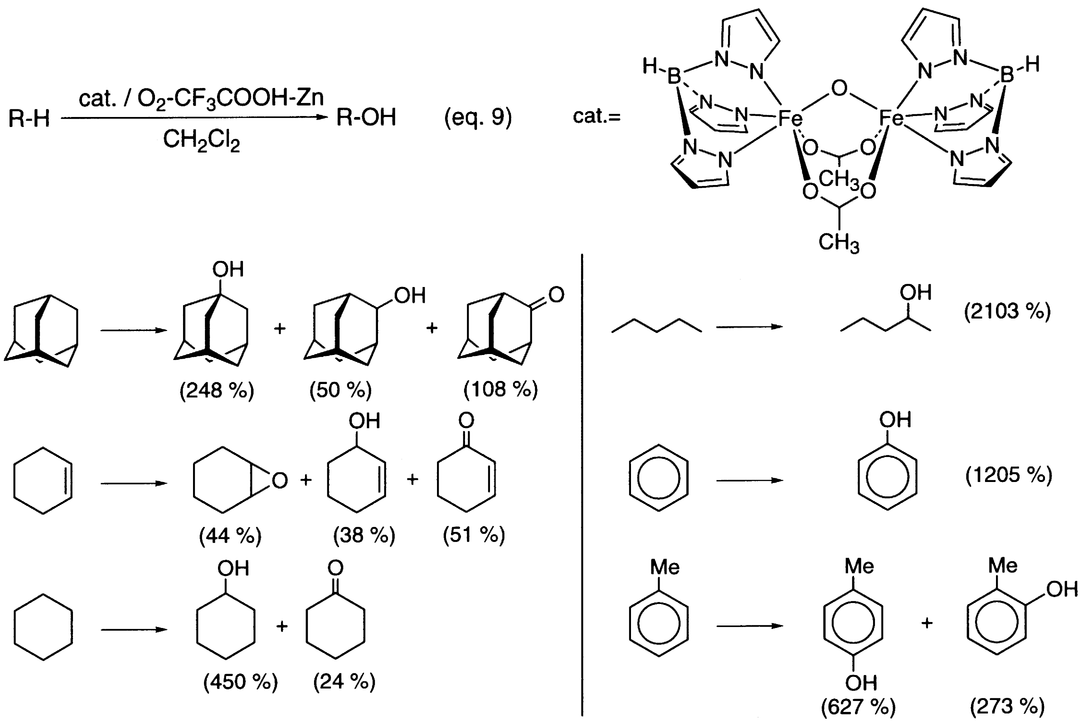
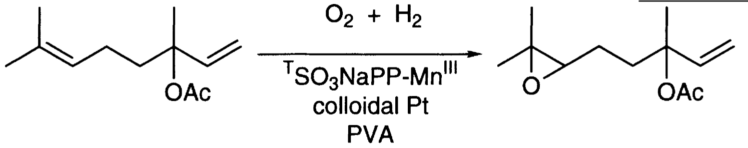


Table 2
Thermochemistry of O_2-activation

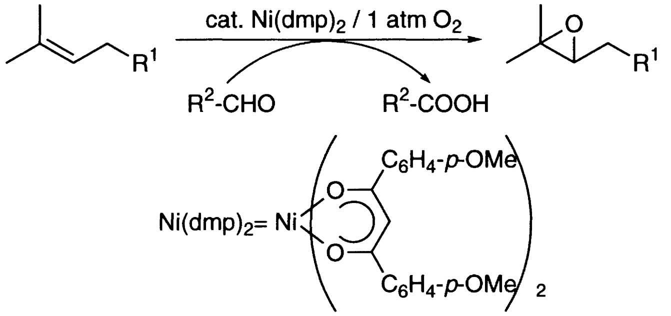
O_2-activation	ΔH (Kcal/mol)
$O_2 \rightarrow 2O$	119
$O_2+2H^+ +2e^- \rightarrow O+H_2O$	−730
$O_2+H_2 \rightarrow O+H_2O$	1.4
$O_2+CO \rightarrow O+CO_2$	−8
$O_2+CH_3CHO \rightarrow O+CH_3COOH$	−10

Thus the utilization of cheaper reducing agents such as hydrogen, carbon monoxide and aldehyde has been challenged and a number of new reductive oxidations have been reported in the last decade. The reaction mechanism differs depending on the system and oxene-like species is not necessary involved in the reaction. However, it is clear from the simple calculation of thermochemistry in Table 2 that the dissociation energy of dioxygen to produce an electrophilic atomic oxygen is decreased remarkably by using reducing agents and oxidizing ability of dioxygen enhanced kinetically by the participation of them [1].

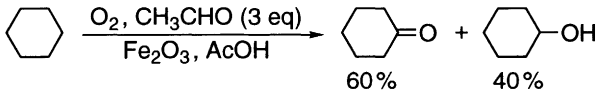
Aerobic epoxidation of olefin with hydrogen gas was first demonstrated by Tabushi et al. [45,46] using Mn tetraphenylporphyrin complex and colloidal platinum as the model of cytochrome P-450. Cyclohexene and geraniol were epoxidized selectively with molecular oxygen and regioselectivity of the epoxidation of geraniol suggested that active species of oxygen is electrophilic (Eq. (10)). The reaction was demonstrated as a model of monooxygenase but a serious defect for the application of the Tabushi's system to synthetic chemistry arises from that too much hydrogen is consumed independently from the epoxidation. More effective epoxidation was developed by Yamada and Mukaiyama [47] using acetaldehyde as reducing agent (Eq. (11)). The system is applicable to most kinds of olefin and may offer an useful aerobic epoxidation method for organic synthesis. Murahashi et al. [48] have also developed useful organic synthesis by using acetaldehyde as reductant (Eqs. (12) and (13)). Aerobic epoxidation of propylene was also reported by the system, $O_2/H_2/Au–TiO_2$ at room temperature though the space time yield was quite low (Eq. (14)) [49].



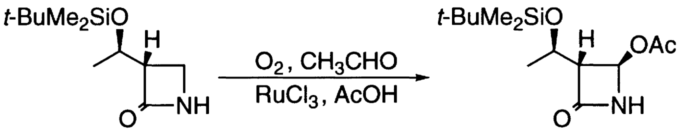
(eq. 10)



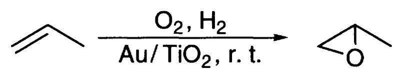
(eq. 11)



(eq. 12)

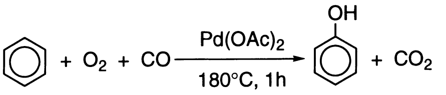


(eq. 13)



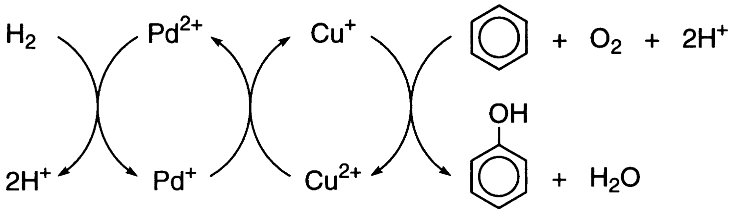
(eq. 14)

Direct hydroxylation of aromatics to phenols with molecular oxygen was found by Sasaki et al. [50] in $Cu(I)/O_2/H_2SO_4$ system. Cu(I) is consumed stoichiometrically in the earlier system but the reaction proceeds catalytically when Cu(II) is reduced to Cu(I) by molecular hydrogen in the presence of a palladium cocatalyst (Scheme 4) [51]. The aerobic oxidation of benzene to phenol was also demonstrated by using carbon monoxide at elevated temperature [52,53–55]. The catalyst system seems to be far from enzyme but ^{18}O tracer experiment showed that one atom of dioxygen is incorporated into phenol and the other to carbon dioxide just like the reaction of monooxygenase (Eq. (15)).



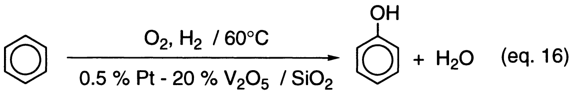
(eq. 15)

The most effective hydroxylation of aromatics with molecular oxygen was recently developed by Miyake et al. [56] employing hydrogen gas as reductant (Eq. (16)). Benzene is oxidized to phenol selectively without forming any carbon oxide on supported platinum catalyst with vanadium pentoxide or palladium cocatalyst. The reaction proceeds both in liquid phase in the presence of acetic acid at 20–60°C and in gas phase at elevated temperature. Although sufficient space time yield for industrial production of phenol was obtained, still the consumption of hydrogen gas was not satisfactory. The efficiency of oxygen to form



Scheme 4.

phenol is 30–40% meaning that 7–8 mol of hydrogen is consumed to form one mol of phenol. Nevertheless, the reductive activation of oxygen is expected to develop new industrial oxidation process for future technology.



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)

6. Conclusion

At the present stage, the most prospective oxidation process for the direct functionalization of inactive hydrocarbon may be (amm)oxidation of propane [57] and hydroxylation of benzene. The latter has been mainly investigated by oxygen transfer reaction and reductive oxidation. On the other hand, the former has been studied by the conventional activation method of dioxygen on the mixed oxide catalysts. Different from the hydroxylation of benzene, it has been suggested for the oxidation of propane that the activation of propane is also important as well as dioxygen and some acidic site may be involved in the first rate-determining abstraction of hydrogen from propane [58].

In spite of extensive investigations, conclusive process has not been established yet for these reactions. How to activate dioxygen still be a key factor to establish new oxidation process and it is expected that both reactions will be industrially realized in near future by employing most effective method for the activation of dioxygen molecule.

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