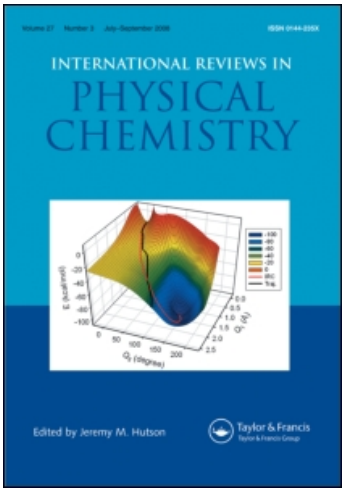

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Transition metal dioxygen complexes as intermediates in homogeneous catalytic oxidations

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Transition metal dioxygen complexes as intermediates in homogeneous catalytic oxidations

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The formation and main structural properties of superoxo and peroxo complexes are briefly described. These complexes are involved in catalytic oxidations (oxygenations) by dioxygen occurring under mild conditions in the presence of iron, cobalt, manganese, rhodium and other transition metal complexes. Examples of catalytic systems are taken from cytochrome P-450 models with specific reference to the mechanisms involved. Metalloporphyrin-catalysed oxidations of hydrocarbons involve free-radical chain processes in most cases. Added reducing agents modify the mechanism of oxidation by pumping electrons into key intermediates. They help the formation of oxometal species, which may transfer oxygen atoms to substrates, thereby improving the selectivity. Olefin oxidation is a difficult task for the homogeneous catalysts described: only a few working systems are available, based mainly on rhodium phosphine complexes. Peroxometalacycles are presumably formed, whose decomposition involves co-oxidation of a phosphine molecule. The oxidation of hindered phenols catalysed by cobalt (II) Schiff-base complexes points to the involvement of superoxocobalt species abstracting a H-atom from the phenol. Complex reaction patterns emerge from the oxidation of *o*-disubstituted phenols. The synthetic potential of homogeneous catalytic oxidation is illustrated on examples including various types of organic compounds.

1. Dioxygen complexes of transition metals

The subject of this review is the role of a class of compounds referred to as *dioxygen complexes* in homogeneous catalytic oxidations with molecular oxygen (dioxygen) in the presence of transition metal complexes. They are typically formed from a transition metal complex L_nM (where M is a metal ion and L is a unidentate or multidentate ligand) and molecular oxygen in a two-step reversible reaction. For reviews, see for example Jones *et al.* (1979) and Sheldon and Kochi (1981):

$$L_nM \underset{\longleftarrow}{\overset{O_2}{\longrightarrow}} L_nM{-}O_2 \underset{\longleftarrow}{\overset{L_nM}{\longrightarrow}} L_nM{-}O_2{-}ML_n. \qquad (1)$$

The name 'synthetic oxygen carrier' has been coined to indicate that similarity is observed with natural oxygen carriers, such as haemoglobin or myoglobin, operative in the respiratory cycle of living organisms. The degree of reversibility depends very strongly on the metal ion and the ligand in the complex. There have been very successful early attempts to synthesise oxygen carriers that can withstand dozens of oxygenation–deoxygenation cycles without appreciable degradation. The irreversible conversion of the oxygen carriers was at that time considered as a singularly undesirable drawback. Much effort has been expended to suppress these undesirable 'side reactions'. Later it has been recognised that these effects are the key to the synthetic application of homogeneous catalytic oxidations with molecular oxygen as

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terminal oxidant. The forward and reverse reactions leading to and from a metal–dioxygen complex are called oxygenation and deoxygenation respectively (see equation (1)). The dioxygen complexes formed in (1) involve the shift of electron density toward the O_2 moiety. In a simplified manner, this may be regarded as one of two limiting cases: the transfer of one or two electrons, to form a superoxo (O_2^-) or a peroxo (O_2^{2-}) ligand respectively, coordinated to the metal. Alternative routes to dioxygen complexes, especially those of Co^{3+} and Fe^{3+}, are from superoxide and (hydrogen) peroxide (Taube 1986):

$$LCo(H_2O)^{3+} + O_2^- \rightarrow LCoO_2^{2+} + H_2O, \quad (2)$$

$$2L'_nCo^{3+} + H_2O_2 \rightarrow [L'_nCo{-}O_2{-}CoL'_n]^{4+} + 2H^+. \quad (3)$$

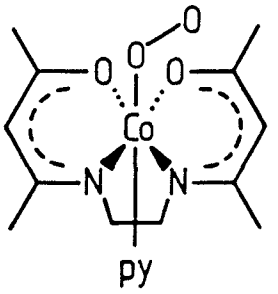
In his review, Vaska (1976) was the first to give a classification scheme for dioxygen complexes known at that time. It was based on the geometry of the metal–dioxygen moiety and the formal charge on the O_2 ligand. Dioxygen complexes may contain one or two metal centres per O_2 group (mono- and dinuclear complexes), and may have either a superoxo or a peroxo ligand. All of the four combinations are known. The main structural types of dioxygen complexes are summarised in table 1. The formation of dioxygen complexes is observed primarily for Group 8 metal ions also having other ligands simultaneously coordinated to them. Typically, complexes of cobalt(II) with various chelating ligands such as Schiff bases and their derivatives, such as porphyrins, polyamines and glyoximes, would react with O_2 to form relatively stable dioxygen complexes according to equation (1) (M = Co).

The vast majority of known dioxygen complexes directly synthesised using O_2 contain cobalt, iron, manganese, rhodium and iridium as the central ion. Numerous molybdenum(VI) and tungsten(VI) peroxo complexes have been prepared from H_2O_2 and metal oxide (Chaumette *et al.* 1983). Representative examples are structures 1–3.

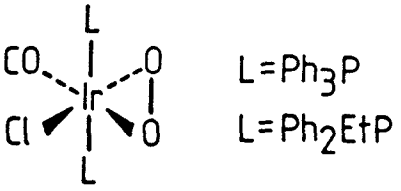
The amount of work done on the oxidation of various substrates by dioxygen in the presence of transition metal complexes as catalysts is too extensive for even a nearly comprehensive review in this survey. Therefore emphasis will be placed on mechanistic features and evidence, where available, indicating the participation of dioxygen complexes in such reactions. Examples will be selected which are believed to be typical and illustrative, as well as of general interest. In a number of cases, although oxidation is catalytic, mechanisms not involving dioxygen complexes are operative. It is important to distinguish between these alternatives in order to obtain a picture of the synthetic potential of dioxygen activation.

Table 1. Structural classification of dioxygen complexes.

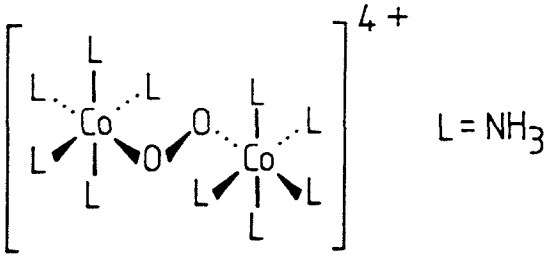
Structure type	Vaska's classification	Example	Reference
	Type Ia (superoxo)	$[Co(CN)_5O_2]^{3-}$	Brown and Raymond (1975)
	Type IIa (peroxo)	$(Ph_3P)_2PtO_2$	Cheng *et al.* (1971)
	Type Ib (μ-superoxo)	$[(H_3N)_5CoO_2Co(NH_3)_5]^{5+}$	Marsch and Schaefer (1968)
	Type IIb (μ-peroxo)	$[(H_3N)_5CoO_2Co(NH_3)_5]^{4+}$	Fronczek (1974)



Structure 1



Structure 2



Structure 3

2. Catalytic oxidation of hydrocarbons by O_2

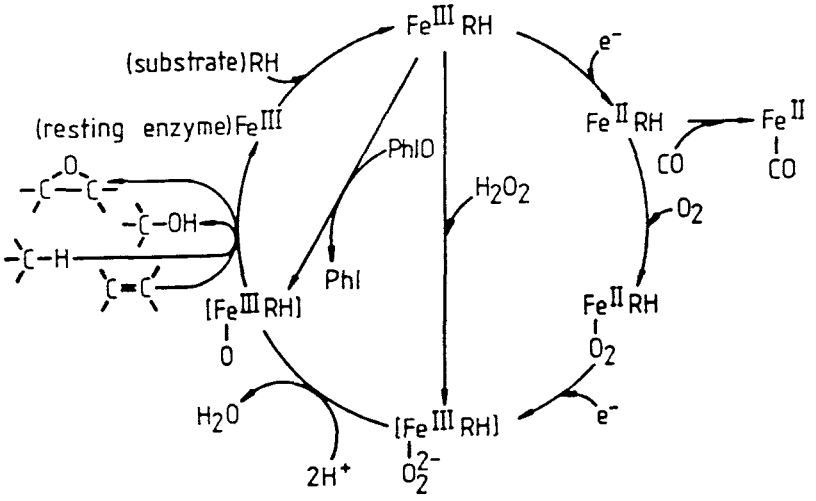
In this review, the term 'hydrocarbon' will be applied to substrates whose oxidation involves one or more C–H bonds, regardless of the presence of other atoms in the molecule. Thus aldehydes, ketones, alcohols, and so on may come under this heading.

2.1. *Cytochrome P-450 models as catalysts*

The study and modelling of haemoglobin active sites has played a decisive role in development of the chemistry of reversible synthetic dioxygen carriers. The objective has been to understand and mimic the extensive reversibility of the oxygenation–deoxygenation cycle without causing or permitting irreversible autoxidation of the ligand and/or metal. Modification of the haem type bonding site has been very successful and many useful analogues have emerged.

It is remarkable that Nature has been able to build two completely different kinds of biological function on the same structural unit, the iron–porphyrin (haem) moiety. Various haem-containing mono-oxygenase enzymes, especially cytochrome P-450, play a central role in oxidative conversions of foreign substances entering living organisms. Metabolic transformations of harmful materials lead to easily discharged hydrophilic compounds. For example, cytochrome P-450 oxidatively converts alkylamines to aldehydes, epoxidises olefins and hydroxylates aromatic compounds.

The active site of cytochrome P-450 is now rather well established: a single haem iron is bonded to the protein by a cysteine thiolato group. The substrate to be oxidized is attached to the porphyrin ring side opposite to the coordinated sulphur atom. Dioxygen is bound at the iron immediately adjacent to the site of substrate oxygenation.

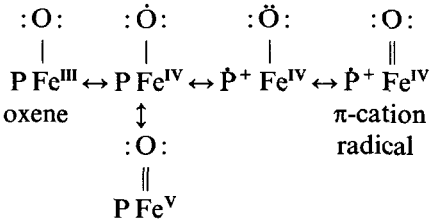


Scheme 1

A schematic outline of the chemical steps believed to be involved in dioxygen activation and oxygen transfer by the enzyme is given in Scheme 1 (Coon and White 1980, Groves 1985, Dolphin 1985).

The resting ferric enzyme binds a typical (hydrocarbon) substrate via hydrophobic interaction with the protein. One-electron reduction to the ferrous state is effected by NADPH. The enzyme is then ready to bind O_2 and subsequently take up a second electron. The peroxo-iron(III) complex formed undergoes proton-assisted heterolytic splitting to yield water and a very reactive 'activated oxygen' species, which can transfer an oxygen atom to C–H bonds or olefins, yielding alcohols or epoxides, the enzyme returning to the resting state.

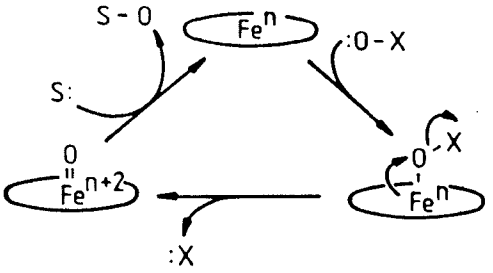
The equivalence of this O-insertion process to similar reactions of carbenes and nitrenes prompted Hamilton (1974) to coin the term 'oxenoid mechanism', and Lichtenberger *et al.* (1976) to describe cytochrome P-450 as an 'oxene transferase'. These terms reflect the ability of the enzyme to remove an O-atom from O_2 and insert it into the substrate via an enzyme–O-atom intermediate. At no stage of this process are free oxygen atoms thought to be present. The resonance structures of the active intermediate involving an O-atom bonded to iron(III) complexed with a porphyrin (P) can be represented by Scheme 2:



Scheme 2

Model studies have been very successful in throwing light on this mechanism, especially after the second one-electron reduction. The oxo-iron(IV) π-cation radical can be reached from iron–porphyrin model systems by reacting them with peracids or H_2O_2 via the so-called 'peroxide shunt'. This supports the formulation of the second one-electron reduction product as an iron(III)-peroxo complex.

Oxo-iron(IV) π-cation radical intermediates can be directly made from iron(III)-porphyrin model compounds via reaction with O-atom transfer reagents, the most notable of which are iodosylbenzene (PhIO) (Groves and Nemo 1983, Groves *et al.* 1981) and peroxyacids (Groves and Watanabe 1988). Oxygen-atom transfer to a substrate S from the oxo-iron(IV) intermediate can be described in a simplified way by the 'oxygen rebound' mechanism in Scheme 3:



Scheme 3

Heterolytic cleavage of the O–X bond of a suitable oxygen donor leads to a reactive oxometal species which is capable of transferring its O-atom to the substrate (Groves *et al.* 1978). Relevant to this feature is that the reactivity of $Fe^{III}(TPP)(O_2^{2-})$, where TPP is the tetraphenylporphyrinato(2−) ligand, in cyclohexane oxidation is enhanced by acetic anhydride (Khenkin and Shteinman 1982, 1984), which probably forms a peroxyacetato complex, $(TPP)FeOOC(O)CH_3$. The latter decomposes to yield the active FeO intermediate. Alkylperoxocobalt porphyrins were recently reported to form from alkylcobalt(III) porphyrins via a dissociative mechanism (Kendrick and Al-Akhdar 1987):

$$RCo^{III}(OEP)L \rightleftarrows Co^{II}(OEP)L + R^{\cdot}, \tag{4}$$

$$R^{\cdot} + O_2 \rightarrow ROO^{\cdot}, \tag{5}$$

$$Co^{II}(OEP)L + ROO^{\cdot} \rightarrow ROOCo^{III}(OEP)L, \tag{6}$$

where OEP is the octaethylporphyrinato(2−) ligand. The product may be employed in catalytic oxidation of hydrocarbons via O-atom transfer.

The epoxidation and hydroxylation of hydrocarbons can also be carried out by metalloporphyrin-catalysed O-atom transfer from single oxygen donors other than PhIO, such as sodium hypochlorite, alkyl hydroperoxides, hydrogen peroxide, amine N-oxides or potassium hydrogen persulphate. The rich chemistry of these reactions has been recently reviewed by Meunier (1986).

Cytochrome P-450 analogues consisting of manganese 'picket basket' porphyrins have been designed and synthesised (Collman *et al.* 1988). These compounds epoxidise olefins by shape selective catalysis using oxygen atom donors, but the eventual objective is to activate dioxygen.

2.2. *Metalloporphyrin catalysed oxidations by O_2*

Metalloporphyrins act as oxidation catalysts in three types of reactions:

(*a*) Free radical autoxidation of substrates by O_2;
(*b*) Oxidation (oxygenation) of substrates in presence of added reducing agents (e.g. Pt/H_2, $NaBH_4$);
(*c*) Oxygen transfer from a source of O-atoms other than O_2 (e.g. PhIO, NaOCl, ROOH, H_2O_2).

Case (*c*) is beyond the scope of this survey; excellent reviews on the subject have been published by Meunier (1986, 1988).

2.2.1. *Free-radical autoxidations*

The term autoxidation is traditionally used to describe non-catalytic oxidation of hydrocarbons by O_2, in which thermally generated free radicals react with O_2 to form peroxy radicals, which in turn initiate chain reactions. The selectivities in these systems are not particularly good, owing to indiscriminate H-atom abstractions by radicals, reminiscent of combustion type processes. Similar behaviour is observed in direct oxidation of hydrocarbons by high-valent metal ions such as cobalt(III) and manganese(III) species (Sheldon and Kochi 1981).

Porphyrin complexes of transition metals listed in table 2 promote the oxidation of aldehydes, some olefins and activated phenols by dioxygen. The reactions usually occur with an induction period, during which the active catalyst is formed.

It is generally assumed that these oxidations occur by free-radical chain mechanisms and the high-valent metalloporphyrin acts as an initiator generating free

Table 2. Representative examples of metalloporphyrin catalysed oxidations.

Catalyst	Substrate	Main product	Conditions	Reference
CoTPP	Acetaldehyde	Peroxyacetic acid	10°C/AcOEt	Tezuka *et al.* (1976)
	Propionaldehyde	Propionic acid	30°C/Acetone	Apostol *et al.* (1982)
	Indols	Ketoamides	25°C/CH_2Cl_2	Dufour *et al.* (1980)
	Cyclohexene	Cyclohexenone	30°C/AcOEt	Ohkatsu and Tsuruta (1978)
CuTPP	Acetaldehyde	Peroxyacetic acid	10°C/AcOEt	Ohkatsu and Osa (1977)
FeTPP	Cyclohexene	Cyclohexen-2-one	25°C	Paulson *et al.* (1974)
MnTPP	Cyclohexene	Cyclohexen-2-one	25°C/benzene–EtOH	Tabushi and Koga (1979)
NiTPP	Acetaldehyde	Peroxyacetic acid	10°C/AcOEt	Ohkatsu and Osa (1977)
RhTPP	Cyclohexene	Cyclohexene hydroperoxide	25°C	Paulson *et al.* (1974)
VOTPP	2,6-di-*t*-butyl-phenol	3,3′,5,5′-tetra-*t*-butyldipheno-quinone	DMF	Wang *et al.* (1984)

radicals. Short-lived superoxo species may be involved, as in the case of an aldehyde substrate (Enikolopyan *et al.* 1983):

$$\left.\begin{aligned} &Co^{II}TPP + O_2 \rightarrow Co^{III}TPP\cdots O_2^-, \\ &Co^{III}TPP\cdots O_2^- + RCHO \rightarrow Co^{III}TPP\cdots O_2H + R\dot{C}O, \end{aligned}\right\} \text{Initiation} \quad \begin{matrix}(7)\\(8)\end{matrix}$$

$$\left.\begin{aligned} &R\dot{C}O + O_2 \rightarrow RCO_3^{\cdot}, \\ &RCO_3^{\cdot} + RCHO \rightarrow RCO_3H + R\dot{C}O, \end{aligned}\right\} \text{Propagation} \quad \begin{matrix}(9)\\(10)\end{matrix}$$

$$2RCO_3^{\cdot} \rightarrow \text{inert products.} \quad \} \text{Termination} \quad (11)$$

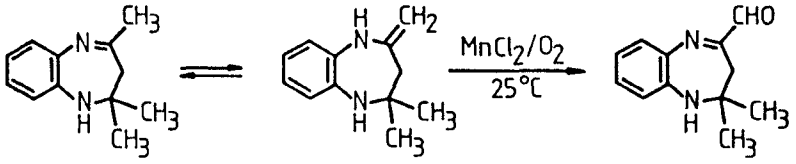
However, despite the ability of most catalytically active metalloporphyrins to form dioxygen complexes, there is no direct evidence for this initiation mechanism (Sheldon and Kochi 1981, Młodniczka 1986).

It is more likely that initiation involves adventitious hydroperoxides, and the metalloporphyrin promotes their decomposition:

$$Co^{II}TPP + ROOH \rightarrow Co^{III}TPP + OH^- + RO^{\cdot}, \quad (12)$$

$$Co^{III}TPP + ROOH \rightarrow Co^{II}TPP + H^+ + ROO^{\cdot}, \quad (13)$$

Generation of free radicals without intervention of O_2 complexes may in some cases lead to facile and selective C–H bond oxidation. For example, conversion of a methyl to a formyl group by O_2 in a trimethyl-1,5-benzodiazepine derivative can be observed in the presence of manganese(II) salts (Szeverènyi and Simándi 1989, Szeverènyi *et al.* 1988). The nearly 100% selectivity is due to the easy abstraction of an electron (or H-atom) from the enamine tautomer on the right-hand side of the equilibrium in Scheme 4:



Structure 4 Scheme 4

Similar monooxygenations in *bis*(1-methylbenzimidazole-2-yl) methane and *bis*(2-pyridyl)methane to yield ketones have been reported (Sprecher and Zuberbühler 1977, Urbach *et al.* 1978).

Another route of dioxygen activation without involvement of dioxygen complexes is that observed for Ru porphyrin systems, wherein outer-sphere electron transfer generates free superoxide, yielding H_2O_2 via protonation (James *et al.* 1987):

$$Ru^{II}(P)L_2 + O_2 \rightleftarrows Ru^{III}(P)L_2^+ + O_2^-, \quad (14)$$

$$O_2^- + H^+ \rightarrow HO_2^{\cdot} \rightarrow \tfrac{1}{2}H_2O_2 + \tfrac{1}{2}O_2. \quad (15)$$

These systems oxidise substrates that are reactive toward H_2O_2, an example being the oxidation of PPh_3 in the presence of $Ru(OEP)(PPh_3)_2$ (OEP = P in equation (14)), affording Ph_3PO via the catalytic cycle (14)–(17):

$$PPh_3 + H_2O_2 \rightarrow Ph_3PO + H^+ + OH^-, \quad (16)$$

$$2\,Ru^{III}(OEP)L_2^+ + PPh_3 + OH^- \rightarrow 2Ru^{II}(OEP)L_2 + Ph_3PO + H^+. \quad (17)$$

This behaviour was first demonstrated for the Pt(0)-catalysed oxidation of PPh_3 (Sen and Halpern 1977), with the difference that peroxide formation occurred in the coordination sphere, followed by displacement by free PPh_3.

2.2.2. *Catalytic oxidation under reducing conditions*

For proper oxidative action, the cytochrome P-450 system requires NADPH as an electron source, the flow of electrons being controlled by a reductase enzyme. The idea of adding an electron source (reducing agent) to a catalytic system designed for oxidation was first implemented by Tabushi and Koga (1979). The oxidation of cyclohexene by O_2 with Mn(TPP)Cl as catalyst was carried out in the presence of $NaBH_4$ as reductant. The product distribution observed did not correspond to a typical autoxidation pattern, where the main product should be cyclohexenol. Instead, cyclohexanol formation occurred, via reduction of the initially formed epoxycyclohexane.

A number of related systems have been reported for other metalloporphyrins and several reducing agents (table 3).

A detailed mechanistic study of reductive dioxygen activation has been reported by Tabushi *et al.* (1985). His artificial cytochrome P-450 enzyme was the iron(II) 'picket-fence' porphyrin (a sterically hindered synthetic derivative) with N-methylimidazole and molecular O_2 as axial ligands, Fe^{II}(TpivPP)(N-MeImd)(O_2) (denoted as PF^{II}–O_2 in the scheme). The artificial P-450 reductase was H_2 with colloidal Pt supported on poly(vinylpyrrolidone).

The decomposition of PFe^{II}–O_2 in ethanol–toluene was followed by stopped-flow spectrophotometry. In the presence of Pt/H_2 the decomposition is faster than spontaneous decay. This reductive decomposition gives PFe^{III} via an iron(V) oxo species, which attacks cyclohexene, giving mostly epoxide and some allylic oxidation product. Thus the function of the reducing agent is to generate an active species which would otherwise not be present in the system. Substrate concentration does not affect the rate of decomposition, indicating that oxidation occurs after the overall rate-determining step. The observed behaviour can be accommodated by the simplified Scheme 5:

$$PFe^{II} \xrightarrow{O_2} PFe^{II}\text{–}O_2 \leftrightarrow PFe^{III}\text{–}O\text{–}O^{\cdot} \leftrightarrow PFe^{IV}\text{–}O\text{–}O^{-},$$

$$PFe^{IV}\text{–}O\text{–}O^{-} \xrightarrow[H^+]{Pt/H_2} PFe^{III}\text{–}O\text{–}OH \xrightarrow[H^+]{-H_2O} PFe^{V}=O,$$

$$PFe^{V}=O \xrightarrow{C=C} PFe^{III} + C\text{—}C.$$

Scheme 5

Benzoic anhydride can stabilise PFe^{III}–O–OH by acetylation to PFe^{III}–O–O–Bz, which decarboxylates to $PFe^{V}=O$, continuing the cycle via an additional route. This highly reactive oxoiron species is not detectable in the strongly reducing medium: in competition with the above route, it also reacts with Pt/H_2. For optimum substrate epoxidation, there is apparently an optimum concentration of the reducing agent.

Table 3. Oxidations by O_2 in the presence of metalloporphyrins and reducing agents.

Catalyst	Reducing agent	Substrate	Product(s)	Reference
Mn(TPP)Cl	$NaBH_4$	Cyclohexene	Cyclohexanol Cyclohexenol	Tabushi and Koga (1979)
Mn(TPP)Cl	Colloidal Pt/H_2	Cyclohexene	Cyclohexanol Cyclohexenol	Tabushi and Yazaki (1981)
Mn(TPP)Cl	$R_4N\ BH_4$	Cyclohexene	Cyclohexanol Cyclohexenol	Perre-Fauvet and Gaudemer (1981)
In(TPP)Cl	Colloidal Pt/H_2	Geraniol acetate	Epoxide	Tabushi and Morimitsu (1984)
Mn(TPP)Cl	Ascorbate	Styrene	Styrene oxide	Fontecave and Mansuy (1984)
		Cyclohexene	Epoxide	
		cis and *trans* Stilbenes	Epoxides	
		cis and *trans* Hex-2-ene	Epoxides	
		2,3-Dimethyl-but-2-ene	Epoxides	
		Cyclohexane	Cyclohexanol Cyclohexanone	
		Heptane	Heptanones	
		Toluene	Benzaldehyde	
		Heptan-4-ol	Heptan-4-one	
		Benzyl alcohol	Benzaldehyde	
		Anisol	Phenol	
		Methylcyclo-hexane	Methylcyclohexanol, Methylcyclohexanone	
Mn(TPP)Cl	$NaBH_4$/crown ether	Cyclohexene	Cyclohexene oxide Cyclohexenol Cyclohexanol Cyclohexanone	Sakurai *et al.* (1985)
Mn(TPP)Cl	Zn and imidazole	Cyclooctene	Epoxide	Battioni *et al.* (1987)
		Cyclooctane	Cyclooctanol	
		Cyclohexene	Cyclohexene oxide	
		Adamantane	Hydroxylation	
Mn(TPPS)	$NaBH_4$	Cyclohexene	Cyclohexanol	Shimizu *et al.* (1988)
Mn(TPPS)	$Bu_4N\ BH_4$	Cyclohexene	Cyclohexanol	
Mn(TPPS)	Sodium ascorbate	Cyclohexene	Cyclohexene oxide	Shimizu *et al.* (1988)
			Cyclohexen-3-one	Shimizu (*et al.*) 1988)
			Cyclohexen-3-ol	Shimizu *et al.* (1988)
Fe(TPPS)	$NaBH_4$	Cyclohexene	Cyclohexanol	Shimizu *et al.* (1988)
Rh(OEP)	$NaBH_4$	Cyclohexene	Cyclohexanol Cyclohexenol Cyclohexenone	Aoyama *et al.* (1983)
Co(TPP)	$NaBH_4$	Arylolefins	Benzylic alcohols	Okamoto and Oka (1984)
Fe(TpivPP)Cl 'picket fence' porphyrin + acetic anhydride	Collodial Pt/H_2	Cyclohexene	Cyclohexene oxide, Cyclohexenol	Tabushi *et al.* (1985)

Mn(TPP) was used in a biphasic system to catalyse monooxygenation of alkanes and olefins by either O_2 or PhIO, using ascorbate as reducing agent (Fontecave and Mansuy 1984). Alkanes are oxidised mainly to alcohols under anaerobic conditions with Mn(TPP)/PhIO. In the presence of O_2 the yield of ketones (aldehydes) increases relative to the small anaerobic values. The mechanism proposed to interpret these results is shown in scheme 6 (Mn denotes (TPP)Mn).

$$Mn^{III}Cl + PhIO \rightleftarrows [ClMn^{IV}(OIPh)]_2O \rightleftarrows Mn^{V}=O,$$

$$Mn^{V}=O + R_1R_2CH_2 \rightarrow [Mn^{IV}\text{–}OH + R_1R_2\dot{C}H] \rightarrow Mn^{III} + R_1R_2CHOH$$

$$\downarrow$$

$$Mn^{IV}\text{–}O\text{–}CHR_1R_2 \xrightarrow{Mn^{V}=O} R_1R_2\dot{C}H \xrightarrow[\text{or } Mn^{IV}OH]{Mn^{III}OH} \begin{matrix} Mn^{II}OH \\ \text{or} \\ Mn^{III}OH \end{matrix} + R_1R_2CHOH$$

$$\downarrow -Mn^{II} \qquad +O_2 \downarrow$$

$$R_1R_2C=O \qquad \leftarrow\leftarrow R_1R_2CHO_2^{\cdot}.$$

Scheme 6

The intermediate free radical $R_1R_2\dot{C}H$ generated by the active $Mn^{V}=O$ intermediate can be further oxidised to a ketone via two routes: (*i*) directly by the oxomanganese(V), or (*ii*) by reacting first with O_2 (if it is present) to give a peroxy radical, which abstracts an H-atom and eliminates water, affording the ketone. The formation of $R_1R_2\dot{C}H$ occurs similarly to the 'oxygen rebound' mechanism, proposed by Groves and co-workers (Groves and McClusky 1976, Groves and Van der Puy 1976) for cyclohexanol hydroxylation with an iron(II)/H_2O_2 system.

The active $Mn^{V}=O$ species was first suggested by Groves *et al.* (1980). It is in equilibrium with a Mn^{IV}-oxo dimer (Smegal and Hill 1983). In alkene oxidation under reductive conditions, epoxides are the main products with some allylic oxidation where possible (see table 3).

A review on non-radical olefin oxidations in the presence of reducing agents has appeared (Enikolopyan and Soloveva 1988).

2.3. *Oxidations with various catalysts*

2.3.1. *Oxidation of olefins*

The classical oxidation of ethylene to acetaldehyde with dioxygen, catalysed by Pd(II)/Cu(II) systems, known also as the Wacker process, does not involve dioxygen complexes. Detailed mechanistic studies have revealed that the olefin coordinated to palladium undergoes oxidative hydroxylation and the reduced palladium is re-oxidised by copper(II) or other oxidants. The extensive chemistry of this and related reactions has been reviewed by Henry (1980).

2.3.1.1 *Rhodium complexes as catalysts*

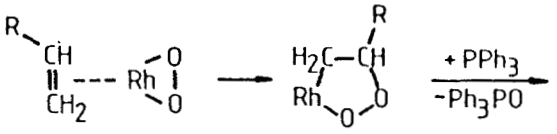
The first example of catalytic olefin oxidation without interference of free radical species was reported by Read and co-workers (Dudley and Read 1972, Dudley *et al.* 1977). Co-oxygenation of terminal olefins, such as octene-1, with Ph_3P in the presence of $RhCl(PPh_3)_3$ led to the formation of methyl ketones and Ph_3PO in benzene solution. In this system, one atom of O_2 is incorporated into the olefin while the other is transferred to the co-reducing agent Ph_3P. The reaction is unaffected by radical chain inhibitors and co-oxygenation is not enhanced by small amounts of water. These data

rule out Haber–Weiss-type radical chain oxygenation and Wacker-type hydration of the olefin. A side-on peroxo complex is formed in the system, to which an alkene molecule is subsequently coordinated:

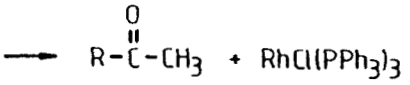
$$RhCl(PPh_3)_3 \xrightarrow{O_2} RhCl(Ph_3P)_3O_2, \tag{18}$$

$$RhCl(Ph_3P)_3O_2 \underset{+PPh_3}{\overset{-PPh_3}{\rightleftharpoons}} RhCl(PPh_3)_2(S)(alkene)O_2. \tag{19}$$

In the rate-determining breakdown of the latter intermediate, the olefin is inserted into one of the Rh–O bonds to yield a peroxometalacycle, which is attacked by PPh_3, resulting in hetero-co-oxygenation:



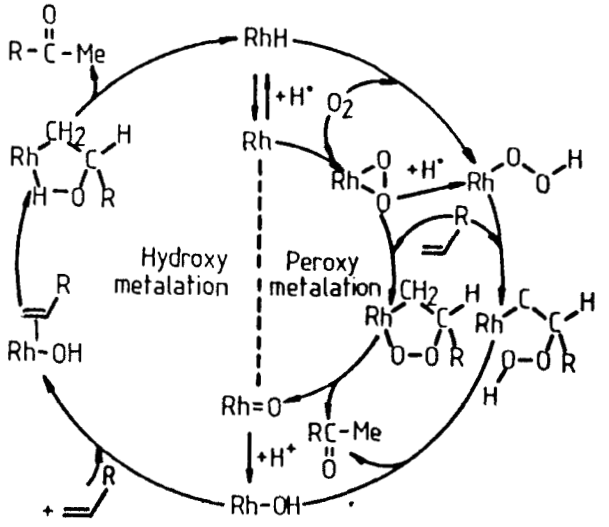
(20)



(21)

Each molecule of olefin oxidised requires the oxidation of a PPh_3 molecule. The involvement of the peroxo complex in the catalytic cycle has later been demonstrated for a number of substrates, among them cycloolefins (Atlay *et al.* 1983a, b Read and Urgelles 1985, Read 1988).

A different system, based on rhodium(III) chloride in combination with copper(II) perchlorate, has been reported to oxidise terminal olefins to methyl ketones, using O_2 and operating in dry alcohols without co-reducing agent (PPh_3) (Mimoun *et al.* 1978, Mimoun 1981). Both O-atoms of O_2 are incorporated into the olefin, which should be



Scheme 7

able to form a π-complex with Rh(I). Two complementary reactions occurring in a coupled mode (scheme 7) explain the observed pattern:

(i) dioxygen activation by Rh(I) to form a side-on peroxo complex, followed by transfer of one of the peroxidic oxygens to the coordinated olefin (cyclic peroxymetallation);
(ii) Wacker-type *cis*-hydroxymetallation of a second coordinated olefin by a hydroxorhodium(III) species (derived from oxo-rhodium(III) via protonation).

Deuterium labelling experiments on the oxidation of oct-1-ene to octan-2-one catalysed by $RhCl_3/Cu(NO_3)_2$/HMPT in dry ethanol rule out β-hydrogen carbon–carbon shift and favour β-hetero elimination (proton abstraction) by the solvent (Bortolini *et al.* 1984).

It has been found that in these rhodium systems (with or without copper), the source of oxygen for olefin oxidation may also be H_2O_2 or *t*-BuOOH (Drago *et al.* 1985).

Rhodium(II) acetate induces the free-radical autoxidation of 1,4-cyclohexadienes to aromatic compounds (Doyle *et al.* 1984).

2.3.1.2. *Cobalt complexes as catalysts*

If Z in the p-substituted 2,6-di-*t*-butylphenol is an olefinic side chain, incorporation of dioxygen occurs at the double bond with some cleavage at that site (Nishinaga *et al.* 1986). This process shows the characteristics of a free radical reaction.

The cobalt(II) Schiff-base complex Co(smdtp), previously employed in phenol oxidation (*vide infra*) has been reported to catalyse the oxidation of terminal olefins, such as hex-1-ene, styrene and 3-methyl-hex-1-ene, to methyl ketones and 2-alcohols in ethanol or ethanol-containing solvents (Zombeck *et al.* 1982). According to the mechanism proposed for the reaction (Hamilton *et al.* 1987), olefin oxidation actually requires H_2O_2 as the key intermediate. It is produced by free-radical chain oxidation of the alcohol (EtOH) solvent:

$$In^{\cdot} + CH_3CH_2OH \rightarrow CH_3\dot{C}HOH + InH \quad \} \text{ Initiation} \tag{22}$$

$$CH_3\dot{C}HOH + O_2 \rightarrow CH_3\underset{\displaystyle OO^{\cdot}}{\underset{|}{C}}HOH \rightarrow CH_3CHO + HO_2^{\cdot} \quad \} \text{ Propagation} \tag{23}$$

$$HO_2^{\cdot} + CH_3CH_2OH \rightarrow H_2O + CH_3\dot{C}HOH \quad \} \text{ Propagation} \tag{24}$$

$$2HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \quad \} \text{ Termination} \tag{25}$$

Addition of H_2O_2 eliminates the induction period which is observed in the presence of O_2. Co(smdtp) reacts with H_2O_2 via a Haber–Weiss-type mechanism to produce the actual catalyst of olefin oxidation, the hydroperoxo complex (smdtp)$Co^{III}OOH$:

$$Co^{II} + H_2O_2 \rightarrow Co^{III} + HO^{\cdot} + OH^-, \tag{26}$$

$$Co^{III} + H_2O_2 \rightarrow Co^{III}OOH + H^+ \tag{27}$$

(smdtp is omitted for brevity). $Co^{III}OOH$ can also form from $HO_2^{\cdot}$ and Co^{II}. The hydroperoxo complex adds to the double bond:

$$Co^{III}OOH + RCH{=}CH_2 \rightarrow Co^{II} + RCH\underset{\displaystyle HOO}{\underset{|}{-}}\dot{C}H_2. \tag{28}$$

The resulting hydroperoxy-substituted radical affords the methylketone product via Haber–Weiss decomposition.

An alternative to this mechanism involves a hydridocobalt species, which adds across the double bond to afford an alkylcobalt. Dioxygen insertion into the Co–C bond leads to an alkylperoxocobalt complex, which is the precursor of the observed products (Mimoun 1985).

The oxygenation of styrene catalysed by optically active cobalt(III) Schiff base complexes shows asymmetric induction (Nishinaga *et al.* 1988a, b). The proposed mechanism involves addition of a hydridocobalt complex across the double bond followed by decomposition of the 1-phenylethyl hydroperoxide formed.

Olefin oxidation with C=C bond cleavage in the presence of Co(smdpt) and O_2 has been reported for isoeugenol (Drago *et al.* 1986, Bailey and Drago 1987). Attack by Co–O_2 could lead to a dioxetane intermediate, affording vanillin and acetaldehyde.

2.3.1.3. *Complexes of other metals as catalysts*

Conversion of cyclohexene to 2-cycohexen-1-one and 2-cyclohexen-1-ol in dry organic solvents has been observed in the presence of $[(bpy)_2(PPh_3)Ru^{II}(H_2O)](ClO_4)_2$ as catalyst (Leising and Takeuchi 1987). Presumably the water ligand is replaced by O_2 to afford a μ-peroxo species, which undergoes homolytic cleavage to the active Ru^{IV}–oxo complex. In the oxygenation of cyclooctene to cyclooctanone catalysed by iridium complexes Ir(OOH)-type intermediates are involved (Atlay *et al.* 1982a, b), which are formed via protonation of peroxometal species (Sue and James 1988).

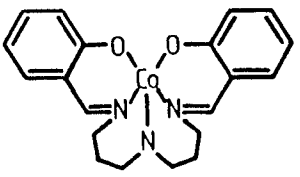
A radical chain mechanism has been suggested for cyclohexene oxidation with layered graphite intercalated with $MoCl_5$ (Kovtyukhova *et al.* 1987).

An interesting combination of three redox couples, namely Pd(II)/Pd(O)–*p*-benzoquinone/hydroquinone–Co(0)(TPP)/Co(TTP), constitutes a catalyst for conversion of cyclohexa-1,3-diene to 1,4-diacetoxy-2-cyclohexene via 1,4-oxidation (Bäckvall *et al.* 1987).

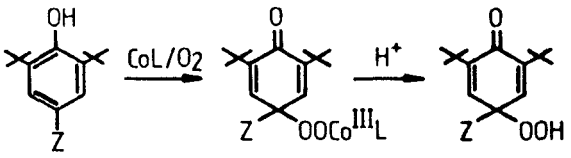
2.3.2. *Oxidation of benzene derivatives*

2.3.2.1. *Oxidation of 2,6-di-t-butylphenols catalysed by cobalt(III) Schiff base complexes*

Complexes of various Schiff bases, such as Co(salpr) (structure 5), promote the oxygenation of *p*-substituted 2,6-di-*t*-butylphenols (structure 6) with regioselective incorporation of a hydroperoxy group in *ortho* or *para* position, depending on the nature of Z. If Z is an alkyl group, the *p*-derivative is formed via an isolable peroxocobalt(III) intermediate (structure 7) (Nishinaga *et al.* 1981, Nishinaga and Tomita 1980).



Structure 5



Structure 6 Structure 7

Scheme 8

Identification of the peroxy-*o*-quinolatocobalt(III) intermediate clearly demonstrates that the corresponding superoxocobalt(III) complex is involved in the reaction. If Z is an aromatic group, the reactive centre is the *o*-position.

In the absence of a *p*-substituent, the $Cu(OAc)_2$–LiBr catalyst system converts 2,6-di-*t*-butylphenol (DTBP) to 4,4′-diphenoquinone via tail-to-tail radical dimerisation (Mamalis *et al.* 1988). The active catalyst is regarded as a copper–chloro cluster but no O_2-complexes have been identified.

A detailed mechanistic picture with a number of rate constants for 2,6-di-*t*-butylphenol oxidation using cobalt(II)-polyamine complexes as catalysts has been given by Martell (1983). Superoxocobalt(III) and peroxodicobalt(III) species are key intermediates attacking the *para* position of the substrate, affording quinonoid products.

A similar catalyst, Co(smdtp), carrying a Me group at the central N-atom of Co(salpr), (structure 5), has been used by Drago *et al.* (1980) and Zombeck *et al.* (1981) in a detailed mechanistic study of DTBP oxidation. The superoxocobalt(III) complex is involved in the reaction, abstracting an H-atom from the phenol. New features in the proposed mechanism are (*i*) hydrogen-bonding interaction of coordinated dioxygen with the OH group of DTBP before formation of the phenoxy radical, (*ii*) after H-atom transfer, a free $HO_2^{\cdot}$ radical is formed, which is assumed to decompose very rapidly to H_2O_2 and O_2, and (*iii*) the $LCoO_2$ species attacks the phenoxy radicals in the *p*-position.

2.3.2.2. *Oxygenation (dehydrogenation) of* o-*disubstituted benzenes*

Interest in this class of substrates stems from the attempts made at modelling dioxygenase enzymes, which effect the cleavage of aromatic and indole rings, as well as dihydroxylations. A characteristic feature if the incorporation of both O-atoms of O_2 into the substrate, which was first demonstrated by Hayaishi *et al.* (1955) in catechol oxygenation by pyrocatechase. In model studies a convenient substrate is catalysed by complexes of copper (Demmin *et al.* 1981, Tsuji and Takayanagi 1980, Gampp *et al.* 1984, Speier 1986), iron (Tyson and Martell 1970, Funabiki *et al.* 1986), cobalt (Tsuruya *et al.* 1986) and some other metals.

Oxidation of DTBC catalysed by an iron(III) (py) (bpy) complex has been investigated in great detail (Funabiki *et al.* 1986). The oxygenation mechanism proposed involves formation of a 1 : 1 iron–catechol complex, followed by attack of O_2 to form a peroxy group in coordinated catechol. The oxygen atoms are then inserted in a step-wise manner to give both intradiol and extradiol cleavage products. This mechanism represents a case when catalysis involves coordination of both dioxygen and substrate to the metal ion.

The first step in catechol dioxygenase model reactions is often assumed to be dehydrogenation of the ene-diol moiety to an *o*-quinonoid structure. This has created interest in the behaviour of *o*-disubstituted benzenes under oxidative conditions.

With the aim of modelling tyrosinase, which has a dicopper site for catechol oxidation to *o*-quinone, copper catecholato complexes have been tested and found active as catalysts (Kida *et al.* 1983, Karlin *et al.* 1985, Speier 1986, Karlin and Gultneh 1987). Catalytic activity can be ascribed to dinuclear copper complexes, which permit simultaneous coordination of the catecholate ligand to both metal ions (Kida *et al.* 1983). Mononuclear complexes are less active or inactive even if they have their redox potentials in the same range as the dinuclear species. Kinetic studies on the oxidation of DTBC using the Cu(I)-pyridine catalyst system show second-order kinetics in the catalyst, zero-order kinetics in DTBC and first-order kinetics in dioxygen. This is in accordance with the key role of dinuclear complexes; the formation of a μ-peroxo complex is rate-determining. When *bis*(1,3,5-triketonato)dicopper(II) complexes are used as catalysts for DTBC oxidation, the rate is first-order with respect to the dimeric complex, in line with the same concept as above (Tsuruya and Lintvedt 1978).

Structurally related substrates are 1,2-disubstituted benzenes containing NH_2, OH and SH groups in various combinations. The *o*-phenylenediamine (OPD) complexes of Cu(II) and Co(II) react with dioxygen under mild conditions to yield a variety of products. The ligand in the catalyst complex and the substrate are the same, namely OPD. The oxidation of copper(II)–OPD complexes yields 2,3-diaminophenazine (Balogh-Hergovich *et al.* 1981), with the *o*-quinonediimine as a likely intermediate. The same product is observed in the cobalt(II)–OPD system (Zehnder and Löliger 1980, Nèmeth and Simándi 1982a, b, 1983, 1984). In acetone solution, with *bis*(dimethylglyoximato)-cobalt(II) derivatives (cobaloximes) as catalysts, substituted benzimidazoles are produced (Nèmeth and Simándi 1982a, b). Cobaloxime(II) is known to form superoxo and μ-peroxo complexes (Schrauzer and Lee 1970), so these are likely intermediates in the oxidations.

Stopped-flow kinetic studies on the O_2 rate of the Co(II)–OPD system have revealed the transient formation of both superoxo and μ-peroxocobalt(III) complexes containing two molecules of OPD per Co atom (Nèmeth and Simándi 1983). These species decompose by a complex route involving oxidative dehydrogenation and addition steps. In combination with cobalt(II) salts, *o*-aminophenol affords similar oxidative condensation products via transient dioxygen complexes. Dehydrogenation of *o*-aminothiophenol to the corresponding disulphide occurs without detectable formation of dioxygen complexes (Nèmeth *et al.* 1987). N-alkylidene-2-hydroxyanilines are oxidised to 2-substituted benzoxazoles by the CuCl/py system (Speier 1987b). A transient superoxocopper(II) is assumed to be involved in this reaction.

2.3.2.3. *Aromatic hydroxylation*

The hydroxylation of aromatic compounds can be effected in very modest yields by Fe(II)/ascorbic acid/edta systems (Udenfriend *et al.* 1954, Sheldon and Kochi 1981). Recently reports have appeared on benzene hydroxylation to phenol using Cu_2Cl_2 (Ito *et al.* 1988) and a Pd/CO/1,10-phenanthroline catalyst (Jintoku *et al.* 1987), and on naphthol oxygenation (Duchstein *et al.* 1988), but no dioxygen complexes seem to be involved. The hydroxylation of an aromatic ring in a dinuclear copper complex of a pyridine substituted ligand has an extensive chemistry; the involvement of peroxodicopper complexes has been demonstrated (Karlin and Gultneh 1987, Jacobson *et al.* 1988).

3. Oxidation of miscellaneous substrates

The catalytic oxidation of a dialkyl sulphide to sulphoxide has been observed in the presence of Ru(OEP) $(R_2S)_2$. The reaction probably involves steps similar to those given by equations (14)–(17) (James *et al.* 1987).

Complexes of the type *cis*- and *trans*-$RuX_2(Me_2SO)_4$ catalyse the oxidation of dialkyl sulphides to the corresponding sulphoxides by O_2 (Riley and Shumate 1984).

The copper(II) catalysed autoxidation of some diaminouracils has been studied to gain an insight into the action of Cu(II)-containing amine oxidases (Al-Arab and Hamilton 1986). In a ternary complex involving the substrate, Cu(II) and O_2, two electrons are transferred from one substrate molecule to another with the formation of a diiminouracil (formal oxidative dehydrogenation).

In the presence of Cu_2Cl_2, nitroxyls mediate the oxidation of allylic and benzylic alcohols to aldehydes (Semmelhack *et al.* 1984) with no indication of dioxygen complexes being involved.

Glutathione and other thiols are oxidised to disulphides in the presence of iron(III) (Hamed *et al.* 1983). Involvement of a μ-peroxodiiron(III) intermediate has been inferred from kinetic results.

Dioxygenation of 1,2-cyclohexanedionds is catalysed by copper(II) ions. The product 1,5-keto acids are formed via an endoperoxide intermediate. The process is a non-enzymatic analogue of quercetinase action (Utaka *et al.* 1984).

Deoxybenzoin is converted to a mixture of benzyl and bidesyl, and the cleavage products PhCHO and $PhCO_2H$ by the Cu(II)–pyridine system (Sayre and Jin 1984). In the presence of the $[CuClpy_n]$ system, acyloins (e.g. benzoin) are catalytically oxidised to 1,2-dicarbonyls but no C–C cleavage is observed (Speier 1987a). A redox shuttle mechanism was deduced from kinetic data. A μ-peroxodicopper(II) intermediate is proposed but a copper(III)-oxo species is also conceivable.

Adrenalin is dehydrogenated and cyclised to adrenochrome in the presence of VO^{2+} ions and dioxygen (Jameson and Kiss 1986). Peroxide ions are active intermediates of the reaction.

The oxidative condensation of 2-mercaptobenzothiazole with cyclohexylamine gives a sulphenamide. The rate-determining step is presumably the oxidation of Cu(I) by O_2 via intervention of a short-lived superoxocopper species (Hronec and Malik 1986).

Isonitriles are oxidised to isocyanates in the presence of Ni complexes (Otsuka *et al.* 1967) or cobaloximes (Nèmeth and Simándi 1982a, b). Cobaloximes also catalyse the oxygenation of nitrobenzene to nitrobenzene (Nèmeth and Simándi 1982a, b).

Cobalt(II)–dipeptide complexes (e.g. with glycylglycine or glycylalanine) react with dioxygen and the peroxodicobalt(III) species formed produce oxidised derivatives of the ligand, containing imine group(s) (Martell 1983). Successive dehydrogenation steps in Co(II) macrocyclic Schiff-base complexes lead to an entirely conjugated ligand (Black and Hartshorn 1974).

Alpha-amino acids are oxidised to keto-acids in the presence of pyridoxal and transition metal ions as catalysts. A ternary complex containing dioxygen, and the Schiff base formed from pyridoxal and the amino acid, coordinated to the metal ion is responsible for the catalytic effect (Martell 1983).

3-substituted indoles are dioxygenated with C=C bond cleavage in the presence of Co(Salen) (Nishinaga 1975), Co(II) porphyrin complexes (Dufour-Ricroch and Gaudemer 1976), $FeCl_2$/py/bpy systems (Ohkubo *et al.* 1985), or the CuCl/py system (Speier and Tyeklár 1983).

Diethylamine is dehydrogenated to the corresponding imine with Ru(III) ion or Ru(III)-edta as catalyst (Taqui Khan *et al.* 1987). Intramolecular β-hydride abstraction affords a hydridoruthenium species, which is rapidly oxidised to the starting catalyst. This mechanism is similar to those proposed for other secondary amines (Murahashi *et al.* 1985, Marino and Larsen 1981).

The catalytic oxidative dehydrogenation of hydrazobenzene to azobenzene in the presence of cobaloxime(II) derivatives occurs via a novel oxo-cobaloxime(IV) species, which is formed by simultaneous abstraction of the two N-bonded H-atoms within a H-bonded intermediate. No H_2O_2 is formed even transiently, water being the sole reduction product from O_2 (Simándi *et al.* 1988). Similar mechanisms may be involved in other dehydrogenations where only that reduction product is detected.

1,2-phenylhydrazine is oxidised to azobenzene with O_2 under ambient conditions also, in the presence of macrocyclic cobalt(II) complexes (Sakata *et al.* 1988) as catalysts. The Co(III)-porphyrin catalysed oxidation of hydrazine has been reported (Bratushko *et al.* 1987).

D-fructose undergoes photochemically induced oxidative degradation to give *D*-erythrose and other fragments in the presence of Mn(II) ions (Araki and Shiraishi 1986). It seems that no dioxygen complexes are involved.

4. Conclusions

Studies on metal-ion activation of dioxygen are motivated by (*i*) biological relevance, and (*ii*) possible synthetic applications. Mechanistic studies and the nature of active intermediates have been the centre of attention during the last decade. Model systems of metalloporphyrin-mediated oxidations with oxygen atom sources other than dioxygen (such as PhIO and NaClO) have been very useful in providing a deeper insight into the intricate mechanism of olefin epoxidation and aromatic hydroxylation. The importance of oxometal species capable of O-atom transfer to the substrate in such reactions has been conclusively established. Dioxygen complexes of the superoxo or peroxo type have been shown in a number of cases to be intimately involved in the catalytic process, mostly via initiating the reaction by H-atom abstraction. Catalytic oxidation in the presence of added reducing agents is a new development with further potential for applications. Irreversible oxidative decay of the catalyst complex often precludes unequivocal conclusions on the mechanism, as well as synthetic application. Much effort has been expended on discovering new catalytic systems based on known or specially designed metal complexes with ligands resistant to oxidation under catalytic conditions.

The field of dioxygen activation is in a state of progress. Our understanding of these reactions is still far from satisfactory. Future advances can be expected in the areas of reaction mechanisms, new more selective catalysts, easily handled oxygen sources, and complex catalysts on solid carriers. New developments can be foreseen in interdisciplinary areas such as photochemical and electrochemical dioxygen activation.

Appendix. List of symbols

bpy	2,2′-bipyridine
DTBC	3,5-di-*t*-butylcatechol
DTBP	2,6-di-*t*-butylphenol
edta	ethylenediaminetetraacetato(4-) ligand
HMPT	hexamethylphosphoramide

N-MeImd	N-methylimidazole
OEP	octaethylporphyrinato(2-) ligand
OPD	*o*-phenylenediamine
py	pyridine
salpr	*bis*(salicylidene-γ-iminopropyl)amine(2-),
smtdp	*bis*(salicylidene-γ-iminopropyl)methylamine(2-),
TPP	tetraphenylporphyrinato(2-) ligand,
TPPS	tetrakis(*p*-sulphonatophenyl)porphyrinato(2-),
TpivPP	*meso*-tetra(α,α,α,α-*o*-pivalamidophenyl)porphyrinato(2-) ligand

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