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ORGANOMETALLIC COMPLEXES AS CATALYSTS IN OXIDATION OF C–H COMPOUNDS

GEORGIY B. SHUL'PIN

Department of Kinetics and Catalysis, Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia

1.1 INTRODUCTION

Organometallic (i.e., containing π or σ metal–carbon bonds) derivatives of transition metals are known as *excellent catalysts* in reactions that do not involve the insertion of oxygen atoms [1]. They are used in (selected examples of recent publications are given) hydrogen/deuterium (H/D) exchange [2a], dehydrogenation [2b–e], homogeneous syngas conversion [2f], hydrosilylation [2g], carbonylation [2h], and homogeneous water gas shift reaction [2i]. In other recent works, complex [(Cp*)Ru(IPr*)Cl], where Cp* = η^5-C_5Me_5 and IPr* = 1,3-bis(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene, was used as a catalyst in the racemization of chiral alcohols [2j], neutral η^6-arene ruthenium complexes with monodentate P-donor ligands found to catalyze the transfer hydrogenation reaction [2k].

Organometallic catalysts were employed in oxidation reactions of some organic compounds. Thus, complex [$CpMo(CO)_3CF_3$] is a precatalyst for olefin epoxidation [3a], heterodinuclear ruthenium–iron complexes showed high activity for the catalytic oxidation of secondary alcohols with *tert*-butyl hydroperoxide to give ketones in aqueous media [3b]. In contrast, organometallic complexes were very rarely used as (pre)catalysts in oxygenation reactions of aromatic and saturated hydrocarbons [4a–e] (the latter can be called *noble gases of organic chemistry* because of their known inertness).

In various C–H oxygenation reactions, organometallic complexes can play the role of precatalyst. Compounds bearing carbon–metal bonds can also be some of intermediate compounds in the catalytic cycles. In this chapter, we discuss reactions in which an organometallic complex catalyzes the insertion of oxygen atoms into C–H bonds of hydrocarbons or other organic compounds. The focus will be made on the author's own works.

1.2 OXYGENATION REACTIONS WITH OXIDANTS OTHER THAN PEROXIDES

The first example of a metal-catalyzed oxygen atom insertion into the C–H bond was the reaction found by Shilov and Shteinman and their coworkers in 1972 (for reviews, see References 1h and 5). These authors demonstrated that $Pt^{II}Cl_4^{2-}$ ion could catalyze H/D exchange in methane in a D_2O/CD_3COOD solution and, if $Pt^{IV}Cl_6^{2-}$ is added, the latter oxidizes methane to methanol (Shilov chemistry). The catalytic cycle in which σ-methyl complexes of platinum(II) and platinum(IV) are involved is shown in Fig. 1.1.

Later, Periana and coworkers proposed (2,2′-bipyrimidyl)platinum(II)dichloride as a catalyst ("Periana system"; see a recent review [4d]). Fuming sulfuric acid is the oxidant in this case. A simplified scheme of the catalytic cycle is shown in Fig. 1.2. It can be seen that some intermediates contain σ-methyl-platinum bonds.

Complexes containing the fragment Cp*Ir (Cp* is pentamethylcyclopentadienyl) are active precatalysts in the C–H oxidation of *cis*-decalin and cyclooctane. Ceric ammonium nitrate was a sacrificial oxidant and water was the oxygen source

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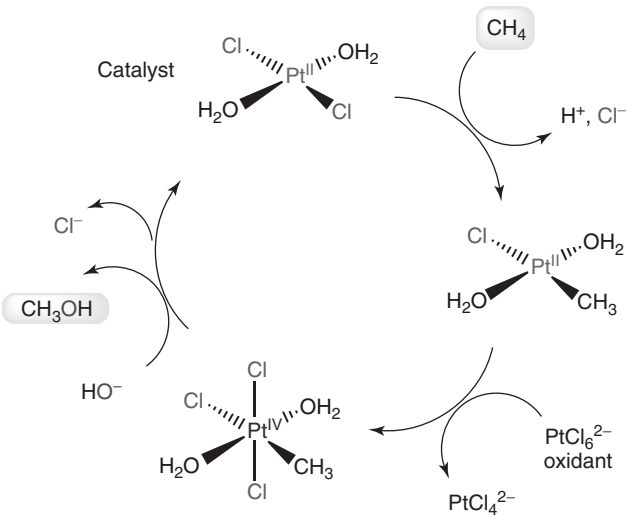

Figure 1.1 The catalytic cycle proposed for the methane oxidation to methanol by $Pt^{IV}Cl_6^{2-}$ catalyzed by $Pt^{II}Cl_4^{2-}$.

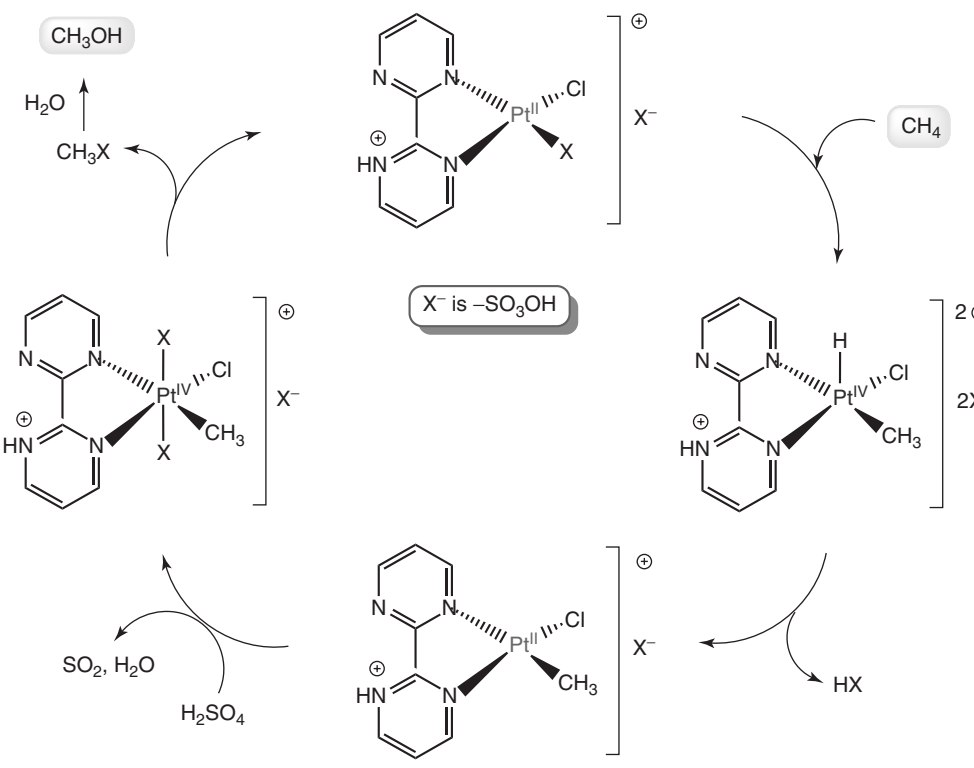

Figure 1.2 The simplified catalytic cycle for the methane oxidation by the Periana system. Adapted from Reference 4d.

(Fig. 1.3). Calculations using the Density functional theory (DFT) method showed that the C–H oxidation of *cis*-decalin by $Cp^*Ir(ppy)(Cl)$ (ppy = *o*-phenylpyridine) follows a direct oxygen insertion mechanism on the singlet potential energy surface [6]. The authors proposed that some of intermediate species contain the Cp^* ring coordinated to the iridium ion. The authors also made a general conclusion: oxidation catalysis by organometallic species can be hard to interpret because of the possibility that the real catalyst is an oxidation product of the precursor.

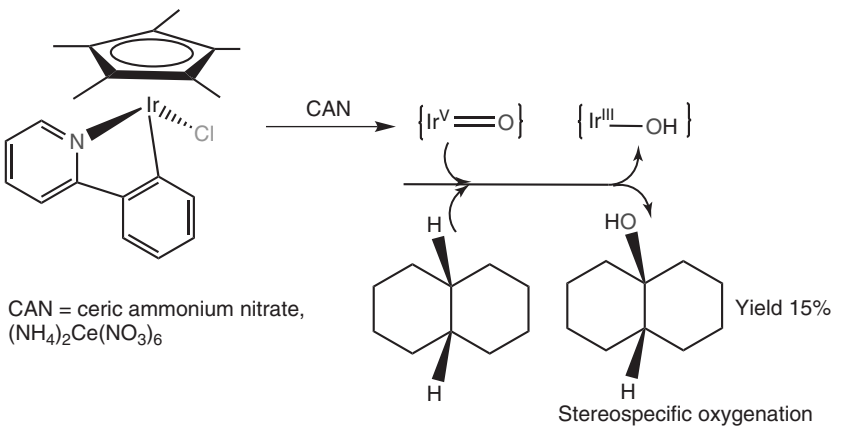

Figure 1.3 Stereospecific oxygenation of *cis*-decalin catalyzed by the Ir organometallic derivative [6].

Indeed, organometallic precatalysts can be transformed during an induction period into catalytically active species that do not contain metal–carbon bonds. For example, molybdenum [7a] and tungsten [7b] carbonyls catalyze aerobic photooxygenation of cyclohexane to cyclohexyl hydroperoxide (primary product) and cyclohexanol and cyclohexanone (Fig. 1.4). The proposed mechanism is shown in Fig. 1.5. It includes the formation during the induction period of an oxo derivative. Complexes $CpFe(\pi\text{-PhH})BF_4$ and $(\pi\text{-durene})_2Fe(BF_4)_2$ also catalyzed the aerobic alkane photooxygenation [7c]. The mechanism has not been studied.

1.3 OXYGENATION OF C–H BONDS WITH PEROXIDES

In the course of our systematic studies of hydrocarbon oxidation with peroxides, we have found a few organometallic catalysts and systems based on organometallic compounds. In some cases, these systems turned out to be extremely efficient, much more efficient than systems containing "simple" salts of transition metals.

Recently, we have discovered [8], for the first time, that ferrocene (catalyst **1.1**) is an efficient (pre)catalyst for several types of oxidative transformations, namely, the oxidation of alkanes and benzene by H_2O_2 or *tert*-butyl hydroperoxide. The oxidation of gaseous and liquid alkanes to alkyl hydroperoxides by H_2O_2 proceeds in MeCN at 50 °C. An obligatory cocatalyst is pyrazine-2-carboxylic acid (PCA, or Hpca, where H is a proton and pca is the anion of PCA). In the cyclohexane oxidation, the yield and TON after 1.5 h attained 32% and 1200, respectively. In the ethane oxidation, TON reached 970. Maximum yield (58% based on the alkane) was obtained for the *n*-butane oxidation after 4 h.

The simplest kinetic scheme of the alkane oxygenation based on the kinetic data was proposed. In the first stage, ferrocene $FeCp_2$ is oxidized to ferricenium cation $(FeCp_2)^+$, which is in turn transformed into species ***Fe*** that is a fragment containing one iron ion.

$$FeCp_2 + H_2O_2 \xrightarrow{H^+} (FeCp_2)^+,$$

$$(FeCp_2)^+ \rightarrow \boldsymbol{Fe}.$$

These are the fast stages of the generation from $FeCp_2$ and H_2O_2 the main species, which is active in the catalytic process. Produced fragment ***Fe*** interacts with a PCA molecule to form the complex ***Fe***(PCA):

$$\boldsymbol{Fe} + \mathrm{PCA} \rightleftharpoons \boldsymbol{Fe}(\mathrm{PCA}). \qquad (K_1)$$

Here (PCA) is a PCA fragment (possibly pyrazinecarboxylate, pca). The formed complex can react with the second PCA molecule yielding in this case an adduct containing two PCA fragments per one Fe ion:

$$\boldsymbol{Fe}(\mathrm{PCA}) + \mathrm{PCA} \rightleftharpoons \boldsymbol{Fe}(\mathrm{PCA})_2. \qquad (K_2)$$

Two adducts ***Fe***(PCA) can dimerize to afford the dinuclear complex $\boldsymbol{Fe}_2(\mathrm{PCA})_2$:

$$\boldsymbol{Fe}(\mathrm{PCA}) + \boldsymbol{Fe}(\mathrm{PCA}) \rightleftharpoons \boldsymbol{Fe}_2(\mathrm{PCA})_2. \qquad (K_3)$$

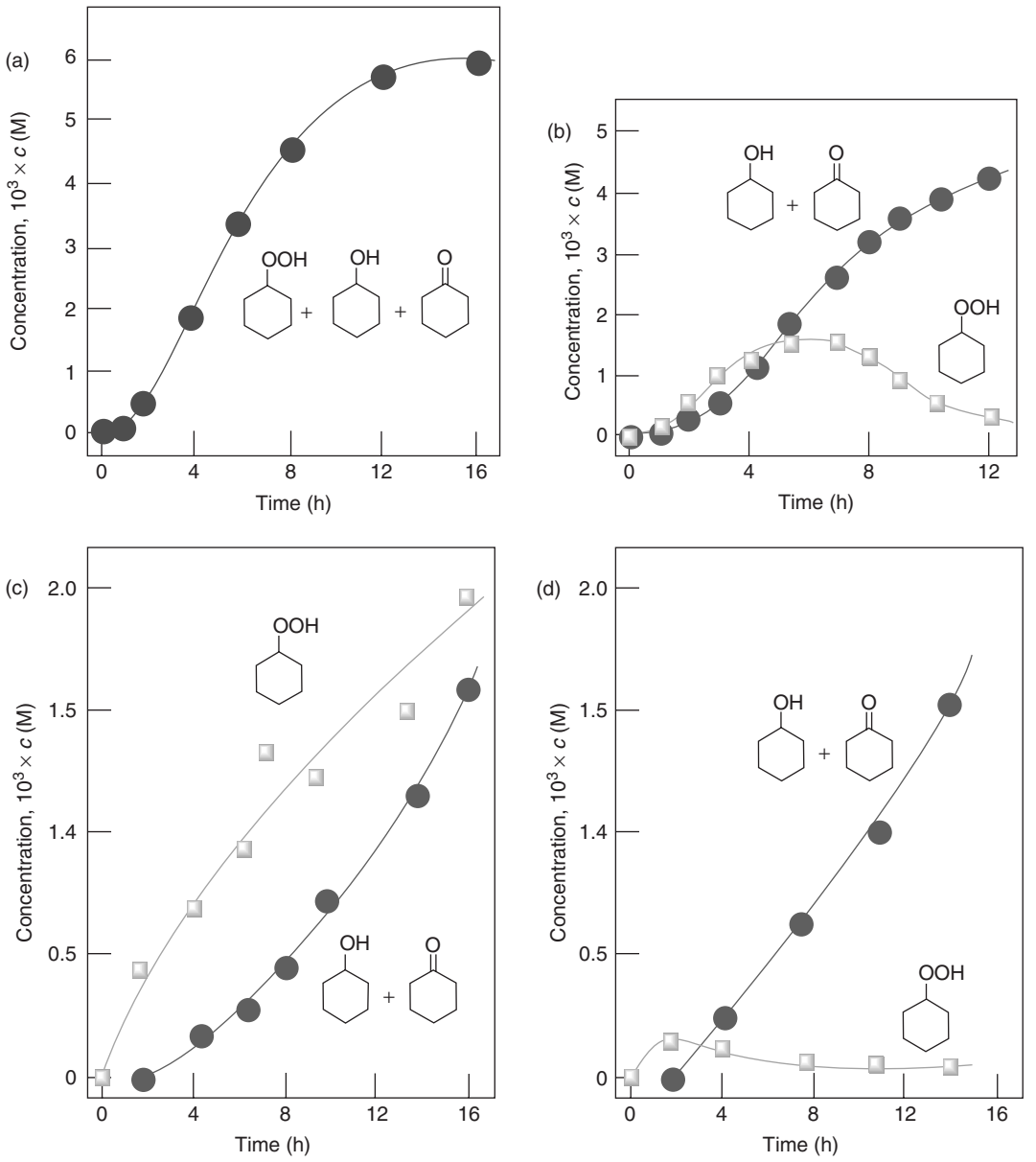

Figure 1.4 Oxidation of cyclohexane (CyH, 0.46 M) to cyclohexyl hydroperoxide, cyclohexanol, and cyclohexanone with air under irradiation with full light of high pressure Hg arc (1000 W) in MeCN (15 °C). Photocatalysts (5×10^{-4} M) : $M(CO)_6$ (where M = Mo, graph a [7a] and W, graph b [7b]) and complexes $CpFe(\pi\text{-PhH})BF_4$ (graph c) and $(\pi\text{-durene})_2Fe(BF_4)_2$ (graph d) [7c] are shown.

Complex $\boldsymbol{Fe}_2(PCA)_2$ is a catalytically active species that produces hydroxyl radicals from H_2O_2:

$$\boldsymbol{Fe}_2(PCA)_2 + H_2O_2 \rightarrow HO^{\bullet}. \qquad (k_4)$$

Hydroxyl radicals react in parallel routes with solvent (acetonitrile) and substrate (cyclohexane, RH):

$$HO^{\bullet} + MeCN \rightarrow \text{Products}, \qquad (k_5)$$

$$HO^{\bullet} + RH \rightarrow \ \rightarrow ROOH. \qquad (k_6)$$

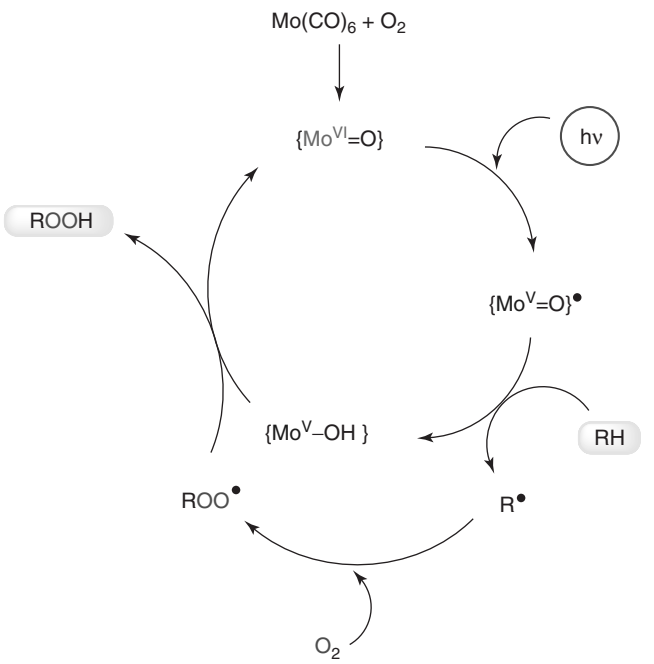

Figure 1.5 Mechanism proposed for the photooxygenation of alkanes, RH, in the presence of Mo or W carbonyls. (*See insert for color representation of the figure*.)

The last reaction is the rate-limiting step in the sequence of alkane transformations into cyclohexyl hydroperoxide. If we assume that the concentration of $HO^{\bullet}$ is quasi-stationary and concentrations of all iron complexes are in quasi-equilibrium and take into account conditions $[\boldsymbol{Fe}(\mathrm{PCA})] \ll [\mathrm{FeCp_2}]_0$ and $[\boldsymbol{Fe}_2(\mathrm{PCA})_2] \ll [\mathrm{FeCp_2}]_0$, we obtain the equation for the initial reaction rate as follows:

$$W_0 = \frac{k_4[\boldsymbol{Fe}_2(\mathrm{PCA})_2][\mathrm{H_2O_2}]_0}{1 + k_5\,[\mathrm{MeCN}]/k_6[RH]_0},$$

where

$$[\boldsymbol{Fe}_2(\mathrm{PCA})_2] = K_3[\boldsymbol{Fe}(\mathrm{PCA})]^2,$$

and

$$[\boldsymbol{Fe}(\mathrm{PCA})] = \frac{K_1[\mathrm{FeCp_2}]_0[\mathrm{PCA}]_0}{1 + K_1K_2[\mathrm{PCA}]_0^2}.$$

We can rewrite the equation for the initial reaction rate in the following form:

$$W_0 = \frac{\alpha[\mathrm{PCA}]_0^2}{\left(1 + \beta\,[\mathrm{PCA}]_0^2\right)^2},$$

where

$$\alpha = \frac{k_4[\mathrm{H_2O_2}]_0(K_1[\mathrm{FeCp_2}]_0)^2}{1 + k_5[\mathrm{MeCN}]/k_6[\mathrm{RH}]_0},$$

and

$$\beta = K_1K_2.$$

The following values $\alpha = 30\,\mathrm{M^{-1}\,s^{-1}}$ and $\beta = 1.1 \times 10^5\,\mathrm{M^{-2}}$ have been calculated for the conditions of our experiments. Using these values for parameters α and β, the initial reaction rates (presented by a dotted curve) have been calculated at different concentrations of PCA under conditions described in the caption of Fig. 1.6b.

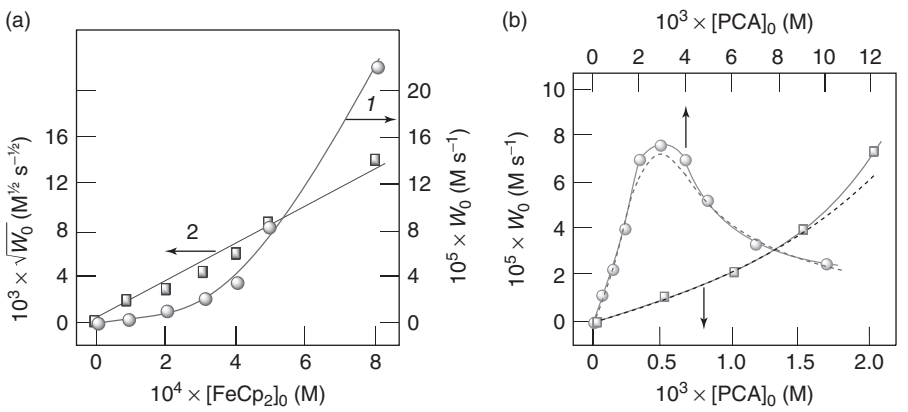

Figure 1.6 (a) Dependence of the initial rate W_0 of oxygenate accumulation in the cyclohexane oxidation with H_2O_2 catalyzed by ferrocene **1.1** in MeCN on the initial concentration of ferrocene (curve 1). Conditions: $[PCA]_0 = 3 \times 10^{-3}$ M, $[H_2O_2]_0 = 0.32$ M, $[\text{cyclohexane}]_0 = 0.37$ M, 50 °C. Curve 2: linearization of curve *1* in coordinates $[FeCp_2]_0 - W_0^{1/2}$. (b) Dependence of the initial rate W_0 of oxygenate accumulation in the cyclohexane oxidation with H_2O_2 catalyzed by **1.1** in MeCN on the initial concentration of PCA (in the intervals $0 - 10 \times 10^{-3}$ M and $0 - 2 \times 10^{-3}$ M). Conditions: $[FeCp_2]_0 = 5.0 \times 10^{-4}$ M, $[H_2O_2]_0 = 0.32$ M, $[\text{cyclohexane}]_0 = 0.37$ M, 50 °C. Dotted curves present the simulated dependences.

tert-Butyl hydroperoxide (0.58 M; 70% aqueous) oxidizes cyclohexane (0.92 M) in MeCN at 50 °C in the presence of **1.1** (1×10^{-3} M) and PCA (25×10^{-3} M), affording (after reduction with PPh_3) cyclohexanol (0.02 M) and cyclohexanone (0.001 M) after 4.5 h. Heating a solution of benzene (0.58 M) with H_2O_2 (1.28 M) in MeCN at 50 °C in the presence of **1.1** (5×10^{-4} M) and PCA (1×10^{-2} M) gave phenol (0.038 M after 1 h). In the presence of 2,2′-bipyridine (4×10^{-3} M) instead of PCA, **1.1** (5×10^{-4} M) catalyzes the oxygenation with H_2O_2 (1.28 M) of benzene (0.58 M) to phenol (0.05 M after 3 h) with a long induction period.

We also found recently [8] the first example of alkane hydrocarboxylation in aqueous acetonitrile with the $CO/S_2O_8^{2-}/H_2O$ system catalyzed by an iron complex, that is, ferrocene (Table 1.1). For example, the reaction of propane (1 atm) with CO (10 atm) at 60 °C during 4 h gave isomeric butyric acids in 60% total yield.

Another metallocene, namely, decamethylosmocene, $(Me_5C_5)_2Os$ (catalyst **1.2**), turned out to be a good precatalyst in a very efficient oxidation of alkanes with hydrogen peroxide in acetonitrile at $20 - 60$ °C [9]. The reaction proceeds with a substantial lag period that can be reduced by the addition of pyridine in a small concentration. Alkanes, RH, are oxidized primarily to the corresponding alkyl hydroperoxides, ROOH. TONs attain 51,000 in the case of cyclohexane (maximum turnover frequency was 6000 h^{-1}) and 3600 in the case of ethane. The oxidation of benzene and styrene afforded phenol and benzaldehyde, respectively. A kinetic study of cyclohexane oxidation catalyzed by **1.2** and selectivity parameters (measured in the oxidation of *n*-heptane, methylcyclohexane, isooctane, *cis*-dimethylcyclohexane, and *trans*-dimethylcyclohexane) indicated that the oxidation of saturated, olefinic, and aromatic hydrocarbons proceeds with the participation of hydroxyl radicals.

We discovered [10] that triosmium dodecacarbonyl (compound **1.3**, Fig. 1.7) catalyzes a very efficient oxidation of alkanes by H_2O_2 in MeCN to afford alkyl hydroperoxides (primary products) as well as alcohols and ketones (aldehydes) at 60 °C if pyridine is added in a low concentration. TONs attained 60,000 (Fig. 1.8a) and turnover frequencies were up to $24,000$ h^{-1}. A plateau in the dependence of W_0 on initial concentration of cyclooctane, [RH] (Fig. 1.8b), indicates that there is a competition between RH and another component of the reaction mixture for a transient oxidizing species. Indeed, at high concentration of the hydrocarbon, all oxidizing species are accepted by RH and the maximum possible oxidation rate is attained. This concurrence can be described by the following kinetic scheme:

$$H_2O_2 + \text{Catalyst} \rightarrow X \quad W_i, \tag{i}$$

$$X + RH \rightarrow \text{Products} \quad k_1, \tag{1}$$

$$X + py \rightarrow \text{Products} \quad k_2, \tag{2}$$

TABLE 1.1 Hydrocarboxylation of Alkanes by the 1.1/CO/$K_2S_2O_8$ System[a]

Alkane[b], atm; mmol	CO, atm	Products	Yield, %	Total Yield, %
Cyclohexane[c]				
1.0	20	*c*-$C_6H_{11}COOH$	18.3	19.4
		c-$C_6H_{11}OH$	0.8	
		c-$C_6H_{10}O$	0.3	
n-Heptane[d]				
1.0	20	$Me(CH_2)_6COOH$	0.3	9.2
		$MeCH(COOH)(CH_2)_4Me$	3.6	
		$EtCH(COOH)(CH_2)_3Me$	3.5	
		$Me(CH_2)_2CH(COOH)(CH_2)_2Me$	1.8	
n-Hexane[d]				
1.0	20	$Me(CH_2)_5COOH$	0.4	8.3
		$MeCH(COOH)(CH_2)_3Me$	4.0	
		$EtCH(COOH)(CH_2)_2Me$	3.9	
n-Pentane[d]				
1.0	20	$Me(CH_2)_4COOH$	0.8	12.6
		$MeCH(COOH)(CH_2)_2Me$	8.2	
		EtCH(COOH)Et	3.6	
n-Butane				
0.75[e]	10	EtCH(Me)COOH	19	21
		$Me(CH_2)_3COOH$	2	
Propane				
6	20	$Me_2CHCOOH$	17	19
		$Me(CH_2)_2COOH$	2	
1[e]	10	$Me_2CHCOOH$	51	60
		$Me(CH_2)_2COOH$	9	
Ethane				
10	20	EtCOOH	9	9
1[e]	10	EtCOOH	15	15

Adapted from Reference 8.
[a]Conditions. Amounts: ferrocene **1.1**, 4×10^{-3} mmol; $K_2S_2O_8$, 1.5 mmol; MeCN, 4 ml; H_2O, 2 ml; 60 °C, 4 h. Volume of the autoclave was 13 ml. Yield is based on the alkane.
[b]Amounts as pressure for gaseous ethane, propane, and *n*-butane and as mmol for other alkanes are given.
[c]At 50 °C; CH_3CN, 3 ml; H_2O, 3 ml.
[d]Regioselectivity parameters C(1) : C(2) : C(3) : C(4) for pentane, hexane, and heptane are 1 : 15 : 14, 1 : 15 : 15, and 1 : 18 : 18 : 18, respectively.
[e]$K_2S_2O_8$, 1.0 mmol.

$$X + H_2O_2 \rightarrow \text{Products} \quad k_3, \tag{3}$$

$$X + MeCN \rightarrow \text{Products} \quad k_4, \tag{4}$$

where W_i is the rate of generation of oxidizing species X. The analysis of this scheme in a quasi-stationary approximation relative to species X leads to the following equation:

$$W_0 = \frac{d[ROOH]}{dt} = \frac{W_i}{1 + \dfrac{k_2[py] + k_3[H_2O_2] + k_4[MeCN]}{k_1[RH]}}.$$

In accord with the last equation, we can see the linear dependence of the experimentally measured reciprocal parameter $1/W_0$ on reciprocal concentration $1/[RH]_0$ (Fig. 1.8c). The tangent of this straight line slope angle corresponds to the value

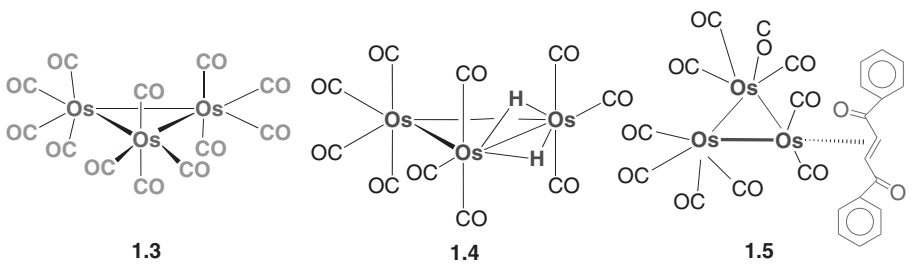

Figure 1.7 Efficient oxidation catalysts based on osmium carbonyls.

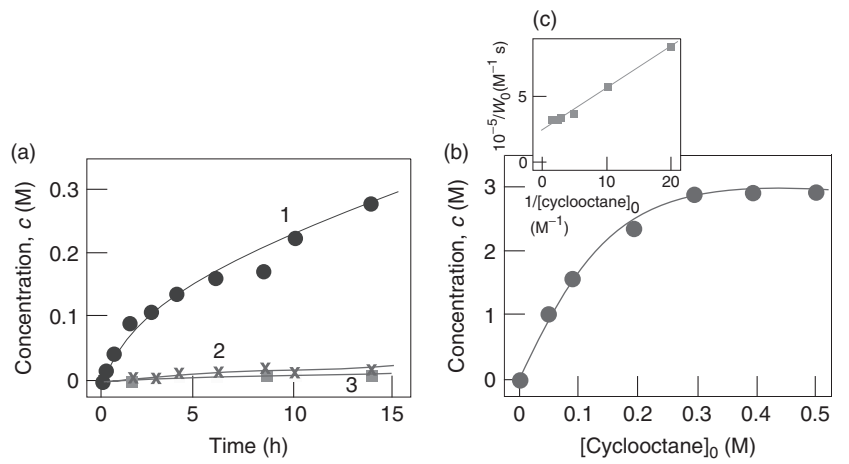

Figure 1.8 (a) Kinetic curves of accumulation of cyclooctyl hydroperoxide (curve 1), cyclooctanone (curve 2), and cyclooctanol (curve 3) in the cyclooctane (0.5 M) oxidation with H_2O_2 catalyzed by $Os_3(CO)_{12}$ (**1.3**) in MeCN at 60 °C. Concentrations of the three products were measured using a simple method, previously developed by us [10–12] with the reduction of samples with PPh_3. (b) Dependence of W_0 on the initial concentration of cyclooctane ($[\mathbf{1.3}]_0 = 5 \times 10^{-5}$ M). (c) Linearization of dependence shown in (b) using coordinates $1/W_0 - 1/[\text{cyclooctane}]_0$. Adapted from Reference 10(a).

$(k_2[\text{py}] + k_3[\text{H}_2\text{O}_2] + k_4[\text{MeCN}])/k_1 W_\text{i}$. The segment that is cut off by the line on Y-axis is equal to $1/W_\text{i}$. Thus, we can calculate the following value:

$$\frac{k_2[\text{py}] + k_3[\text{H}_2\text{O}_2] + k_4[\text{MeCN}]}{k_1} = 0.14.$$

At our conditions [py] = 0.1 M, $[\text{H}_2\text{O}_2] = 2$ M, and [MeCN] $\approx$ 18 M, we can calculate the following parameters (s^{-1}) for different data found in the literature: $k_2[\text{py}] = 2.3 \times 10^8$ or 4.5×10^8, $k_3[\text{H}_2\text{O}_2] = (9 \pm 2.8) \times 10^7$, and $k_4[\text{MeCN}] = 6.4 \times 10^7$ or 3.9×10^8. It follows from this estimation that the most probable competitors of cyclooctane for hydroxyl radicals are pyridine and acetonitrile. Rate constants ($M^{-1}\,s^{-1}$) can be calculated as follows: $k_1 = 1.6 \times 10^9$ or 3.2×10^9 in the case of pyridine and $k_1 = 4.5 \times 10^8$ or 2.8×10^9 in the case of acetonitrile. These values are typical for the reactions of hydroxyl radicals with alkanes: $k_1 = 1.2 \times 10^9$ for cyclopentane, $k_1 = 1.3 \times 10^9$ for cyclohexane, and $k_1 = 1.6 \times 10^9$ for cycloheptane in aqueous solution. It can be seen that the experimentally found competition is in good agreement with the assumption that the oxidizing species in our system is hydroxyl radical. Radical $HO^\bullet$ attacks the hydrocarbon RH to generate alkyl radical $R^\bullet$, which very rapidly reacts with molecular oxygen.

Similar trinuclear carbonyl hydride cluster, $Os_3(CO)_{10}$ (μ-H)$_2$ (compound **1.4**), catalyzes the oxidation of cyclooctane to cyclooctyl hydroperoxide by hydrogen peroxide in acetonitrile solution [12]. Selectivity parameters obtained in oxidations of various linear and branched alkanes as well as kinetic features of the reaction indicated that the alkane oxidation occurs with the participation of hydroxyl radicals. A similar mechanism operates in the transformation of benzene into phenol and styrene into benzaldehyde. The system also oxidizes 1-phenylethanol to acetophenone. The kinetic study

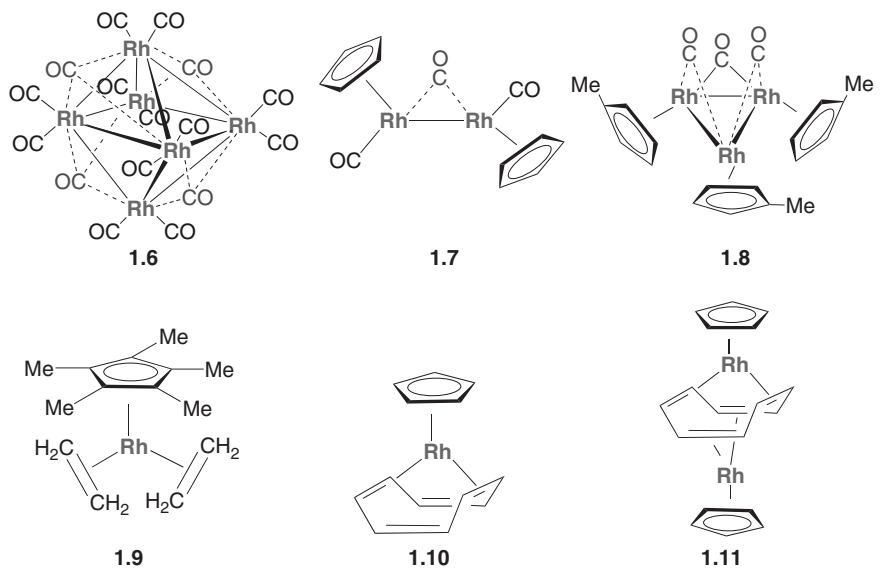

Figure 1.9 Compound **1.6** is an efficient catalyst for the benzene oxidation, compounds **1.7** and **1.8** are less efficient, and compounds **1.9**, **1.10**, and **1.11** are inactive.

led to a conclusion that the oxidation of alcohols does not involve hydroxyl radicals as the main oxidizing species and apparently proceeds with the participation of osmyl species, "Os = O." Finally, a carbonyl osmium(0) complex with π-coordinated olefin, (2, 3-η-1,4-diphenylbut-2-en-1,4-dione)undecacarbonyl triangulotriosmium (**1.5**, Fig. 1.7), catalyzes the oxygenation of alkanes (cyclohexane, cyclooctane, *n*-heptane, isooctane, etc.) with hydrogen peroxide, as well as with *tert*-butyl hydroperoxide and *meta*-chloroperoxybenzoic acid in acetonitrile solution [13]. "Simple" osmium salts ($OsCl_3$, Na_2OsCl_6) also catalyze (especially in the presence of pyridine or other N-bases) alkane hydroperoxidation with H_2O_2 in acetonitrile [14a] or water [14b], but these reactions are less efficient in comparison with processes catalyzed by organoosmium compounds.

Hexanuclear rhodium carbonyl cluster, $Rh_6(CO)_{16}$ (compound **1.6**, Fig. 1.9), catalyzes benzene hydroxylation with hydrogen peroxide in acetonitrile solution [15a]. Phenol and quinone (in less concentration) are formed with the maximum attained total yield and TON of 17% and 683, respectively. It is noteworthy that certain other rhodium carbonyl complexes, containing cyclopentadienyl ligands, $Rh_2Cp_2(CO)_3$ (**1.7**) and $Rh_3(CpMe)_3(CO)_3$ (**1.8**), are less efficient catalysts, whereas cyclopentadienyl derivatives of rhodium, which do not contain the carbonyl ligands, $Rh(CpMe_5)(CH_2 = CH_2)_2$ (**1.9**), RhCp(cyclooctatetraene) (**1.10**) and Rh_2Cp_2(cyclooctatetraene) (**1.11**), turned out to be absolutely inactive in the benzene hydroxylation. In the presence of compound **1.6**, styrene is transformed into benzaldehyde and (in less concentration) acetophenone and 1-phenylethanol. Addition of acids is known to accelerate some metal-catalyzed oxidation reactions. In our case, when trifluoroacetic acid was added to the reaction solution catalyzed by cluster **1.6**, the initial reaction rate was approximately three times higher. It should be emphasized that no oxygenated products have been detected when alkanes were used as substrates in the **1.6**-catalyzed oxidation. Ethyl groups in ethylbenzene were also not oxygenated. It has been tentatively assumed that the interaction of cluster **1.6** with hydrogen peroxide leads to splitting Rh–Rh and Rh–CO bonds to form vacant sites that coordinate benzene molecules. Possibly, the ***Rh***–CO fragment is oxidized in the initial period of the reaction to afford ***Rh***–C(O)OH and ***Rh***–C(O)OOH species. The catalytic cycle presented in Fig. 1.10 was proposed for the oxidation reaction. In the initial period, a rhodium complex under the action of hydrogen peroxide and water is transformed into a hydroxy derivative **A**. The interaction of species **A** with hydrogen peroxide affords a hydroperoxo derivative **B**. The latter forms a π-arene complex **C**. Species **C** can be converted into rhodadioxolane **D**, which decomposes further to produce phenol and initial catalytically active species **A**.

Cyclopentadienylbenzeneiridium(III) tetrafluoroborate [π-C_5H_5)Ir(π-C_6H_6)]$(BF_4)_2$ (complex **1.12**) was completely inactive in oxidation with hydrogen peroxide and *tert*-butyl hydroperoxide but exhibited a moderate activity in oxidation with *m*-chloroperoxybenzoic acid at room temperature [15b]. The H_2O_2–**1.12** system showed a moderate activity in the oxidation of secondary alcohols. For example, cyclohexanol was oxidized at room temperature to cyclohexanone (30% yield for 6 h) when a fourfold excess of PCA as a cocatalyst was added to the reaction solution.

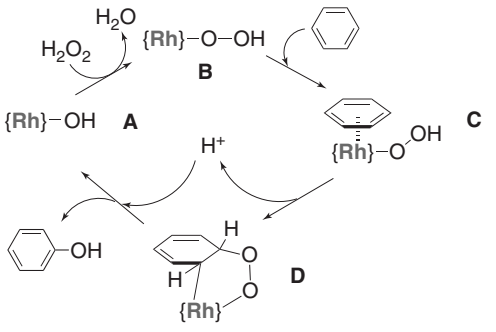

Figure 1.10 A catalytic cycle proposed for the benzene hydroxylation catalyzed by a rhodium complex ({**Rh**} is a Rh-containing fragment). Adapted from Reference 15a.

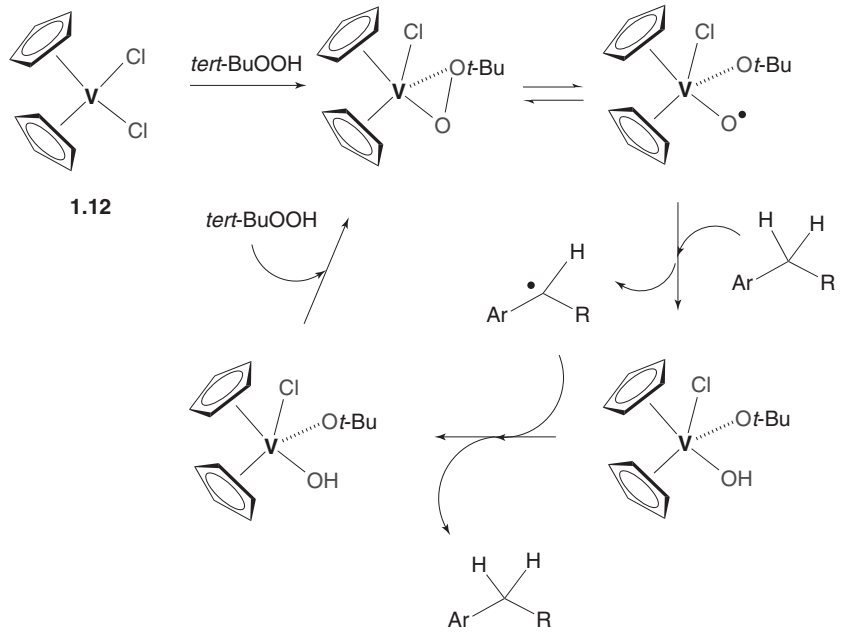

Figure 1.11 A catalytic cycle proposed for the benzyl hydroxylation catalyzed by vanadium complex **1.12**. Adapted from Reference 16.

It has been shown recently that cyclopentadienyl vanadium complexes catalyze the oxidation of benzylic groups by *tert*-BuOOH [16]. Compound Cp_2VCl_2 (**1.12**) catalyzes benzylic C–H oxidation selectively and effectively, giving no aromatic oxidation products. The authors assume that intermediate catalytically active species contain Cp rings (Fig. 1.11).

1.4 CONCLUSIONS AND OUTLOOK

It is clearly seen from this chapter that organometallic complexes are not leading catalysts for various reactions that afford valuable oxygenates from hydrocarbons and other C–H compounds. Such complexes are usually expensive and their synthesis is often not simple. However, in some cases, organometallics outrival commercially available inorganic salts in activity and selectivity. One can expect that the research on the application of organometallic catalysts in oxidation reactions will continue in the future.

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