

CHAPTER IX

HOMOGENEOUS CATALYTIC OXIDATION OF HYDROCARBONS BY MOLECULAR OXYGEN

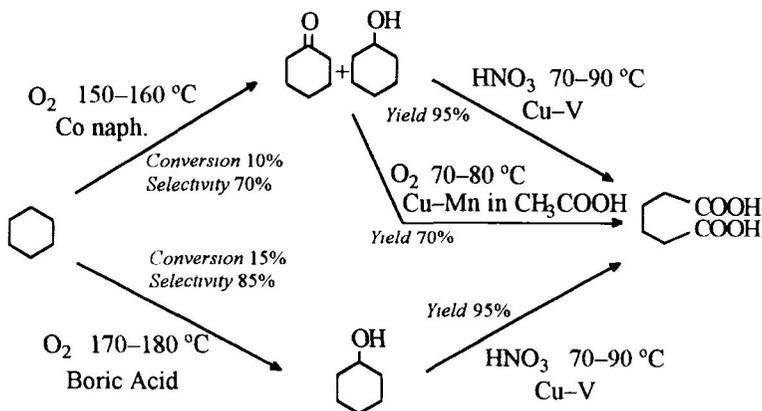
The oxidation of hydrocarbons by molecular oxygen in the absence of metal complexes has been discussed in Chapter II. The oxidation of hydrocarbons with molecular oxygen, as well as with donors of an oxygen atom (hydrogen peroxide, alkyl hydroperoxides and some other compounds), is a very important field since many industrial processes are based on these reactions [1]. In many cases, chain radical non-catalyzed autoxidation of saturated hydrocarbons is not very selective and the yields of valuable products are often low. The use of salts and complexes of transition metals creates great possibilities for solving problems of selective oxidation, as has been demonstrated for a number of important processes.

IX.1. TRANSITION METAL COMPLEXES IN THE THERMAL AUTOXIDATION OF HYDROCARBONS

IX.1.A. CLASSICAL RADICAL-CHAIN AUTOXIDATION

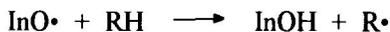
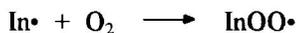
Alkanes and alkyl aromatic hydrocarbons can be oxidized when heated at rather high (usually above 100 °C) temperatures under oxygen. A long induction period can be reduced or eliminated if a donor of free radicals is present. The formation of oxygen-containing products from hydrocarbons and molecular oxygen is always thermodynamically allowed due to the high exothermicity of oxidation reactions. However, this same fact makes these processes usually unselective. The main problem is to prevent various parallel and consecutive oxidation reactions to produce numerous byproducts. Destruction of the carbon

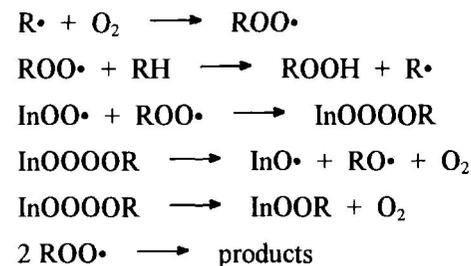
chain is one of the possible routes in the oxidation [2a]. For example, adipic acid is prepared commercially from cyclohexane by a two-step oxidation, first with air and then with nitric acid (Scheme IX. 1) [2b].



Scheme IX.1. Industrial process for the conversion of cyclohexane to adipic acid.

Autoxidation of saturated hydrocarbons or fragments occurs as a free radical-chain process. Azobis(isobutyronitrile) (AIBN, In-N=N-In) is frequently used as an initiator of radical-chain reactions [3]. For example, heptane (RH) is oxidized according to the following scheme [3c]:



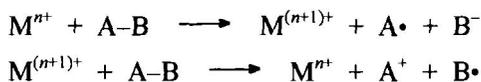


Any additive which could react with free radicals formed in such processes to yield stable adducts will inhibit the oxidation [4].

Mechanism of Catalysis by Transition Metal Salts

Ions of transition metals (homogeneously or in some cases supported on polymers [5]) also effectively catalyze the autoxidation. Salts of cobalt, manganese, iron, copper, chromium, lead, and nickel are used as catalysts that allow the reactions to be carried out at lower temperatures, therefore increasing the selectivity of the oxidation (see, for example, [6]). However, it is more important that the catalyst itself may regulate the selectivity of the process, leading to the formation of a particular product. The studies of the mechanism of the transition metal salt involvement have shown their role to consist, in most cases, of enhancing the formation of free radicals in the interaction with the initial and intermediate species.

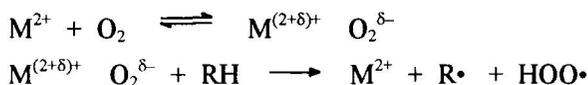
The common mechanism of catalysis by transition metal salts was formulated at the beginning of the thirties by Haber and Willstätter [7]. They proposed a scheme involving a metal ion interaction with a molecule (A–B) involving a change of ion oxidation state and free radical formation:



According to this scheme, a metal ion alternatively increasing and decreasing its valency can participate in the formation of a large number of free radicals, thus playing the role of a catalyst. The study of the participation of metal ions in the

chain reactions of oxidation shows them to take part in all the stages of the reaction, i.e. chain initiation, branching, propagation, and termination. In effect, small additions of transition metal complexes increase the initial rate of chain reactions and decrease the induction period, which is characteristic of non-catalytic oxidation. For example, naphthenates of cobalt, chromium and manganese reduce the induction period in cyclohexane oxidation. The same action is displayed by cobalt stearate, the induction period being shorter if more catalyst is introduced.

Formation of free radicals in the presence of transition metal compounds may be the result of their interaction with hydrocarbon or dioxygen. Such catalysts as cobalt and manganese salts are usually introduced in the bivalent state. An increase of chain initiation rate here may be connected with the activation of dioxygen by a metal complex via the following reaction [8]:



If the catalyst is in a high-valent state, chain initiation can proceed in the reaction:



This mechanism was unequally established for the case of benzaldehyde oxidation at room temperature in solutions of glacial acetic acid [9]. The kinetic equation obtained for the reaction is

$$v = k [\text{RCHO}]^{3/2} [\text{catalyst}]^{1/2}.$$

For the chain termination of the second order, the chain reaction rate is

$$v = \text{const} [\text{RH}] v_i^{1/2}$$

which leads to:

$$v_i = k_1 [\text{RCHO}] [\text{catalyst}]$$

The rate constant of chain initiation was determined from the special experiments with the introduction of an inhibitor. It was found to be

$$k = 3 \times 10^9 \exp(-14800/RT) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

The rate constant of the reaction of cobalt(III) acetate with benzaldehyde in the absence of dioxygen was determined in independent experiments. It turned out to be virtually the same as the rate constant of the chain initiation in the oxidation reaction in the presence of O_2 . However, the contribution of chain initiation to the radical formation is insignificant in the developed oxidation process. The radicals are mainly formed in the reactions of the intermediates in the process of degenerate chain branching. These reactions are also catalyzed by transition metal ions. Especially well studied is the acceleration of radical decomposition of intermediately formed hydroperoxides (see, e.g., [10]).

As early as 1932, Haber and Weiss [11] suggested a mechanism of interaction between hydrogen peroxide and iron(II) ions where electron transfer to the peroxide molecule led to the formation of a free hydroxyl radical:



The reaction of iron(II) ions with hydroperoxides proceeds similarly [12]:



Other ions, such as Co^{2+} and Mn^{2+} can react in the same way:



The newly formed high-valent ions can further react with hydroperoxide, e.g.,

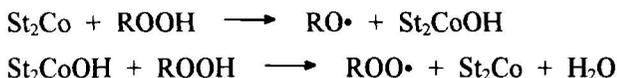


Therefore transition metal salts, in particular those of cobalt, can catalyze the decomposition of hydroperoxides into free radicals:



In this case, the time taken to reach the maximum rate, as well as the steady-state concentration of hydroperoxide, will be reduced.

In non-polar hydrocarbon media the reaction of hydroperoxide proceeds with undissociated salt, for example cobalt(II) stearate, which can be present in solution in small concentrations:



Such a reaction obviously proceeds more slowly than in aqueous or other polar media, but much faster than does thermal hydroperoxide decomposition. This results in a sharp drop of the steady-state concentration of the hydroperoxide in the hydrocarbon oxidation in the presence of a transition metal salt. Here, a decrease of hydroperoxide concentration will be compensated by an increase of its specific rate of decomposition so that the maximum oxidation rate will remain the same as in non-catalytic oxidations. In effect, the maximum rate

$$v_{\max} = (-d[\text{RH}]/dt)_{\max} = f^{-1} k_2 [\text{ROO}\cdot]_{\max} [\text{RH}]$$

will be reached under the condition that

$$nk_2 [\text{ROO}\cdot] [\text{RH}] = 2 k_6 [\text{ROO}\cdot]^2$$

that is [13]:

$$v_{\max} = (n/f)(k_2^2/k_6) [\text{RH}]$$

The same expression was obtained for non-catalytic reactions, i.e., the catalyst does not increase the maximum rate but merely reduces the induction period. This seemingly paradoxical conclusion is based on the fact that in both cases the maximum rate is determined by the equality of catalyst-independent reaction rates of chain propagation which, in the maximum, are equal to the rate of chain branching and termination. The existence of a maximum rate was quantitatively confirmed for the oxidation of some hydrocarbons (tetralin, ethylbenzene, diphenylmethane, etc.) [14a].

The maximum rate of dioxygen consumption

$$-d[\text{O}_2]/dt = k_{\text{eff}} [\text{RH}]^2$$

was found to be independent of the catalyst concentration and the value k_{eff} was found to coincide quantitatively with the parameter $k_2^2/2k_6$, measured independently. Chemiluminescent techniques have shown the hydroperoxide formation rate in these systems to be equal to that of dioxygen consumption. This is the evidence that the process proceeds entirely via the hydroperoxide formation [14b].

Hydroperoxide decomposition in the presence of transition metal compounds may be, in effect, more complicated than the above simple radical scheme suggests. It may involve, for example, the formation of intermediate complexes between the catalyst and hydroperoxide. The reaction may result in the formation of molecular products without the participation of free radicals or proceed itself by a radical chain mechanism [15].

The classical radical-chain mechanism leads to a variety of products in hydrocarbon oxidation due to the high temperature of the process and low selectivity of the interacting radicals. In view of developing selective industrial processes based on these reactions for the production of various substances, their low selectivity is an important shortcoming. The rate of oxidation usually increases in the order



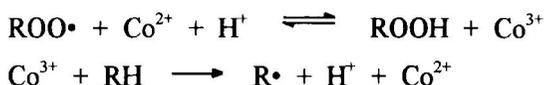
Thus, oxidation products are oxidized in their turn faster than the hydrocarbons themselves, and therefore the yields of the required intermediate products are usually low. In many cases the catalyst merely decreases the induction period, changing neither the mechanism nor the maximum rate of the process. This is typical of low catalyst concentrations in hydrocarbon media when the metal salt concentration, due to low solubility, does not exceed several hundredths of one percent. The use of polar solvents, e.g., acetic acid, trifluoroacetic acid, etc., allows for a considerable increase (100–1000 times) of the catalyst concentration. In this case the reaction can acquire new features. Not only the ratio but also the kinetics of the process can be markedly changed. Especially important is

the fact that the process very often becomes highly selective, which allows it to be used on the industrial scale.

Cobalt compounds are among the most efficient catalysts of alkane and aryl alkane autoxidation [16]. Toluene oxidation by dioxygen at 60 °C in acetic acid in the presence of Co(III) at the initial stages gives exclusively benzaldehyde [16d]. The reaction proceeds without an induction period, reaching the maximum rate at the beginning of the reaction. The kinetic equation for the oxidation is

$$-d[\text{O}_2]/dt = k [\text{PhCH}_3] [\text{Co(III)}]^2 [\text{Co(II)}]^{-1}$$

It is noteworthy that the reaction rate increases sharply on the addition of sodium acetate, which may mean that the primary interaction of Co(III) with toluene, which the authors of [16d] represented as electron transfer from toluene to Co(III), actually proceeds through electron transfer with synchronous elimination of the proton with the participation of a base (in this case, acetate). Since Co^{3+} can rather effectively oxidize a number of hydrocarbons, the following catalytic pathway:



is presumably realized in the presence of high cobalt salt concentrations. It is important that in some reactions of alkanes, an unusual selectivity is observed in the presence of cobalt compounds with or without dioxygen. This is strikingly different from that observed in radical reactions and implicates the direct interaction of Co(III) with hydrocarbons.

Butane oxidation in the presence of cobalt(III) acetate in acetic acid occurs at temperatures of 100–125 °C. Acetic acid is the reaction product with 83% selectivity (at 80% conversion) [1j, 17]. These data are markedly different from those observed for butane autoxidation at low initiator concentrations, where temperatures up to 170 °C and higher are required and acetic acid is produced with 40% selectivity. Cyclohexane oxidation in the presence of cobalt(II) acetate in acetic acid gives adipic acid in one step as the main product with 75% selectivity at more than 80% cyclohexane conversion [2b]. The induction period

which is observed in the reaction decreases on the addition of promoters, such as acetaldehyde, or disappears completely if the cobalt salt is introduced in the three-valent state.

The kinetics of dioxygen consumption are described by the equation which is common for reactions with Co(III) participation

$$-d[\text{O}_2]/dt = k [\text{RH}] [\text{Co(III)}]^2 [\text{Co(II)}]^{-1}$$

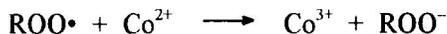
It is noteworthy that benzene under these conditions is not oxidized and is an appropriate solvent for cyclohexane oxidation. However, in a mixture of benzene – acetic acid the rate is 40% higher than that in acetic acid alone.

The alkanes containing a tertiary C–H bond appear to be less reactive than normal alkanes (the same is observed in the absence of dioxygen) and the reactivity surprisingly decreases with the increase of the hydrocarbon chain length. Thus, under similar conditions, isobutane reacts slower than butane, *n*-butane is more reactive than *n*-pentane, and undecane is completely unreactive [17]. It is difficult, as yet, to find any plausible explanation for these results. Heptane oxidation by cobalt(III) acetate in trifluoroacetic acid proceeds selectively without dioxygen in position 2, and in the presence of dioxygen results in 2-heptanone with 83% selectivity [18]. Undoubtedly, the alkane in these reactions interacts with the cobalt(III) salt and the selectivity observed, as has been pointed out, is of special interest, indicating the significant role of steric factors. The kinetics of the reaction, however, seem to be complicated by the oxidation of substances produced from alkanes. These secondary reactions might proceed according to a mechanism different from the mechanism of alkane oxidation.

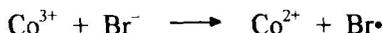
Cobalt-Bromide Catalysis

The oxidation of alkylaromatic hydrocarbons proceeds particularly easily in the presence of both cobalt and bromide ions (a so-called “cobalt-bromide catalysis”). Carboxylic acids are the final products of the reaction. For example, terephthalic acid is selectively formed from *p*-xylene, the whole process being used in the industrial production of the acid [1k, 19]. Despite the large number of works on cobalt-bromide catalysis, its mechanism has long remained speculative.

The process has interesting kinetic characteristics, specifically, in the presence of bromide ions the methylbenzenes oxidation rate is of second order with respect to cobalt. The rate does not depend on dioxygen concentration and depends only very insignificantly on the concentration of the compound being oxidized. To elucidate the "cobalt-bromide catalysis", a variety of schemes has been suggested. The reaction undoubtedly follows the chain mechanism (though some non-chain schemes were also suggested, some of them even without free radicals). The catalytic effect of cobalt and bromide ions is connected with their participation in chain propagation. Cobalt(II) ions can interact with hydroperoxide radicals:



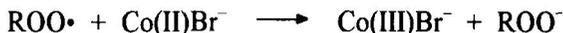
Cobalt(III) ions are again reduced to Co(II) by Br^- ions, the latter converting into bromine atoms:



Bromine atoms further react with hydrocarbons causing H elimination and forming a free radical:



The bromide ions may enter the coordination sphere of Co(II) as ligands, facilitating the process of cobalt oxidation:



Then Br^- oxidation occurs in the coordination sphere of Co(III):



The reaction with hydrocarbons is suggested to proceed without $\text{Br}\cdot$ atoms leaving the coordination sphere of Co(II):

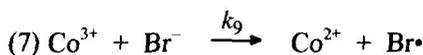
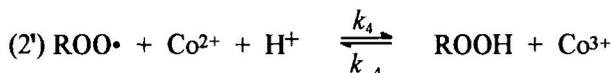


Table IX.1 gives the data on the relative rates of hydrocarbon oxidation obtained in the mixed oxidation of two hydrocarbons (usually the second hydrocarbon is ethylbenzene). For comparison, the relative reactivity for radicals and bromine atoms is also given in this table.

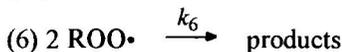
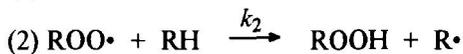
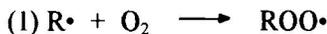
Table IX.1. The relative reactivity of hydrocarbons (per one reactive H atom) in the reaction with active species and in the autoxidation in the presence of Co(II) and Br⁻ in acetic acid.

RH	Co(OAc) ₂ + NaBr (60 °C)	Cumylperoxy radicals (30 °C)	Br atoms (40 °C)
Cyclohexane	0.33	0.1	0.0074
<i>p</i> -Chlorotoluene	0.42		
Toluene	1.00	1.00	1.00
Mesitylene	1.17		
<i>p</i> -Xylene	1.50	1.60	
Pseudocumene	2.54		
<i>p</i> -Methoxytoluene	3.42		
Durene	3.83		
Ethylbenzene	8.33	9.3	17
Cumene	16.8	15.9	37
Tetralin	34.2	36.4	

Kinetic studies, combined with measurements of chemiluminescence resulting from the process of the recombination of two radicals ROO•, allow for the proposal of a scheme where cobaltous, cobaltic and bromide ions enter the chain propagation [19b, 20]:



The other stages are similar to those of the mechanism with participation of small catalytic concentrations



Thus a slow reaction of chain propagation in the absence of the catalyst, or when its concentration is small, is replaced by the more rapid reactions 2', 7 and 8 (in fact, reactions 2', 7 and 8 are a catalytic pathway of the reaction 2) with catalyst participation. In this case, the maximum rate is reached if

$$2k_2 [\text{ROO}\cdot] [\text{Co}^{2+}] = 2k_6 [\text{ROO}\cdot]^2$$

Hence, in agreement with the experimental results

$$v = -d[\text{O}_2]/dt = (2k_2^2/k_6) [\text{Co}^{2+}]^2$$

Taking into account that hydroperoxide formation occurs in the reactions of $\text{ROO}\cdot$ not only with cobaltous ions but with hydrocarbons as well, we have, for steady-state conditions

$$2k_2 [\text{ROO}\cdot] [\text{RH}] + 2k_2 [\text{ROO}\cdot] [\text{Co}^{2+}] = 2k_6 [\text{ROO}\cdot]^2$$

and

$$v = (2/k_6)(k_2 [\text{RH}] + k_2' [\text{Co}^{2+}])^2$$

In accordance with the last formula, the relation is linear, with the slope of the straight line corresponding to the ratio $k_2(2/k_6)^{1/2}$. The mechanism suggested is also supported by the fact that, in the case of alkylbenzenes, the dioxygen consumption rate coincides with that of the catalytic hydroperoxide decom-

position. Moreover, the hydroperoxide radical recombination rate, measured by the chemiluminescence technique, is practically the same as that of dioxygen consumption.

In the suggested scheme, Br^- catalyzes an electron transfer from RH to Co^{3+} :



The mechanism via bromine atoms is supported by molecular bromine formation in the interaction of Co^{3+} with Br^- in the absence of a hydrocarbon (Br_2 is apparently formed by bromine atom recombination). This mechanism is also consistent with the fact that bromide ions, while catalyzing the oxidation in the case of alkylaromatic compounds, are not particularly effective in the case of simple alkanes. This corresponds to the difference of bromine atom reactivity with respect to alkylaromatic and aliphatic hydrocarbons. The bond energy in the H-Br molecule (85 kcal mole⁻¹) is practically equal to the energy of the C-H bond in the α -position to the aromatic ring, so that the reaction



for alkylaromatic hydrocarbons is close to thermoneutrality. For aliphatic hydrocarbons, this reaction is endothermic and its activation energy is considerably higher with bromine ions ceasing to be an effective catalyst of electron transfer from RH to Co^{3+} . The question arises as to why the reaction

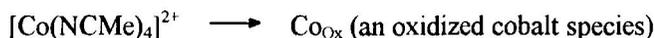


proceeds much slower without the catalyst and why its rate is enhanced by Br^- ions. Probably the answer is that a direct electron transfer from RH to Co^{3+} requires a hydrocarbon molecule to approach Co^{3+} with H^+ being synchronously eliminated by the base. Apparently this is of rather low probability. At the same time, a negative bromine ion can easily enter the coordination sphere of a positive cobalt(III) ion and the bromine atom produced will react with the hydrocarbon molecule without serious steric hindrance. It is obvious that such catalysis reflects the characteristics of the $\text{Br}\cdot/\text{Br}^-$ pair for which the redox potential, for the optimum case, must be close to those of the $\text{Co}^{3+}/\text{Co}^{2+}$ and $(\text{R}\cdot + \text{H}^+)/\text{RH}$ pairs.

IX. 1. B. SOME NEW AUTOXIDATION PROCESSES

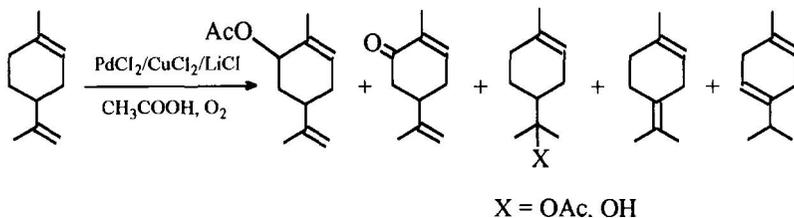
During the last decades some reactions between hydrocarbons and molecular oxygen have been described. These processes are often chain radical autoxidations, but in some cases the mechanisms of the reactions are not fully clear.

A weakly solvated complex containing acetonitrile, $[\text{Co}(\text{NCMe})_4](\text{PF}_6)_2$, catalyzes the air oxidation of cyclohexane and adamantane at 75 °C and 3 atm [21]. The commercial catalyst for cyclohexane oxidation does not function under these conditions. The metal ion functions both as an initiator and as a hydroperoxide decomposition catalyst. The following steps have been proposed for the oxidation reaction:



Cobalt chloride in diglyme is a useful catalyst for benzylic [22a] and allylic [22b] oxidation under mild conditions. The addition of sodium azide to oxidations catalyzed by transition metal acetylacetonates, heteropolyacids, phthalocyanines, bis-(pyridylimino)isoindolines, porphyrins and Schiff bases significantly enhances the rates of the low-temperature catalytic oxidation of alkanes [22c]. Ethylbenzene is slowly oxidized by air in MeCN in the presence of catalytic amount of chromium trioxide [23]. Complexes of Fe(III) and Co(II)

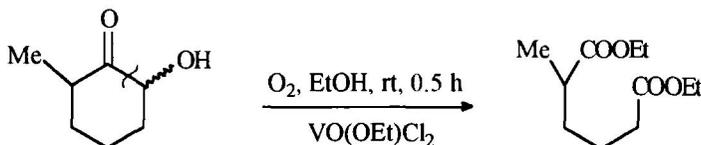
with dipyriddy- and acetylacetonate-functionalized polymers showed a high degree of activity and selectivity in the oxidation of ethylbenzene by oxygen [24]. Limonene can be efficiently and selectively oxidized by molecular oxygen in the presence of the $\text{PdCl}_2\text{-CuCl}_2$ catalytic combination [25]:



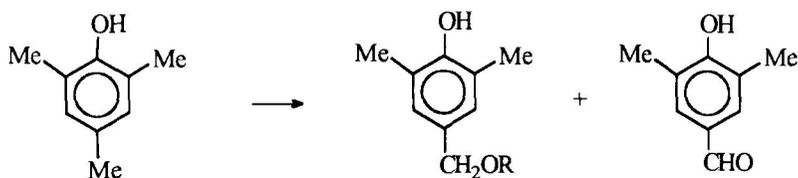
The system Ru(III)-EDTA catalyzes the oxidation of cyclohexane by molecular oxygen [26]. In the presence of manganese(II) acetate and molecular oxygen, alkenes and active methylene compounds react to yield cyclic peroxides [27]. α -Substituted cycloalkanones are oxidized to oxo acids by the copper(II) nitrate-dioxygen-acetic acid-water system [28a]:



α -Hydroxy ketones can be cleaved with a catalytic amount of dichloroethoxyoxovanadium under an oxygen atmosphere [28b]:

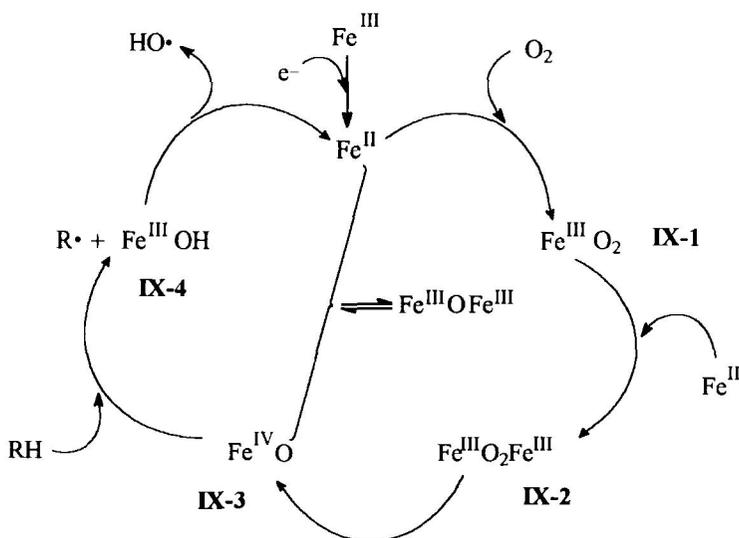


Copper(II) chloride, in combination with acetoxime, catalyzes the oxidation of a methyl group in 2,4,6-trimethylphenol in alcohols, ROH , at ambient temperature [29]:



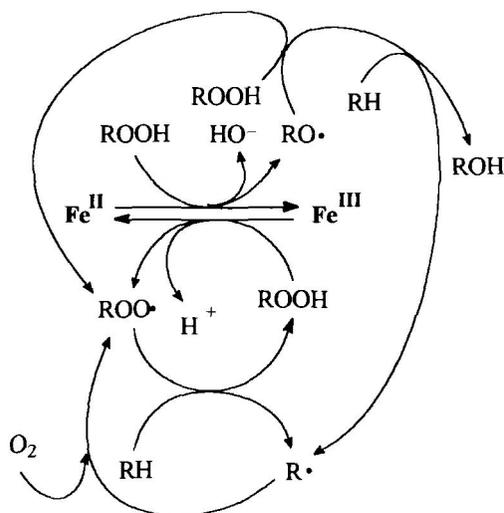
Oxygenation Catalyzed by Metalloporphyrins

Halogenated metalloporphyrins are effective catalysts for selective air oxidation of light alkanes [30] as well as of olefins [31]. The postulated mechanism of the reaction (Scheme IX.2) [30c] is similar to those proposed for biological oxidation (by cytochrome P450 and methanemmonooxygenase, see Chapter XI).



Scheme IX.2. The mechanism postulated for the air oxidation of alkanes catalyzed by halogenated metalloporphyrins.

This mechanism involves the reduction of Fe(III) followed by the addition of dioxygen to produce dioxo species **IX-1**. This species reacts with a second molecule of catalyst (intermediate **IX-2**) giving two molecules of the monooxo complex **IX-3**, which is capable of oxidizing the alkane. Species **IX-3** abstracts a hydrogen atom from the alkane to generate an alkyl radical and the hydroxy derivative **IX-4**. However, the alternative mechanism does not consider Fe(II)-O₂ species and assumes the conventional radical-chain autoxidation [30d]. Such a mechanism is depicted in Scheme IX.3.

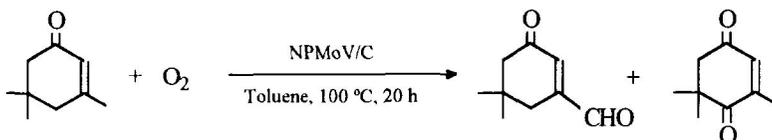


Scheme IX.3. The alternative mechanism for the air oxidation of alkanes assuming a radical-chain autoxidation.

Oxidations Catalyzed by Polymetalates

Heteropolyanions have been shown to effectively catalyze the oxidation of alkanes into the corresponding alcohols and ketones [32]. Thus, the compound $[\text{PW}_9\text{O}_{37}][\text{Fe}_2\text{Ni}(\text{OAc})_3]^{10-}$ catalyzes [32b] the transformation of adamantane into 1-adamantanol (76%), 2-adamantanol (12%) and 2-adamantanone (12%) with a total turnover number of 25 and a 29% conversion. The mixed-addenda hetero-

polyanion $[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]^{5-}$ catalyzes the aerobic oxidative dehydrogenation of α -terpinene to *p*-cumene [32d]. Transition metal substituted Keggin type polyoxomolybdates have been shown to be catalysts for the autoxidation of cumene or cyclohexene to afford alkylhydroperoxides which are used in the same reaction to epoxidize alkenes [32e]. Alkylbenzenes and alkanes can be oxygenated by dioxygen when ammonium molybdovanadophosphate is used as a catalyst [32f]. Finally, isophorone has been smoothly oxidized with O_2 in the presence of molybdovanadophosphate supported on active carbon [32g].



It is interesting that the regioselectivity of the oxidation is opposite to that of the conventional oxidations.

The Ishii Oxidation Reaction

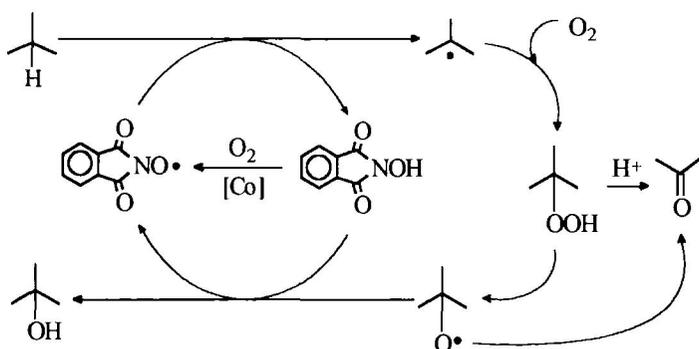
An oxidation of alkanes by molecular oxygen, which is catalyzed by *N*-hydroxyphthalimide (NHPI) combined with $\text{Co}(\text{acac})_n$ ($n = 2, 3$) or transition metal salts, has been described by Ishii and coworkers (see a review [33] and original papers [34]; in some cases NHPI also efficiently catalyzes the oxidation in the absence of metal derivatives [35]). For example, the oxidation of isobutane in the presence of catalytic amounts of NHPI and $\text{Co}(\text{acac})_2$ under an air atmosphere in benzonitrile at 100 °C gave *tert*-butyl alcohol (yield 84%) as well as acetone (13%) [34d]. The co-catalytic effects of various metal compounds are compared in Table IX.2. The proposed mechanism of the Ishii oxidation reaction involves hydrogen abstraction from isobutane (or any other compound with reactive C–H bonds) by the phthalimidoxy radical (PINO) (Scheme IX.4) [34d].

Direct conversion of cyclohexane into adipic acid has been achieved under the Ishii oxidation reaction conditions [34e]. The selectivity of adipic acid formation was 73% at 73% conversion in the presence of NHPI and $\text{Mn}(\text{acac})_2$ at 100 °C for 20 h. The oxidation of other cycloalkanes is presented in Table IX.3 [34e].

Table IX.2. The aerobic oxidation of isobutane in the presence of NHPI and various metal acetylacetonates ^a.

Catalyst	Yield, %	
	(CH ₃) ₃ COH	CH ₃ COCH ₃
None	3	4
TiO(acac) ₂	6	2
V(acac) ₂	18	9
Cr(acac) ₃	52	9
Mn(acac) ₂	28	8
Mn(acac) ₃	48	12
Fe(acac) ₃	52	9
Co(acac) ₂	84	13
Co(acac) ₃	58	10
Ni(acac) ₂	25	6
Cu(acac) ₂	47	11
Zn(acac) ₂	2	1

^a Reaction conditions: isobutane (5 mmol) was allowed to react in the presence of NHPI (10 mol %) and metal acetylacetonate (0.25 %) under a pressure of air (10 atm) in benzonitrile (10 mL) at 100 °C for 8 h.



Scheme IX.4. The mechanism of *tert*-butyl alcohol formation from isobutane in the Ishii oxidation reaction.

Table IX.3. The aerobic oxidation of cycloalkanes in the presence of NHPI and $Mn(acac)_2$ at 100 °C .

Substrate	Conversion, %	Products (%)	
		Cycloalkanone	Dicarboxylic acid
Cyclohexane	70	Cyclohexanone (~0)	Adipic acid (60) ^a
Cyclooctane	83	Cyclooctanone (2) ^b	Suberic acid (53) ^b
Cyclodecane	90	Cyclodecanone (2) ^b	Sebacic acid (55) ^b
Cyclododecane ^c	81	Cyclododecanone (3) ^b	Dodecanedioic acid (68) ^b

^a Selectivity.

^b Yield based on substrate reacted.

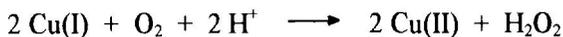
^c At 70 °C .

Oxygenation of Aromatic Hydrocarbons

Methods for hydroxylation of arenes by dioxygen to phenols have been developed in recent years. For example, the liquid-phase oxidation of benzene with molecular oxygen over the iron-heteropolyacid system gave phenol [36]. The following yields of phenol based on benzene have been obtained for various catalysts (300 K, 10 h):

Catalyst	Yield, %
$FeCl_2$	Trace
$H_3PW_{12}O_{40} + FeCl_2$	27.0
$H_0_5Fe_{1.25}PW_{12}O_{40}$	14.0
$H_0_5Fe_{1.25}PMo_{12}O_{40}$	4.2
$H_0_5Fe_{1.75}SiW_{12}O_{40}$	2.5

Copper(I) chloride promotes the oxidation of benzene to phenols with molecular oxygen [37a]. The active species is proposed to be a hydroxyl radical generated in the following manner:



Analogously, in the presence of silica-supported palladium catalysts, benzene is oxidized under ambient conditions to give phenol, benzoquinone, hydroquinone and catechol [37b]. Palladium chloride, used for the catalyst preparation, is believed to be converted into metallic palladium. The synthesis of phenol from benzene and molecular oxygen via direct activation of a C–H bond by the catalytic system Pd(OAc)_2 -phenanthroline in the presence of carbon monoxide has been described [38]. The proposed mechanism includes the electrophilic attack of benzene by an active palladium-containing species to produce a σ -phenyl complex of palladium(II). Subsequent activation of dioxygen by the Pd-phen–CO complex to form a Pd–OPh complex and its reaction with acetic acid yields phenol. The oxidation of propenoidic phenols by molecular oxygen is catalyzed by [*N,N'*-bis(salicylidene)ethane-1,2-diaminato]cobalt(II)[Co(salen)] [39].

IX.2. COUPLED OXIDATION OF HYDROCARBONS

The oxidation of organic compounds by dioxygen, including hydrocarbons, is known to be a strongly exothermic process with a large negative free energy. For a certain mechanism to correspond to an appropriate reaction rate, the intermediate stages must be advantageous enough thermodynamically, i.e., they should not require too much energy. The probability of this will be generally higher in the case of overall strongly exothermic processes, including oxidation of hydrocarbons by molecular oxygen, than in the case of less exothermic or thermoneutral process.

There are a number of mechanisms to provide a high rate of the whole process in the case of oxidation of hydrocarbons, particularly in coupled oxidation. They are mechanisms with chemically active species, such as free radicals, readily reacting with hydrocarbons. These free radicals may be formed as intermediates in metal ion oxidation.

IX.2.A. EARLIER WORKS

The coupled oxidation was described first in the middle of the past century. Schönbein discovered the phenomenon of so-called "active oxygen" [40], i.e., oxidation of some substances by molecular oxygen only when there is a parallel oxidation of other substances present. For example, the formation of iodine from potassium iodide or the discoloring of indigo are induced by zinc or a zinc amalgam. Ferrous oxide is among the number of organic and inorganic substances whose oxidation induces the oxidation of more inert substances. A thorough review of the oxidation reactions known at that time is given in the book by N. A. Shilov, which appeared in 1905 [41]. Several theories of active oxygen already existed then. According to N. A. Shilov, "All of them come to an assumption that the coupled oxidation by molecular oxygen is conditioned by the formation of an intermediate product. Some authors consider this intermediate substance to be free oxygen atoms or ion; the others, on the contrary, suppose that the oxygen molecule in the first stage of the oxidation preserves the atomic complex $-O-O-$, forming this or that holoxide. This last group of theories elucidates the experimental evidence in the best way". Here holoxide is a substance of the type:



The suggestion of peroxide formation in the first stage of the oxidation by molecular oxygen was made by Schönbein, their intermediate formation being confirmed in the works of Traube, Bach, Engler and others. For the coupled oxidation of a number of substances by strong oxidizing agents (for example, H_2CrO_4 or $HMnO_4$) in the presence of ferrous oxide, Manchot [42] suggested an intermediate formation of high-valent iron oxide, Fe_2O_5 .

According to Bach and Engler's peroxide theory [43], the coupling in oxidation reactions is explained in terms of intermediate formation of a peroxide. If of two substances, **A** and **B**, only one (e.g., **A**) reacts with molecular oxygen to give a peroxide (AO_2) (substance **A** is then called an "inductor"), then substance **B** ("acceptor") may be oxidized by this peroxide:

* ————— *



However, later it became clear that in most cases the assumption of the stable peroxide cannot by itself explain the phenomena observed. For example, though benzaldehyde oxidation initiates the coupled oxidation of indigo, specially synthesized peroxybenzoic acid can hardly oxidize indigo, and if so, the reaction proceeds far slower than it does in the process of coupled oxidation.

The development of the chain theory has produced a simple explanation of these facts in terms of the intermediate formation of radicals. The latter react with molecules much more readily than stable hydroperoxide molecules. The formation of free radicals was further established for many cases of oxidation of metal ions and complexes.

Hydroxylation of Hydrocarbons Coupled with the Oxidation of Metal Ions and Complexes

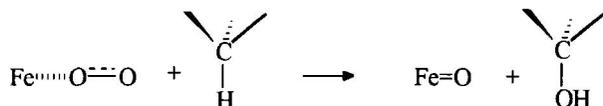
It is well-known that the biological oxidation of hydrocarbons (see Chapter XI) catalyzed by monooxygenases is coupled with the oxidation of electron donors, such as NADH or NADPH, in the presence of iron complexes. The donor in biological oxidation is believed to transfer its electrons initially to the metal ion, which is subsequently oxidized by an oxygen molecule. The fact of metal ion participation in most enzyme systems, which hydroxylate organic compounds, was the reason behind many attempts to create analogous purely chemical systems. It turned out that metal ion oxidation by molecular oxygen induces the oxidation of hydrocarbons (alkanes among them) introduced into the system. The formation of alkane oxidation products, at least with low yields, has been observed in many cases even in the oxidation of simple ions in various media.

Udenfriend suggested a simple non-enzymatic system as a possible model of monooxygenase [44]. It involves an iron(II) complex with EDTA and ascorbic acid and is capable of hydroxylating aromatic compounds. Later, Hamilton found that this system was able to hydroxylate cyclohexane (however, with very low yield) and epoxidize cyclohexene [45]. Afterwards, a number of similar systems were proposed. For example, Ullrich found two models which are more effective than the Udenfriend system. One of them includes a Sn(II) phosphate complex

dissolved in water [46a], and the other one an iron(II) complex with mercaptobenzoic acid in an aqueous solution of acetone [46b]. The reactions are analogous to those catalyzed by monooxygenase: hydroxylation of alkanes and aromatic compounds, and in some cases, epoxidation of olefins.

Ascorbic acid in the Udenfriend system may be replaced by pyrimidine derivatives which resemble tetrahydropteridines; the latter may be used as donors both in the model and enzyme systems. The reaction occurs at room temperature at pH 7.

Hamilton suggested that the model systems (at least some of them) interact with the substrates via a so-called oxenoid mechanism similar to that of monooxygenase functioning. Since the reaction, in many aspects, parallels the processes with carbenes (addition to the multiple bond, insertion into the C-H bond), in the oxenoid mechanism an oxygen atom (oxene) inserts into the C-H bond without an intermediate formation of free radicals:



At the same time, there are some essential differences which may be noted between biological oxidation and process occurring in the model systems. The latter have no NIH-shift (migration of a hydrogen atom to the position next to the point of oxygen insertion), which is characteristic of biological systems in the hydroxylation of aromatic molecules. The model systems are mostly less selective in the reactions with aromatic compounds (a large amount of *meta*-substituted product is formed); they do not show stereospecificity in the hydroxylation of alkanes (e.g., a mixture of both possible isomers in the hydroxylation of *cis*- and *trans*-dimethylcyclohexane is formed). Evidently, the participation of reducing agents, which are analogues of biological electron donors, is not very essential. In effect, simple chlorides of some metallic ions are already active enough in organic solvents.

Thus, the coupled oxidation of C₁-C₄ alkanes and SnCl₂ was found to proceed in acetonitrile at room temperature [47a]. The yields of alcohols, which are the oxidation products, reach 7-15% per SnCl₂. Comparatively high yields of the products of cyclohexane oxidation are obtained in the presence of oxidizing

tin(II) or iron(II) chlorides, when the reaction is carried out in acetonitrile as solvent [47b]. The yield, if based on the amount of metal salt present, may be further increased when the MCl_2 concentration is decreased. Under the optimum conditions of $[MCl_2] \rightarrow 0$, the yield of products grows up to 20% with $SnCl_2$ and up to 30% with $FeCl_2$.

Table IX.4. Parameter $1^\circ : 2^\circ : 3^\circ$ for the hydroxylation of isopentane by various systems.

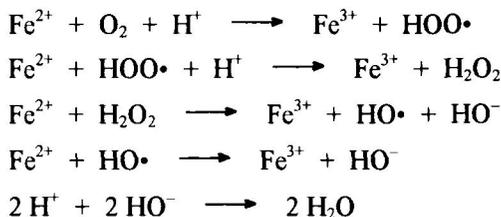
System	Solvent	$1^\circ : 2^\circ : 3^\circ$
Heme + MBA ^a + O ₂	CH ₃ COCH ₃ + H ₂ O	1 : 5.7 : 14
Fe ²⁺ + MBA ^a + O ₂	CH ₃ COCH ₃ + H ₂ O	1 : 4.1 : 12.8
SnCl ₂ + O ₂	CH ₃ CN + H ₂ O	1 : 5.1 : 12.5
FeCl ₂ + O ₂	CH ₃ CN	1 : 4.3 : 13.0
H ₂ O ₂ + <i>hν</i>	CH ₃ CN	1 : 4.5 : 11.2
CF ₃ COOOH	RH	1 : 60 : 720
Pyridine- <i>N</i> -oxide	CH ₂ Cl ₂	1 : 8 : 68

^a MBA = mercaptobenzoic acid.

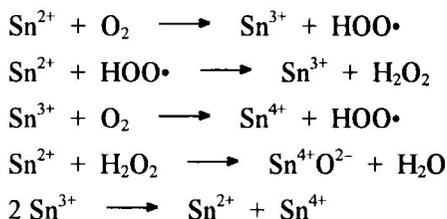
Table IX.4 gives the distribution of isopentane hydroxylation products in various systems, including photochemical hydroxylation by hydrogen peroxide, where free hydroxyl radicals are known to be formed as intermediates. It is clear that the ratios of selectivities with respect to the site of attack ($1^\circ : 2^\circ : 3^\circ$) in the systems involving Fe^{2+} and Sn^{2+} ions are very close to each other and to the selectivity observed for the attack by hydroxyl. This leads to the conclusion [47c] that the same active species (presumably hydroxyl radicals) participates in all these systems. This is also supported by a low isotope effect ($k_H/k_D \approx 1.2-1.3$, when comparing reactions of C_6H_{12} and C_6D_{12}). The yield of cyclohexane hydroxylation products depends on the nature of the solvent. The high yields in acetonitrile as compared with the other solvents are to be expected, provided the hydroxyl radicals are the intermediate active species. The rate constant of the hydroxyl radical reaction with cyclohexane is $5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, with

acetonitrile $2.1 \times 10^6 \text{ s}^{-1}$, with acetone $8.1 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and with methanol $7 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [48]. In the case of cyclohexane in acetonitrile, this means that the reaction of $\text{HO}\cdot$ with the solvent at $[\text{C}_6\text{H}_{12}] > 10^{-2} \text{ mol dm}^{-3}$ may be neglected. For the other organic solvents, it is necessary to take into account the competitive reaction of $\text{HO}\cdot$ with solvent, which reduces the yield of cyclohexane hydroxylation products.

In the case of iron salts, the accepted mechanism includes the formation of hydroxyl radicals:



For stannous chloride, the scheme of unbranched chain reaction without the participation of $\text{HO}\cdot$ radicals has been proposed [49a].



However, a detailed study of this reaction showed that it proceeds with chain branching and that it involves hydroxyl radicals (see below). The yield of oxidation products per metal ion may be increased if the reaction is carried out in the presence of specially added simple inorganic reducing agents. For example, if

the coupled oxidation of SnCl_2 and C_6H_{12} is carried out in the presence of metallic tin, then the yield of cyclohexanol can be increased six times. For FeCl_2 -containing systems, metallic mercury may be used as a reducing agent. This increases the yield of hydroxylation products.

In the systems involving such donors of electrons as hydrazobenzene or *o*-phenyldiamine (besides metal compounds), the yield of hydroxylation products may exceed the amount of the metal compound taken [49b]. Cyclohexane produces cyclohexanol and cyclohexanone, whereas cyclohex-1-ene-3-ol is mainly produced in the case of cyclohexene (with epoxide formation). Hydroxylation of 2-methylbutane produces isomeric alcohols, the selectivity with respect to the site of attack following the order: $3^\circ > 2^\circ > 1^\circ$. In toluene hydroxylation, the formation of both benzyl alcohol and isomeric cresols is observed, *o*- and *p*-isomers prevailing appreciably. An oxenoid mechanism of hydroxylation has been suggested. However, it is difficult to reconcile this mechanism with the fact that the yield of cyclohexane hydroxylation products depends so insignificantly on the nature of the metal ion (for FeCl_2 , VCl_2 , MnCl_2 , NiCl_2 , CuCl_2 the yield differs no more than 4 times; while for FeCl_2 , MnCl_2 , VCl_2 it is almost the same). The formation of the same intermediate active species, for example $\text{HOO}\cdot$, seems to be a more natural alternative.

A particularly active system was observed when mixing copper dichloride with phenylhydrazine in various organic solvents and water [49c]. Under optimum conditions, the yield reaches up to 40% per oxidized phenylhydrazine with the copper salt acting as a catalyst. The yield of products may correspond, for example, to forty redox cycles per mole of Cu salt with one portion of the reducing agent, and even several hundred cycles, if new portions of phenyl hydrazine are added after the previous hydrazine has been oxidized.

The Mechanism of Stannous Chloride Autoxidation Coupled with the Oxidation of Cyclohexane

A great number of species participating in the autoxidation of transition metal compounds makes it difficult to select a hydroxylation mechanism. Only in a small number of cases has this mechanism and the one of coupled hydrocarbon hydroxylation been well established. Let us take as an example the coupled oxidation of cyclohexane and stannous chloride.

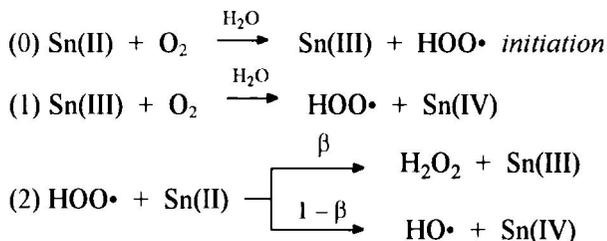
Tin(II) is a typical two-electron reductant since there are only two stable oxidation states for the compounds, Sn(II) and Sn(IV). The redox potential of the pair Sn(IV)/Sn(II) is +0.15 V in aqueous solutions. Thus Sn(II) is a moderately strong reducing agent. The estimation of the redox potential of the pair Sn(III)/Sn(II) gives a value +0.8 V. That means that E_0 for Sn(IV)/Sn(III) is -0.5 V, i.e., Sn(III) should be both a strong reducing agent turning into Sn(IV) and a strong oxidizing agent turning into Sn(II). The disproportionation of two Sn(III) ions is assumed to occur readily upon collision:

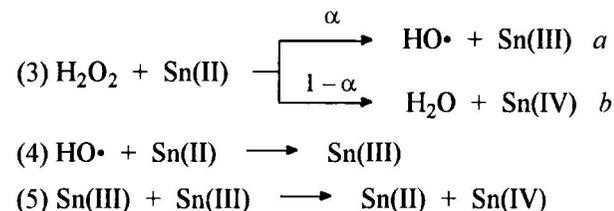


The oxidation of tin(II) salts by dioxygen displays some of the features of a chain process; in particular, it is retarded by certain inhibitors and accelerated when the solution is irradiated. The kinetic behavior of the oxidation reaction of Sn(II) chloride has some peculiarities. The reaction, under certain conditions, has a marked induction period followed by a period of practically constant rate, provided the dioxygen concentration is kept constant. The study of the dependence of the reaction rate on the dioxygen concentration shows that the reaction rate under steady-state conditions can be described by a simple kinetic expression:

$$-d[\text{O}_2]/dt = k [\text{O}_2]^2$$

i.e., the reaction rate does not depend on the Sn(II) concentration. It is clear that such a kinetic expression, though very simple, cannot be explained by a simple mechanism. To explain the kinetic data obtained, a branching chain scheme has been proposed [49d,e]:





Here α and β are the probabilities of one-electron reactions of Sn(II) with H_2O_2 and $\text{HOO}\cdot$, respectively.

In steady-state conditions

$$\alpha\beta k_1 [\text{Sn(III)}] [\text{O}_2] = k_5 [\text{Sn(III)}]^2$$

and the reaction rate is practically equal to that of chain propagation

$$-d[\text{O}_2]/dt = k_1 [\text{Sn(III)}] [\text{O}_2] = (\alpha\beta k_1^2/k_5) [\text{O}_2]^2$$

and, in agreement with the experimental data, depends only on the dioxygen concentration.

The branching chain mechanism is confirmed, for example, by the sensitivity of the reaction to the inhibitor concentration. There exists some limiting inhibitor concentration which practically stops the reaction (the induction period increases to infinity on the addition of a definite amount of an inhibitor). Hydrogen peroxide was detected during the oxidation of Sn(II). Using the reaction scheme, it was possible to estimate the rate constant of the reaction of hydrogen peroxide with Sn(II) by the dependence of H_2O_2 concentration on time. The rate constant found coincided with the value obtained for the reaction of H_2O_2 with Sn(II) determined in a separate investigation, thus confirming the proposed mechanism. Though the probability (α) of a one-electron reaction of hydrogen peroxide with Sn(II) to give a hydroxyl radical is not very high ($\alpha \approx 5 \times 10^{-4}$ for the reaction in acetonitrile), it is quite sufficient for the reaction to ensure the high rate of radical formation in a branched chain reaction under steady-state conditions.

The rate of autoxidation is much lower in acidic aqueous solutions of Sn(II) chloride than in organic solvents (though the addition of water is necessary

because the HO• and HOO• radicals, as well as hydrogen peroxide, participate in the reaction, their formation requiring protons). The rate decrease in aqueous solutions is partially associated with the decrease of dioxygen solubility, which is particularly important since the O₂ concentration enters the kinetic equation as a second-order term. However, the kinetic equation in acidic aqueous media is also different from that found for organic solvents:

$$v(\text{O}_2) = k_{\text{eff}} [\text{Sn(II)}]^{1/2} [\text{O}_2]^{3/2}$$

Detailed studies have shown that the different form of the kinetic equation for aqueous solution is due to the reaction which takes place in water:



and is nonessential for acetonitrile solutions. In other respects the mechanism is the same. Therefore, the autoxidation of stannous salts in a variety of solvents occurs by a branching chain mechanism with the participation of HO• and HOO• radicals. Reactions of the radicals with hydrocarbons should naturally be taken into consideration in the process of their oxidation coupled with the autoxidation of tin(II) salts.

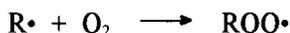
On the introduction of cyclohexane into a Sn(II) aqueous acetonitrile solution, the rate of dioxygen consumption increases and the induction period falls. An increase of cyclohexane concentration decreases the induction period and even causes its complete disappearance. The higher the initial tin concentration, the greater is the cyclohexane concentration necessary to cause the disappearance of the induction period. The rate of hydrogen peroxide production is also increased in the presence of cyclohexane. These data can be understood on the basis of the above chain mechanism of Sn(II) oxidation, where free hydroxyl radicals HO• are intermediately formed. The rate constant of the interaction of the hydroxyl radical with cyclohexane



is $5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Thus all the hydroxyl radicals, with an appropriate hydrocarbon concentration, will interact with the latter to produce hydrocarbon

* ————— *

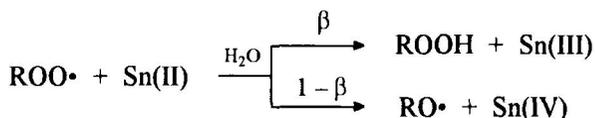
radicals. The radical very readily enters into an addition reaction in the presence of O_2 :



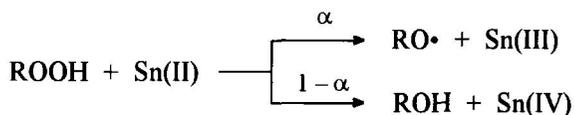
In hydroperoxide oxidation reactions, the radicals usually disappear in a bimolecular disproportionation process:



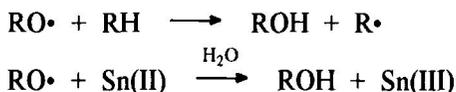
However, in the presence of large Sn(II) concentrations, practically all hydroperoxide radicals interact with the tin in a similar manner to $HOO\cdot$ radicals



The interaction of hydroperoxide with Sn(II) is similar to that of hydrogen peroxide



$RO\cdot$ radicals react with RH and Sn(II):



causing the formation of the alcohol, which is practically the only product. Besides, in aqueous solutions, as in the case of hydroperoxide, it is necessary to take into account the following reaction:



Thus, the participation of Sn(II) in the oxidation process ensures high selectivity of the reaction to produce cyclohexanol as virtually the sole product. It is important that the situation changes if the Sn(II) concentration is low; for example, if instead of dioxygen we add hydrogen peroxide to the Sn(II) solution. In this case Sn(II) quickly disappears, and the reaction of $\text{ROO}\cdot$ disproportionation becomes dominant, yielding a variety of products different from those observed for the oxidation by dioxygen. If we do not differentiate between the differences in reactions with high and low Sn(II) concentrations under the conditions of oxidation, it may lead us to an incorrect conclusion about the non-radical character of hydrocarbon oxidation coupled with Sn(II) oxidation by dioxygen.

It is interesting to note that, provided the RH concentration is sufficient for $\text{RO}\cdot$ radicals to disappear by the reaction with the hydrocarbon, the stoichiometry of the reaction under specified conditions corresponds to the ratio $\text{Sn(II)} : \text{O}_2 : \text{ROH} = 1 : 1 : 1$, which means that it will be the same as the stoichiometry of oxidation in the presence of monooxygenase. This shows that the stoichiometry of the process cannot be used as evidence for its mechanism. The example with Sn(II), treated here so extensively, is further evidence of the danger of drawing conclusions about the models of biological oxidation based merely on formal analogies.

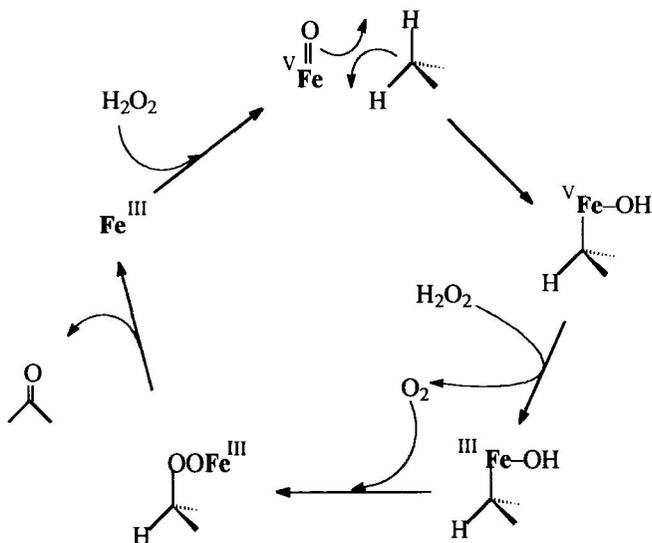
IX.2.B. GIF SYSTEMS

Barton and co-workers have developed a family of systems for oxidation and oxidative functionalization of alkanes under mild conditions exhibiting "unusual" selectivity (see reviews [50], polemics [50d,e], the first publication [51] and some recent publications[52], as well as the papers of other authors concerning these systems[53]). These oxidations occur in pyridine in the presence of an organic acid and are catalyzed by complexes of transition metals (mainly iron). If dioxygen is used as an oxidizing reagent, a reductant must also take part in the reaction. The first such a system was invented in Gif-sur-Yvette [51]. Thus their name: Gif systems. The systems with geographically based names are mentioned in Table IX.5. All Gif systems have the same chemical peculiarities:

1) the major products of the reaction are ketones; it is important that alcohols are not reaction intermediates;

Table IX.5. The nomenclature of Gif systems.

System	Catalyst	Electron source	Oxidant
Gif ^{III}	Fe(II)	Fe (metal)	O ₂
Gif ^{IV}	Fe(II)	Zn (metal)	O ₂
GO (Gif-Orsay)	Fe(II)	Cathode	O ₂
GoAgg ^I	Fe(II)		KO ₂ /Ar
GoAgg ^{II}	Fe(III)		H ₂ O ₂
GoAgg ^{III}	Fe(III)/Picolinic acid		H ₂ O ₂
GoChAgg	Cu(II)		H ₂ O ₂
Cu ⁰ /O ₂	Cu(I)?	Cu(0)	O ₂

**Scheme IX.5.** The proposed mechanism for the Gif GoAgg^{II} oxidation of alkanes.

2) the presence of an excess of some easily oxidizable compounds (e.g., alcohols, aldehydes) does not significantly suppress the alkane oxidation;

3) the selectivity of oxidation of branched hydrocarbons is secondary > tertiary > primary;

4) secondary alkyl free radicals are not reaction intermediates;

5) olefins are not epoxidized;

6) addition of different trapping reagents diverts the formation of ketones to the appropriate monosubstituted alkyl derivatives. For example, in the presence of CBrCl_3 alkyl bromide is formed in quantitative yield.

It should be noted that despite of numerous works devoted to Gif systems the mechanism of their action is not clear (see, for example, a discussion in [50d,e]). The proposed [52a] catalytic cycle for GoAgg^{II} reactions is shown in Scheme IX.5.

IX.2.C. OTHER SYSTEMS INVOLVING O_2 AND A REDUCING REAGENT

In recent years, numerous systems for alkane oxygenation based on molecular oxygen, a reductant and a metal catalyst have been described. Some of these systems will be considered in the present section.

Systems Based on Aldehydes

Olefins can be epoxidized by dioxygen in the presence of an aldehyde and various metal complexes [54]. An analogous oxidation of alkanes gives alcohols, ketones and alkyl hydroperoxides. Examples of oxidations by dioxygen in the presence of various reducing agents catalyzed by transition metal complexes are given in Table IX.6.

A $\text{RuO}_2\text{-CH}_3\text{CHO}$ system catalyzes the oxidative cleavage of C-C double bonds using molecular oxygen [55m]. Carbonyl compounds are formed selectively.

Systems Based on Solid Metals as Reducing Agents

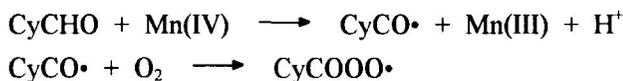
Metals added to various oxidation systems can serve both as reducing reagents and catalysts. Usually transition metals (e.g., iron) are used. If non-tran-

Table IX.6. Catalytic oxidation of hydrocarbons by dioxygen in the presence of aldehydes.

Substrates	Products	Reducing agent	Catalyst	Ref.
Alkanes	Alcohol+ketone	Heptanal	FeCl ₃ , RuCl ₃	55a
Alkanes	Alcohol+ketone	Acetaldehyde	Cu(OH) ₂	55b
Benzene	Phenol	Crotonaldehyde	VO(1,3-diketono) ₂	55c
Alkanes	Alcohol+ketone	Acetaldehyde	Metalloporphyrins	55d
Alkanes	Alcohol+ketone	2-Methyl-propanal	Co(II) Schiff base complex	55e
Cyclohexane	Cyclohexanol + cyclohexanone	Aldehyde	Metalloporphyrins	55f
Alkanes	Alcohol+ketone	Acetaldehyde	Cu-Crown ether	55g
Alkanes, aryl-alkanes	Alcohol+ketone	2-Methyl-propanal	Mo,V-Heteropoly-oxometalates	55h
Alkanes	Alcohol+ketone	Aldehydes	Cu salts	55i
Arylalkanes	Ketone	2-Methyl-propanal	Co(II) cryptate	55j
Alkanes, aryl-alkanes	Alcohol+ketone	3-Methyl-butanal	M(acac) _n M = Pd, Co, Fe, Ni, Cu	55k

sition metals (e.g., zinc) are employed as reducing agents, the catalysts (transition metals complexes) are necessary. In all the reactions, proton donors (carboxylic acids) take part to dissolve the solid metal. Examples of reactions using metals as reducing agents are summarized in Table IX.7.

A binuclear Mn(IV) complex with the 1,4,7-trimethyl-1,4,7-triazacyclononane macrocyclic ligand initiates oxidation of cyclohexancarboxaldehyde with atmospheric oxygen in acetonitrile under heating resulting in the formation of cyclohexanecarboxylic acid and considerable amounts of oxidative decarboxylation products, i.e., cyclohexane, cyclohexanol and cyclohexanone [551]. In the presence of cyclooctane, the reaction gives rise also to the formation of cyclooctanol and cyclooctanone. The following stages of the reaction have been proposed (Cy = cyclohexyl; RH = cyclooctane):



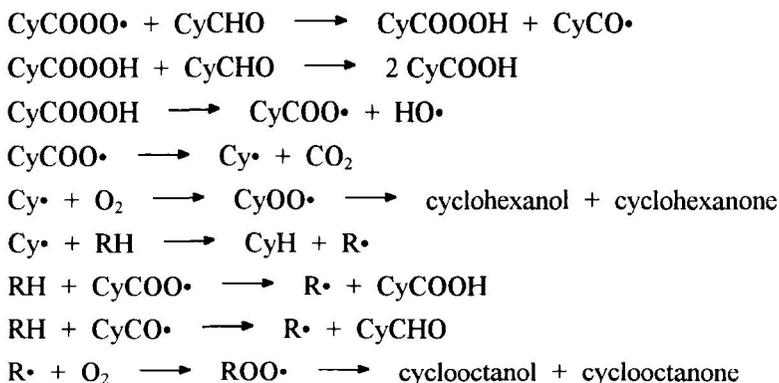


Table IX.7. Catalytic oxidation of hydrocarbons by dioxygen in the presence of solid metals as reducing agents.

Substrates	Products	Reducing agent	Catalyst	Ref.
Arenes	Phenols	Fe	Fe(II)	56a
Cyclohexane	Cyclohexanol + cyclohexanone	Zn powder	Fe(II) on silica gel	56b
Alkanes, arenes	Alcohols, phenols	Zn powder	[{Fe(HBpz ₃)(hfacac)} ₂ O]	56c
Methane	Methanol + formaldehyde	Zn powder	Fe(II) on silica gel	56d,e
Alkanes	Alcohol+ketone	Zn powder	Mn-Porphyrin	56f
Cyclohexane	Cyclohexanol + cyclohexanone	Zn powder	SmCl ₃	56g,h
Alkanes	Alcohol+ketone	Zn powder	EuCl ₃	56i-k
Methane	Methanol	Zn powder	EuCl ₃	56l
Methane	CF ₃ COOCH ₃	Zn powder	VO ₃ ⁻ , VO(acac) ₂	56m

Yamanaka *et al.* have demonstrated that aerobic hydroxylation of methane in trifluoroacetic acid at 40 °C is catalyzed by NH₄VO₃ or VO(acac)₂ if zinc powder is present [56m]. Methyl trifluoroacetate is formed with a turnover number ca. 10 after 1 h. The authors suggested that the active oxygen species in

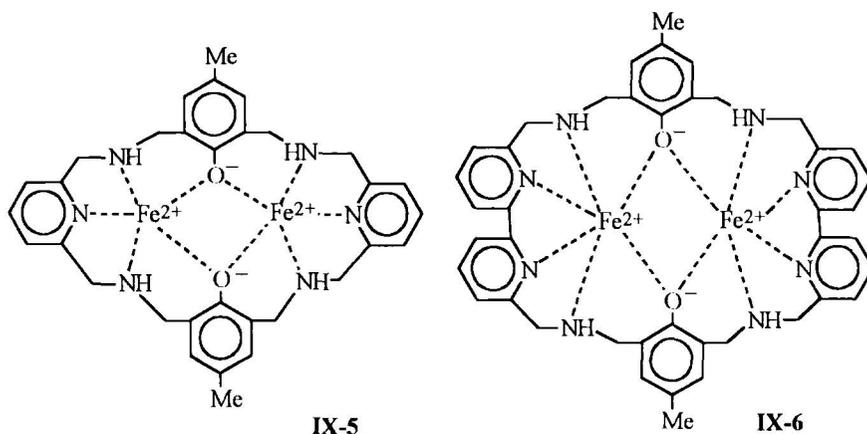
this system is not hydroxyl radicals and proposed that a reduced vanadium species, V(II) or V(III), that was generated by reduction with Zn(0), works as a catalyst for the activation of O₂ and hydroxylation of methane.

Systems Involving Other Reducing Agents

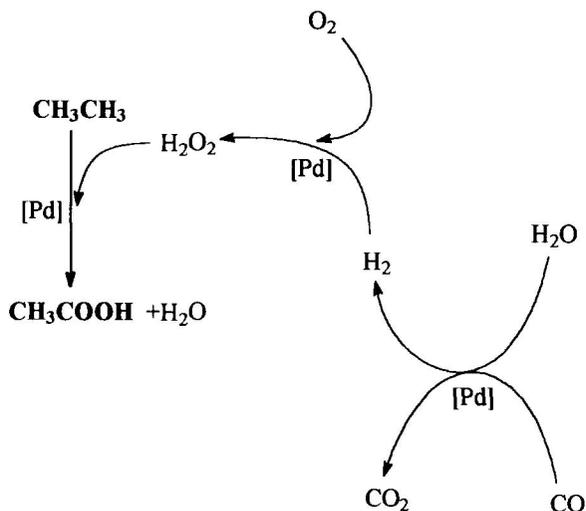
Various other reducing agents have been used in the aerobic coupled oxidations of hydrocarbons. Some examples are presented in Table IX.8.

Table IX.8. Catalytic oxidation of hydrocarbons by dioxygen in the presence of various reducing agents.

Substrates	Products	Reducing agent	Catalyst	Ref.
Alkanes	Alcohols	Hydrazobenzene	Fepy ₄ Cl ₂	57a
Arenes	Phenols	Hydroquinones	Catecholatoiron complex	57b-c
Benzene	Phenol	H ₂	Pd-Ti Silicalites	57d
Alkanes	Alcohol+ketone	H ₂ S	Complexes IX-5 , IX-6	57e



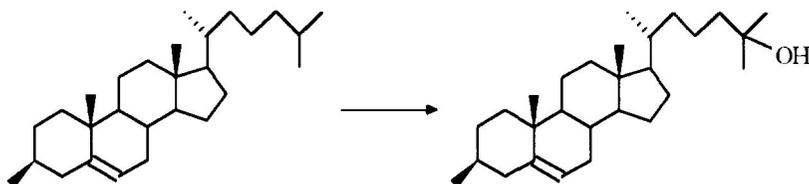
A formal heterogeneous analog of alkane monooxygenases has been described by Lin and Sen [57f]. The system involves a metal catalyst (palladium) and a co-reductant (carbon monoxide). Ethane is transformed into acetic acid at temperatures $< 100\text{ }^{\circ}\text{C}$. The proposed mechanism for this reaction is shown in Scheme IX.6.



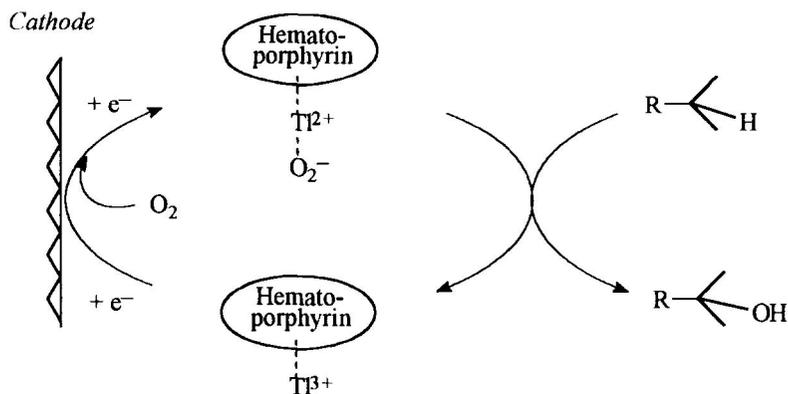
Scheme IX.6. The mechanism proposed for ethane oxidation in the presence of CO.

In some cases, the hydrocarbon oxidation in the presence of a reductant does not need a transition metal complex as catalyst. Thus, a cathode of a carbon whisker has been found to be active for the oxidation of toluene into benzaldehyde and benzyl alcohol during the $\text{H}_2\text{-O}_2$ fuel cell reaction [58a]. During the electrolysis of water at room temperature, the epoxidation of hex-1-ene and hydroxylation of benzene to phenol and hydroquinone occurs simultaneously on the anode and the cathode, respectively [58b]. Finally, selective oxidation of terminal isopropyl groups to the corresponding tertiary alcohols have been carried out by an electrochemical method [58c]. Using the

$\text{Ti}(\text{TFA})_3$ -hematoporphyrin- O_2 -cathode system, cholesterol was converted into the corresponding alcohol:



The authors assumed that Ti^{3+} binds oxygen producing an activated oxygen-like species (Scheme IX.7).



Scheme IX.7. The oxidation of tertiary C-H bonds by the $\text{Ti}(\text{TFA})_3$ -hematoporphyrin- O_2 -cathode system.

IX.3. PHOTOINDUCED METAL-CATALYZED OXIDATION OF HYDROCARBONS BY AIR

A new photochemical catalytic method for the transformation of alkanes and arylalkanes into hydroperoxides has been developed in the recent decade. Iron(III) chloride has been found to be an efficient photocatalyst of alkane

oxidation with atmospheric oxygen [59, 60]. Kinetics of the cyclohexane photooxidation in the presence of a catalytic amount of FeCl_3 as well as some other compounds (see below), are shown in Figure IX. 1 [60g].

Other transition metal chlorides, for example CuCl_2 (Figure IX. 1) [60d,g, 61a,b], AuCl_4^- (Figure IX. 1) [60d,g, 61c,d], PtCl_6^{2-} [60d, 61d,e], and CrCl_3 [61f] also photocatalyze the aerobic oxygenation of alkanes in acetonitrile, methylene chloride or acetic acid (Table IX.9). Methanol ($0.018 \times 10^{-2} \text{ mol dm}^{-3}$) and formaldehyde ($0.17 \times 10^{-2} \text{ mol dm}^{-3}$) were formed upon the slow bubbling of methane and air through a solution of HAuCl_4 in MeCN under irradiation [61c].

Table IX.9. Photocatalytic aerobic oxidation of hydrocarbons in the presence of chloride and bromide metal salts.

Photocatalyst	Substrate	Solvent	Ref.
FeCl_3	Toluene	CH_3COOH	59
FeCl_3 + phenanthroline	Toluene	CH_3COOH	59
FeCl_3	Alkanes, arylalkanes	CH_3CN , CH_3COCH_3	60a
FeCl_3	Alkanes	Alcohols	60e,f
CuCl_2	Alkanes	CH_3CN	60d,g,61a,b
H_2PtCl_6	Cyclohexane	CH_3CN	60d
HAuCl_4	Alkanes, methane	CH_3CN , CH_2Cl_2	60d,61c,d
RhCl_3	Cyclohexane	CH_3CN	60c
RuCl_3	Cyclohexane	CH_3CN	60c
CrCl_3 + $\text{PhCH}_2\text{NEt}_3\text{Cl}$	Alkanes	CH_3CN	61f
FeBr_3	Arylalkanes	CH_3CN	60c
Na_2PtBr_6	Cyclohexane	CH_3CN	60c

The first step of this process is apparently the photoexcitation of the iron chloride species to stimulate homolysis of the Fe–Cl bond [60h]. The chlorine radical (free or in the solvent cage without entering to the solvent) attacks the alkane. The iron(II) derivative that is formed can be oxidized either by molecular oxygen or the alkylperoxy radical (Scheme IX.8).

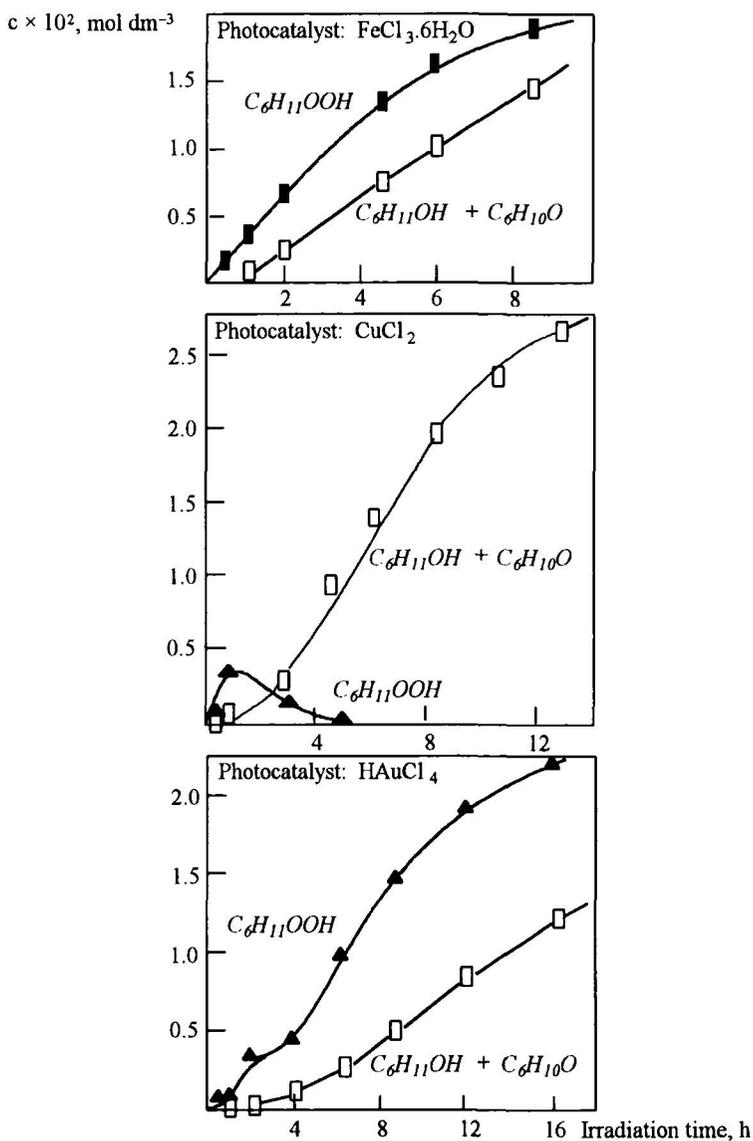
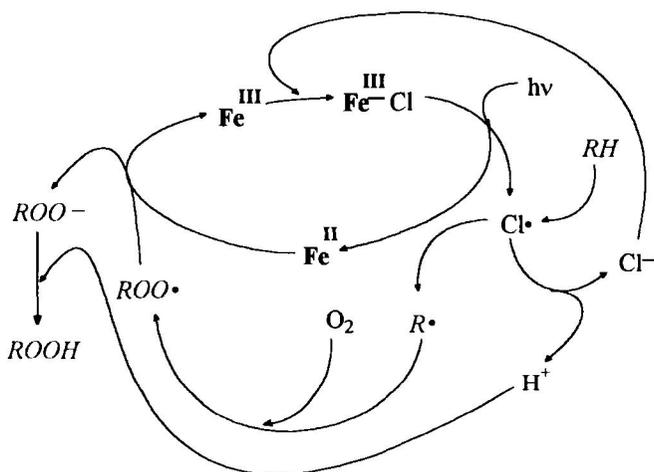
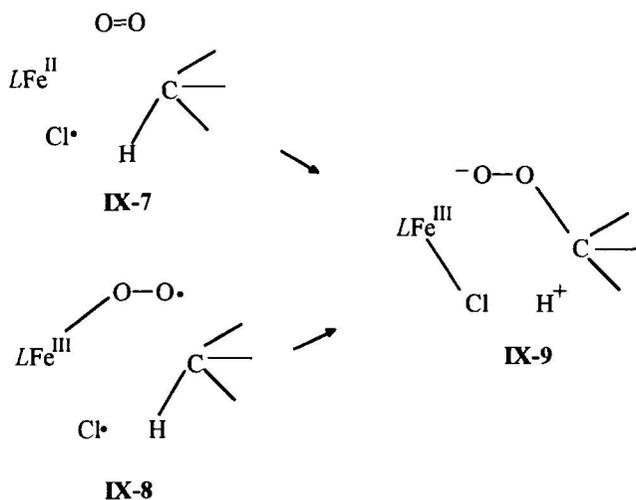


Figure IX.1. The aerobic photooxygenation ($\lambda > 300 \text{ nm}$) of cyclohexane (0.46 mol dm^{-3}) catalyzed by various metal chlorides ($5 \times 10^{-4} \text{ mol dm}^{-3}$) in MeCN at 10°C .



Scheme IX.8. The mechanism proposed for the FeCl_3 -photocatalyzed oxygenation of alkanes, RH , into alkyl hydroperoxides, ROOH .



Scheme IX.9. Possible interactions between photoexcited iron chloride, C-H bond of the alkane and molecular oxygen.

It can be assumed that in one of the possible channels of the alkyl hydroperoxide formation, electron transfer $\text{Cl} \longrightarrow \text{Fe}^{\text{III}}$ and reorganization of bonds occurs within a six-membered structure **IX-7** or **IX-8** (Scheme **IX.9**).

Bromide complexes are also efficient in the photooxidation. However, FeBr_3 photocatalyzes the oxygenation of only alkylbenzenes (Figure IX.2) [60c] and are not effective in the oxidation of alkanes. One can assume that the bromine radical is an active species in this reaction.

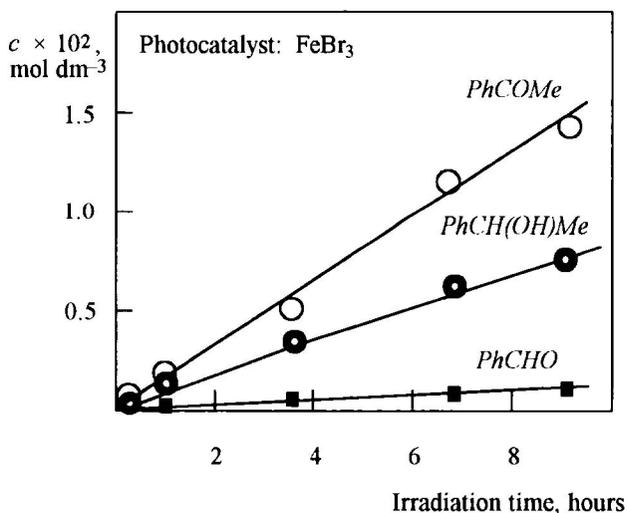


Figure IX.2. Kinetics of aerobic photooxidation ($\lambda > 300 \text{ nm}$) of ethylbenzene (0.41 mol dm^{-3}) in MeCN in the presence of FeBr_3 ($5.0 \times 10^{-4} \text{ mol dm}^{-3}$). The samples were not reduced with PPh_3 before GC analysis.

Kinetics of the photooxidations catalyzed by platinum complexes are shown in Figure IX.3 [60c]. A very long induction period can be noticed in the case of catalysis by PtBr_6^{2-} .

Mechanisms of the photooxygenation reaction in the cases of other than iron metal seems to be different from that postulated for the FeCl_3 -catalyzed process [60h]. Low-valent species are apparently involved in the oxidation. These species can possibly add an oxygen molecule to produce metal peroxo radicals and peroxo

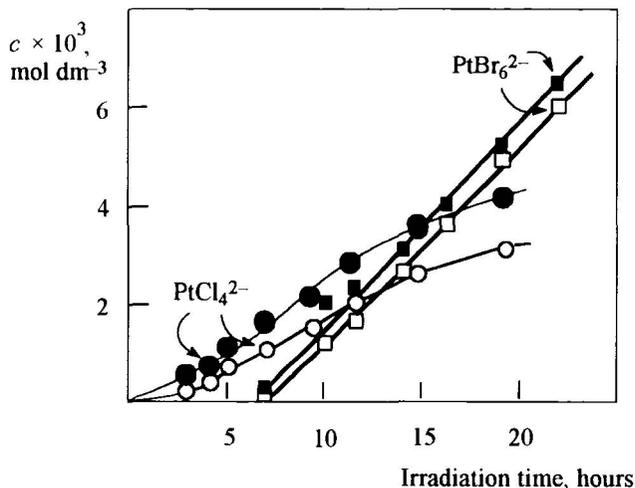
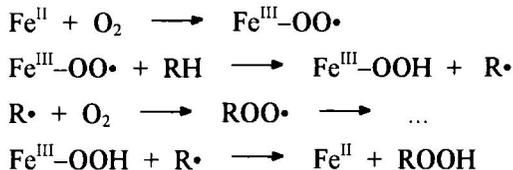


Figure IX.3. Kinetics of aerobic photooxidation ($\lambda > 300$ nm) of cyclohexane (0.46 mol dm^{-3}) in MeCN in the presence of $\text{Na}_2\text{PtCl}_4 \cdot 4\text{H}_2\text{O}$ ($5.0 \times 10^{-4} \text{ mol dm}^{-3}$) (circles) or $\text{Na}_2\text{PtBr}_6 \cdot 6\text{H}_2\text{O}$ ($5.0 \times 10^{-4} \text{ mol dm}^{-3}$) (squares). Concentrations of cyclohexanol (closed symbols) and cyclohexanone (open symbols) determined by GC before the reduction with PPh_3 .

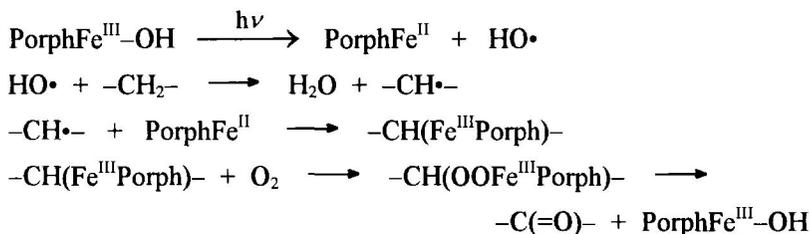
complexes. Such a mechanism has been proposed for the photooxidation of alkanes in acetonitrile in the presence of a catalytic amount of cyclopentadienyliron(II) complexes and bis(arene)iron(II) [62]:



Unlike the oxygenations catalyzed by chloride complexes, the aerobic photooxidation of cyclohexane in the presence of a catalytic system $\text{CrCl}_3\text{-PhCH}_2\text{NEt}_3\text{Cl}$ in MeCN produces the ketone as a main product and only a small

amount of the alcohol [6If], Adding benzene, methylene chloride or ethanol to the cyclohexane solution raises the oxygenation rate and changes the ketone : alcohol ratio. In the presence of a small amount of hydroquinone, the formation rate of cyclohexanone (but not of cyclohexanol) sharply decreases. The kinetic isotope effect in the oxidation of C_6H_{12} and C_6D_{12} is *ca.* 1.0 for cyclohexanol and *ca.* 2.9 for cyclohexanone. Cyclohexanol formation has been assumed to follow a mechanism that does not involve free radicals. Free radicals can participate in the route toward the ketone [6If].

It is interesting that the irradiation of an aqueous cyclohexane emulsion in the presence of an iron(III) salt, e.g. $Fe(ClO_4)_3$, gives rise [63a] also to the formation of cyclohexanone instead of its mixture with cyclohexyl hydroperoxide and cyclohexanol. Likewise, the photooxidation of cycloalkanes by dioxygen catalyzed by the polyhalogenated porphyrinatoiron(III)-hydroxo complex, Porph-Fe-OH, has been reported to produce predominantly cycloalkanones [63b]. The proposed mechanism involves the formation of hydroxyl radicals and an $Fe^{III}-\sigma$ -alkyl complex [63b]:



Examples of "unusual" selectivity in alkane oxygenation (when a ketone is a predominant product) have been discussed above (Gif-type systems) and will be given below when describing alkane ketonization with peroxides and dioxygen. Another photooxidation of alkanes catalyzed by Fe(III)- or Mn(III)-porphyrin occurs in the presence of a reducing agent (triethanolamine) and photosensitizer and gives rise to the "usual" formation of a mixture of alcohol and ketone (the ratio is in the region 0.8–2.7) [63c]. The photocatalytic oxygenation of alkenes with dioxygen and porphyrinatoiron(III) complexes, which affords allylic oxygenation products and/or epoxides, has been proposed to involve the oxoiron(IV) complex, $\text{PorphFe}^{IV}=\text{O}$, as the catalytically active

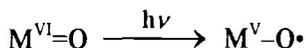
species. This species abstracts an allylic hydrogen atom to initiate autoxidation and "direct" oxygen-transfer reactions [63d]. For other oxygenation reactions by photoexcited iron porphyrins see in refs. [63e,f].

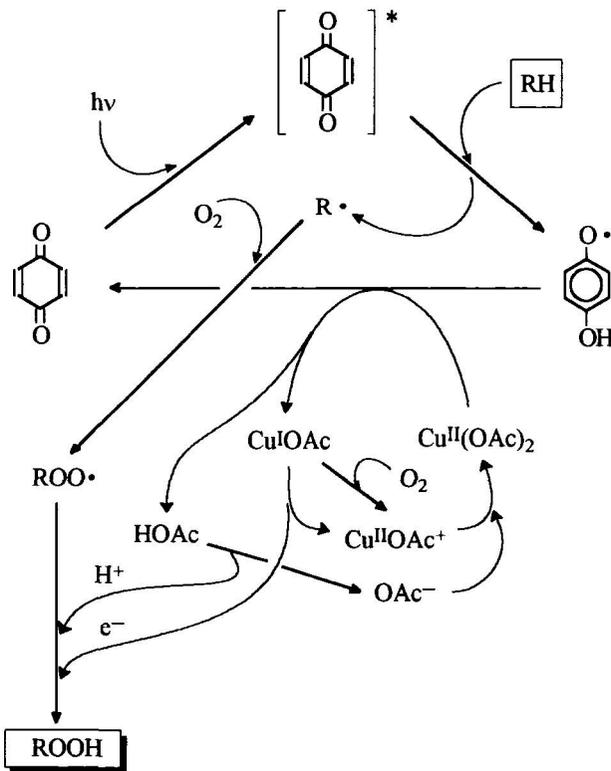
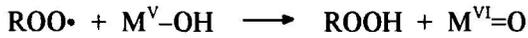
Some other transition metal complexes, e.g., trifluoroacetates of palladium and copper [64a], some platinum derivatives [64b], are known to promote aerobic alkane photooxidation. Mechanisms of these transformations are not clear in detail.

The irradiation of an alkane solution in acetonitrile with visible light in the presence of catalytic amounts of quinone and copper(II) acetate gives rise to the formation of almost pure alkyl hydroperoxide which is decomposed only very slowly under these conditions to produce the ketone and alcohol [64c,d]. It has been proposed [64d] that the first step of the reaction is a hydrogen atom abstraction from the alkane, RH, by a photoexcited quinone species to generate the alkyl radical $R\cdot$ and semiquinone. The former is rapidly transformed into $ROO\cdot$ and then alkyl hydroperoxide, while the latter is reoxidized by Cu(II) into the initial quinone (Scheme IX. 10).

Alkanes and arylalkanes can be transformed into alkyl hydroperoxides as well as ketones and alcohols if their solutions are irradiated in the presence of catalytic amounts of metal oxo complexes. These complexes are heteropolymetalates in methylene chloride [65a], acetic acid, alcohols, acetone, acetonitrile [65b,c], polyoxotungstate $W_{10}O_{32}^{4-}$ in acetonitrile [65d-f] or water [65g] (Table IX. 10). Oxo compounds such as $K_2Cr_2O_7$ in the two-phase solvent water-1,2-dichloroethane [66a], CrO_3 [23], complexes $(n-Bu_4N)_2Cr_2O_7$ ($n-Bu_4N$) $_2Cr_3O_{10}$ and $(n-Bu_4N)Cr_4O_{13}$ [66b], and UO_2Cl_2 [66c] also catalyze the photooxygenation of alkanes. Photooxygenation of alkanes catalyzed by molybdenum or tungsten carbonyl begins apparently from the transformation of the carbonyl into an active oxo species [66d,e]. Some other chromium and vanadium complexes have been reported to be catalysts of alkane photooxidation [66f-j].

The mechanism of aerobic alkane photooxidation catalyzed by metal oxo complexes includes the formation of a photoexcited species which is capable of abstracting a hydrogen atom from an alkane. The alkyl radical thus formed rapidly adds a molecule of oxygen. An alkyl hydroperoxide is partially decomposed to produce a ketone and an alcohol:



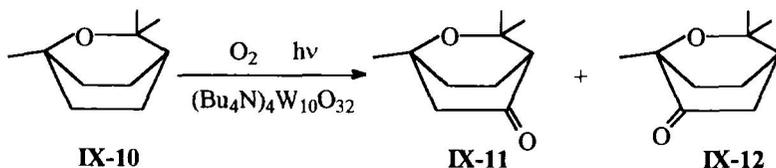


Scheme IX.10. Selective aerobic photochemical alkane hydroperoxidation catalyzed by the system "quinone-copper(II) acetate".

Table IX.10. Photocatalytic aerobic oxidation of hydrocarbons in the presence of metal oxo complexes.

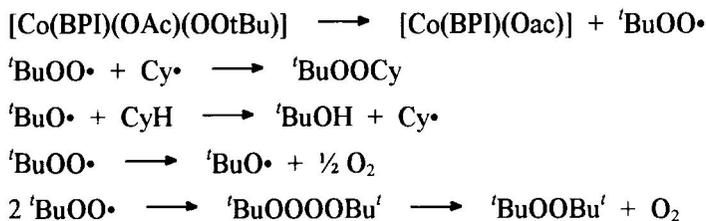
Photocatalyst	Substrate	Solvent	Ref.
CrO ₃ + picolinic acid	Ethylbenzene	CH ₃ CN	23
Oxometalate (NaVO ₃ , H ₃ PW ₁₂ O ₄₀ , Na ₆ V ₁₀ O ₂₈ , Na ₅ H ₇ Mo ₆ V ₅ O ₃₉ , H ₃ PMo ₁₂ O ₄₀ , H ₄ SiMo ₁₂ O ₄₀) + PhCH ₂ NEt ₃ Cl	Cyclohexane	CH ₂ Cl ₂	65a
PW ₁₂ O ₄₀ ³⁻ , PMo ₁₁ VO ₄₀ ⁴⁻ , PMo ₆ V ₅ O ₃₉ ¹²⁻	Alkylbenzenes	CH ₃ COOH, Me ₂ CHOH, CH ₃ OH, CH ₃ COCH ₃ , C ₂ H ₅ OH	65b
(ⁿ Bu ₄ N)W ₁₀ O ₃₂	Cyclohexane	CH ₃ CN+CH ₂ Cl ₂	65f
K ₂ Cr ₂ O ₇ + ⁿ Bu ₄ NBr	Toluene	CH ₂ Cl ₂ -H ₂ O	66a
(ⁿ Bu ₄ N)Cr ₄ O ₁₃	Cyclohexane	CH ₃ CN, CH ₂ Cl ₂	66b
UO ₂ Cl ₂	Alkylbenzenes, alkanes	CH ₃ COOH, CH ₃ CN	66c

Oxidation photocatalyzed by polyoxometalates [66k] has been applied to the functionalization of 1,8-cineole (structure **IX-10**) [66l], widely distributed in the plant kingdom. The photooxygenation of **IX-10** gave a mixture of ketones and alcohols which were transformed by the subsequent action of pyridinium chlorochromate into 5- and 6-keto derivatives in the ratio **IX-11** : **IX-12** = 2.5 : 1. A laser flash photolysis study of the mechanism has been carried out for the decay-state anion catalyzed reaction [66m].



* ————— *

Cobalt(III)-alkylperoxy complexes also promote photooxidation of alkanes [67a]. Irradiation causes homolysis of the Co-O bond of the Co-O-O-Bu' moieties in these complexes to generate ${}^{\bullet}\text{BuOO}$ radicals. Both ${}^{\bullet}\text{BuOO}$ and ${}^{\bullet}\text{BuO}$ are responsible for the oxidation of the C-H bonds:

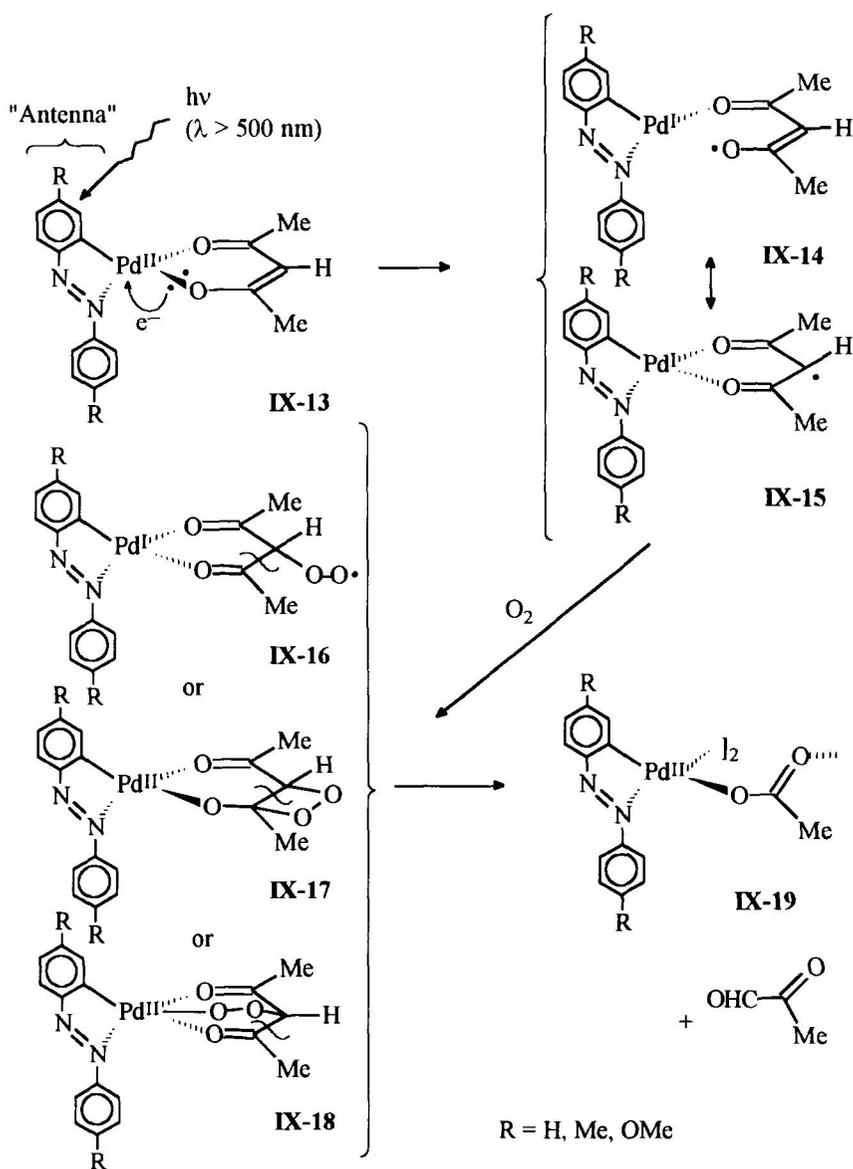


Here BPI is 1,3-bis(2'-pyridylimino)isoindoline, CyH is cyclohexane. Stable final products are formed according to the equations:



Thermal aliphatic C-H bond oxygenation has been achieved by Co(II)-peroxo species [67b]. This oxygenation may proceed via homolysis of the O-O bond of the Co(II)-peroxo species.

Finally, orthometalated (aryloxy)aryl(acetylacetonato)palladium(II) complexes, **IX-13**, can be oxidized by atmospheric oxygen to give the corresponding acetato derivatives, **IX-19**, upon irradiation of their acetone solutions with even long-wavelength visible ($\lambda > 500$ nm) light [68]. The proposed mechanism (Scheme IX.11) includes the light absorption by the arylazo chromophore ("antenna") in complexes **IX-13**. Light energy absorbed by the transition of the azobenzene fragment is intramolecularly transferred to the metal center. The excited palladium ion is capable of promoting electron transfer from an acetylacetonate ligand to produce structures **IX-14** or **IX-15** and the radical-like acetylacetonyl fragment in **IX-15** reacts rapidly with the molecular oxygen present in the solvent to give peroxides **IX-16**, or/and **IX-17**, or/and **IX-18**. These peroxides decompose through C-C and O-O bond cleavage, affording complexes **IX-19**.



Scheme IX.11. The mechanism proposed for the photochemical C-C bond splitting under the action of dioxigen.

References for Chapter IX

- (a) Sheldon, R. A.; Kochi, J. K. *Metal-Catalysed Oxidations of Organic Compounds*; Academic Press: New York, 1981. (b) *Oxygen Complexes and Oxygen Activation by Transition Metals*; Martell, A. E., Sawyer, D. T., Eds.; Plenum Press: New York, 1988. (c) *New Developments in Selective Oxidation*; Centi, G., Trifiro, F., Eds.; Elsevier: Amsterdam, 1990. (d) Sawyer, D. T. *Oxygen Chemistry*; Oxford University Press: Oxford, 1991. (e) *Dioxygen Activation and Homogeneous Catalytic Oxidation*; Simándi, L. I., Ed.; Elsevier: Amsterdam, 1991. (f) Drago, R. S. *Coord. Chem. Rev.* **1992**, *117*, 185. (g) *Catalytic Selective Oxidation*; Oyama, S. T.; Hightower, J. W., Eds.; ACS: Washington, 1993. (h) *The Activation of Dioxygen and Homogeneous Catalytic Oxidation*; Barton, D. H. R.; Martell, A. E., Sawyer, D. T., Eds.; Plenum Press: New York, 1993. (i) Sychev, A. Ya.; Isak, V. G. *Usp. Khim.* **1995**, *64*, 1183 (in Russian), (j) Hobbs, C. C., Jr. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B.; Herrmann, W. A., Eds.; VCH: Weinheim, 1996, p. 521. (k) Schiraldi, D. A. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B.; Herrmann, W. A., Eds.; VCH: Weinheim, 1996, p. 541. (l) *Catalytic Activation and Functionalisation of Light Alkanes*; Derouane, E. G.; Haber, J.; Lemos, F.; Ribeiro, F. R.; Guisnet, M., Eds.; Kluwer Acad. Publ.: Dordrecht, 1998. (m) Sheldon, R. A.; Arends, I. W. C. E.; Lempers, H. E. B. *Catalysis Today* **1998**, *41*, 387.
- (a) Perkel', A. L.; Voronina, S. G.; Freidin, B. G. *Usp. Khim.* **1994**, *63*, 793 (in Russian), (b) Tanaka, K. *CHEMTECH* **1974**, 555.
- (a) Igarashi, J.; Luszytk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 7719. (b) Igarashi, J.; Jensen, R. K.; Luszytk, J.; Korcek, S.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 7727. (c) Goosen, A.; McClelland, C. W.; Morgan, D. H.; O'Connell, J. S.; Ramplin, A. *J. Chem. Soc., Chem. Commun.* **1993**, 401.
- Denisov, E. T.; Khudyakov, I. V. *Chem. Rev.* **1987**, *87*, 1313.
- (a) Hsu, Y. F.; Yen, M. H.; Cheng, C. P. *J. Mol. Catal. A: Chem.* **1996**, *705*, 137. (b) Hsu, Y. F.; Cheng, C. P. *J. Mol. Catal. A: Chem.* **1997**, *720*, 109.
- (a) Emanuel, N. M.; Denisov, E. T.; Maizus, Z. K. *Liquid-Phase Oxidation of Hydrocarbons*; Plenum Press: New York, 1967. (b) Vanoppen, D. L.; De Vos, D. E.; Genet, M. J.; Rouxhet, P. G.; Jacobs, P. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 560. (c) Maschmeyer, T.; Oldroyd, R. D.; Sankar, G.; Thomas, J. M.; Shannon, I. J.; Klepetko, J. A.; Masters, A. F.; Beattie, J. K.; Catlow, C. R. A.

- Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1639. (d) Csanyi, L. J.; Jaky, K. *J. Mol. Catal. A: Chem.* **1997**, *720*, 125. (e) Tugaut, V.; Pellegrini, S.; Castanet, Y.; Mortreux, A. *J. Mol. Catal. A: Chem.* **1997**, *127*, 25.
7. Haber, F.; Willstater, R. *Ber.* **1931**, *64B*, 2844.
 8. Maizus, Z. K.; Skibida, I. P.; Gagarina, A. B. *Zh. Fiz. Khim.* **1975**, *49*, 2491 (in Russian).
 9. (a) Bawn, C. E. K; Jolley, J. *Proc. Roy. Soc.* **1956**, *237A*, 297. (b) Bawn, C. E. H. *Disc. Faraday Soc.* **1953**, *14*, 181.
 10. Barton, D. H. R.; Delanghe, N. C. *Tetrahedron Lett.* **1997**, *36*, 6351.
 11. Haber, F.; Weiss, J. *Naturwiss.* **1932**, *20*, 948.
 12. Kharash, M. S.; Arimoto, F. S.; Nudenberg, W. *J. Org. Chem.* **1951**, *16*, 1556.
 13. Walling, C. *J. Am. Chem. Soc.* **1969**, *91*, 7590.
 14. (a) Kozlova, Z. G.; Tsepalov, V. F.; Shlyapintokh, V. Ya. *Kinet. Katal.* **1964**, *5*, 868 (in Russian), (b) Zakharov, I. V.; Shlyapintokh, V. Ya. *Kinet. Katal.* **1963**, *4*, 706 (in Russian).
 15. Skibida, I. P. *Usp. Khim.* **1975**, *54*, 1729 (in Russian).
 16. (a) Chavez, F. A.; Rowland, J. M.; Olmstead, M. M.; Mascharak, P. K. *J. Am. Chem. Soc.* **1998**, *120*, 9015. (b) Babushkin, D. E.; Talsi, E. P. *J. Mol. Catal. A: Chem.* **1998**, *130*, 131. (c) Bakac, A. *J. Am. Chem. Soc.* **1997**, *119*, 10726. (d) Kamiya, Y.; Kashima, M. *J. Catal.* **1972**, *25*, 326.
 17. (a) Onopchenko, A.; Schultz, J. G. D. *J. Org. Chem.* **1973**, *38*, 909. (b) Onopchenko, A.; Schultz, J. G. D. *J. Org. Chem.* **1973**, *38*, 3727.
 18. Hanotier, J.; Camerman, P.; Hanotier-Bridoux, M.; de Radzitzsky, P. *J. Chem. Soc., Perkin Trans. 2* **1972**, 2247.
 19. (a) Fischer, R. W.; Rohrscheid, F. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B.; Hermann, W. A., Eds.; VCH: Weinheim, 1996, p. 439. (b) Zakharov, I. V. *Kinet. Katal.* **1974**, *15*, 1457 (in Russian), (c) Felzenstein, A.; Goosen, A.; Marsh, C.; McClelland, C. W.; van Sandwyk, K. S. *S. Afr. J. Chem.* **1989**, *42*, 143. (d) Haruštiak, M.; Hronec, M.; Ilavský, J. *J. Mol. Catal.* **1989**, *53*, 209. (e) Dugmore, G. M.; Powels, G. J.; Zeelie, B. *J. Mol. Catal. A: Chem.* **1995**, *99*, 1. (f) Gomez, M. F. T.; Antunes, O. A. C. *J. Mol. Catal. A: Chem.* **1997**, *121*, 145.
 20. Zakharov, I. V.; Geletii, Yu. V. *Neftekhimiya* **1978**, *18*, 615 (in Russian).
 21. Goldstein, A. S.; Drago, R. S. *Inorg. Chem.* **1991**, *30*, 4506.

22. (a) Li, P.; Alper, H. *J. Mol. Catal.* **1990**, *61*, 51. (b) Alper, H.; Harustiak, M. *J. Mol. Catal.* **1993**, *84*, 87. (c) Lyons, J. E.; Ellis, P. E., Jr.; Shaikh, S. N. *Inorg. Chim. Acta* **1998**, *270*, 162.
23. Shul'pin, G. B.; Druzhinina, A. N. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1989**, *38*, 1079.
24. Karakhanov, E. A.; Kardasheva, Yu. S.; Maksimov, A. L.; Predeina, V. V.; Runova, E. A.; Utukin, A. M. *J. Mol. Catal. A: Chem.* **1996**, *107*, 235.
25. Gusevskaya, E.; Gonsalves, J. A. *J. Mol. Catal. A: Chem.* **1997**, *727*, 131.
26. (a) Taqui Khan, M. M.; Shukla, R. S. *J. Mol. Catal.* **1988**, *44*, 85. (b) Taqui Khan, M. M.; Bajaj, H. C.; Shukla, R. S.; Mirza, S. A. *J. Mol. Catal.* **1988**, *45*, 51.
27. (a) Qian, C.-Y.; Yamada, T.; Nishino, H.; Kurosawa, K. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1371. (b) Qian, C.-Y.; Nishino, H.; Kurosawa, K.; Korp, J. D. *J. Org. Chem.* **1993**, *58*, 4448.
28. (a) Altamsani, A.; Brégeault, J.-M. *Synthesis* **1993**, 79. (b) Kirihara, M.; Takizawa, S.; Momose, T. *J. Chem. Soc., Perkin Tram. 1* **1998**, 7.
29. Shimizu, M.; Watanabe, Y.; Orita, H.; Hayakawa, T.; Takehira, K. *Tetrahedron Lett.* **1991**, *32*, 2053.
30. (a) Ellis, P. E., Jr.; Lyons, J. E. *Coord. Chem. Rev.* **1990**, *105*, 181. (b) Lyons, J. E.; Ellis, P. E., Jr. *Catalysis Lett.* **1991**, *8*, 45. (c) Chen, H. L.; Ellis, P. E., Jr.; Wijesekera, T.; Hagan, T. E.; Groh, S. E.; Lyons, J. E.; Ridge, D. P. *J. Am. Chem. Soc.* **1994**, *116*, 1086. (d) Grinstaff, M. W.; Hill, M. G.; Labinger, J. A.; Gray, H. B. *Science* **1994**, *264*, 1311. (e) Huang, J.-W.; Liu, Z.-L.; Gao, X.-R.; Yang, D.; Peng, X.-Y.; Ji, L.-N. *J. Mol. Catal. A: Chem.* **1996**, *111*, 261. (f) Ellis, P. E., Jr.; Wijesekera, T.; Lyons, J. E. *Catalysis Lett.* **1996**, *36*, 69. (g) Böttcher, A.; Birnbaum, E. R.; Day, M. W.; Gray, H. B.; Grinstaff, M. W.; Labinger, J. A. *J. Mol. Catal. A: Chem.* **1997**, *117*, 229. (h) Moore, K. T.; Horvath, I. T.; Therien, M. J. *J. Am. Chem. Soc.* **1997**, *119*, 1791. (i) Bianchini, C. *Chemtracts-Inorg. Chem.* **1997**, 588. (j) Nenoff, T. M.; Showalter, M. C.; Salaz, K. A. *J. Mol. Catal. A: Chem.* **1997**, *121*, 123.
31. (a) Birnbaum, E. R.; Grinstaff, M. W.; Labinger, J. A.; Bercaw, J. E.; Gray, H. B. *J. Mol. Catal. A: Chem.* **1995**, *04*, LI 19. (b) Birnbaum, E. R.; Labinger, J. A.; Bercaw, J. E.; Gray, H. B. *Inorg. Chim. Acta* **1998**, *270*, 433.
32. (a) Mizuno, N.; Nozaki, C.; Hirose, T.; Tateishi, M.; Iwamoto, M. *J. Mol. Catal. A: Chem.* **1997**, *117*, 159. (b) Mizuno, N.; Tateishi, M.; Hirose, T.;

- Iwamoto, M. *Chem. Lett.* **1993**, 2137. (c) Mizuno, N.; Hirose, T.; Tateishi, M.; Iwamoto, M. *J. Mol. Catal.* **1994**, *88*, L125. (d) Neumann, R.; Levin, M. *J. Am. Chem. Soc.* **1992**, *114*, 7278. (e) Neumann, R.; Dahan, M. *J. Chem. Soc., Chem. Commun.* **1995**, 171. (f) Fujibayashi, S.; Nakayama, K.; Hamamoto, M.; Sakaguchi, S.; Nishiyama, Y. Ishii, Y. *J. Mol. Catal. A: Chem.* **1996**, *110*, 105. (g) Hanyu, A.; Sakurai, Y.; Fujibayashi, S.; Ishii, Y. *Tetrahedron Lett.* **1997**, *38*, 5659.
33. Ishii, Y. *J. Mol. Catal. A: Chem.* **1997**, *117*, 123.
34. (a) Ishii, Y.; Kato, S.; Iwahama, T.; Sakaguchi, S. *Tetrahedron Lett.* **1996**, *37*, 4993. (b) Ishii, Y.; Iwahama, T.; Sakaguchi, S.; Nakayama, K.; Nishiyama, Y. *J. Org. Chem.* **1996**, *61*, 4520. (c) Yoshino, Y.; Hayashi, Y.; Iwahama, T.; Sakaguchi, S.; Ishii, Y. *J. Org. Chem.* **1997**, *62*, 6810. (d) Sakaguchi, S.; Kato, S.; Iwahama, T.; Ishii, Y. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1237. (e) Iwahama, T.; Syqjiyo, K.; Sakaguchi, S.; Ishii, Y. *Org. Proc. Res. & Dev.* **1998**, *2*, 255.
35. (a) Ishii, Y.; Nakayama, K.; Takeno, M.; Sakaguchi, S.; Iwahama, T.; Nishiyama, Y. *J. Org. Chem.* **1995**, *60*, 3934. (b) Sakaguchi, S.; Eikawa, M.; Ishii, Y. *Tetrahedron Lett.* **1997**, *38*, 7075. (c) Kato, S.; Iwahama, T.; Sakaguchi, S.; Ishii, Y. *J. Org. Chem.* **1998**, *63*, 222.
36. Seo, Y.-J.; Mukai, Y.; Tagawa, T.; Goto, S. *J. Mol. Catal. A: Chem.* **1997**, *120*, 149.
37. (a) Ito, S.; Yamasaki, T.; Okada, H.; Okino, S.; Sasaki, K. *J. Chem. Soc., Perkin Trans. 2* **1988**, 285. (b) Kitano, T.; Kuroda, Y.; Itoh, A.; Li-Fen, J.; Kunai, A.; Sasaki, K. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1991.
38. (a) Jintoku, T.; Takaki, K.; Fujiwara, Y.; Fuchita, Y.; Hiraki, K. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 438. (b) Jintoku, T.; Nishimura, K.; Takaki, K.; Fujiwara, Y. *Chem. Lett.* **1990**, 1687.
39. Bolzacchini, E.; Canevali, C.; Morazzoni, F.; Orlandi, M.; Rindone, B.; Scotti, R. *J. Chem. Soc., Dalton Trans.* **1997**, 4695.
40. (a) Schonbein, C. F. *Ber. Natur. Ges. Bas.* **1844**, *6*, 16. (b) Schonbein, C. F. *J. Prakt. Chem.* **1852**, *55*, 1.
41. Shilov, N. A. *On the Coupled Oxidation Reactions*, Moscow, 1905 (in Russian).
42. (a) Manchot, W.; Wilhelms, O. *Ber.* **1901**, *34*, 2479. (b) Manchot, W. *Ann.* **1902**, *325*, 93.
43. (a) Bach, A. *Zh. Ross. Fiz.-Khim. Obsch.* **1897**, *29*, 25 (in Russian), (b) Engler, C.; Wild, W. *Ber.* **1897**, *12*, 1669.
44. Udenfriend, S.; Clark, C. T.; Axelrod, J.; Brodie, B. B. *J. Biol. Chem.* **1954**, *208*, 731.

45. Hamilton, G. A.; *J. Am. Chem. Soc.* **1964**, *86*, 3391.
46. (a) Ullrich, V.; Staudinger, H. *Z. Naturforsch.* **1969**, *24b*, 583. (b) Ullrich, V.; *Z. Naturforsch.* **1969**, *24b*, 699.
47. (a) Muradov, N. Z.; Shilov, A. E.; Shteinman, A. A. *Kinet. Katal.* **1972**, *13*, 1357 (in Russian). (b) Karasevich, E. I.; Muradov, N. Z.; Shteinman, A. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1974**, 1805 (in Russian), (c) Muradov, N. Z.; Shteinman, A. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1975**, 2294 (in Russian).
48. Denisov, E. T. *Liquid-Phase Reaction Rate Constants*, Plenum Press: New York, 1974, p. 771.
49. (a) Kutner, E. A.; Matseevskiy, B. P. *Kinet. Katal.* **1969**, *10*, 997 (in Russian). (b) Mimoun, H.; Seree de Roch, I. *Tetrahedron*, **1975**, *31*, 777. (c) Lavrushko, V. V.; Khenkin, A. M.; Shilov, A. E. *Kinet. Katal.* **1980**, *21*, 276 (in Russian). (d) Zakharov, I. V.; Karasevich, E. I.; Shilov, A. E.; Shteinman, A. A. *Kinet. Katal.* **1975**, *16*, 1151 (in Russian), (e) Geletiy, Yu. V.; Zakharov, I. V.; Karasevich, E. I.; Shteinman, A. A. *Kinet. Katal.* **1979**, *20*, 1124 (in Russian).
50. (a) Barton, D. H. R.; Doller, D. *Ace. Chem. Res.* **1992**, *25*, 504. (b) Barton, D. H. R.; Taylor, D. K. *Russ. Chem. Bull.* **1995**, *44*, 575. (c) Barton, D. H. R. *Tetrahedron* **1998**, *54*, 5805. (d) Perkins, M. J. *Chem. Soc. Rev.* **1996**, 229. (e) Barton, D. H. R. *Chem. Soc. Rev.* **1996**, 237.
51. Barton, D. H. R., Gastiger, M. J.; Motherwell, W. B. *J. Chem. Soc., Chem. Commun.* **1983**, 41.
52. (a) Barton, D. H. R.; Bévière, S. D.; Chavasiri, W.; Csuhai, E.; Doller, D.; Liu, W.-G. *J. Am. Chem. Soc.* **1992**, *114*, 2147. (b) Barton, D. H. R.; Beviere, S. D.; Chavasiri, W.; Csuhai, E.; Doller, D. *Tetrahedron* **1992**, *48*, 2895. (c) Barton, D. H. R.; Csuhai, E.; Doller, D. *Tetrahedron* **1992**, *48*, 9195. (d) Barton, D. H. R.; Beviere, S. D.; Chavasiri, W.; Doller, D.; Hu, B. *Tetrahedron Lett.* **1993**, *34*, 567. (e) Barton, D. H. R.; Chavasiri, W.; Hill, D. R.; Hu, B. *New J. Chem.* **1994**, *18*, 611. (f) Barton, D. H. R.; Hill, D. R. *Tetrahedron Lett.* **1994**, *35*, 1431. (g) Barton, D. H. R.; Chabot, B. M.; Delanghe, N. C.; Hu, B.; Le Gloahec, V. N.; Wahl, R. U. R. *Tetrahedron Lett.* **1995**, *36*, 7007. (i) Barton, D. H. R.; Hu, B.; Wahl, R. U. R.; Taylor, D. K. *New J. Chem.* **1996**, *20*, 121. (j) Barton, D. H. R.; Beck, A. H.; Delanghe, N. C. *Tetrahedron Lett.* **1996**, *37*, 1555. (k) Barton, D. H. R.; Chabot, B. M.; Hu, B. *Tetrahedron Lett.* **1996**, *37*, 1755. (l) Barton, D. H. R.; Delanghe, N. C. *Tetrahedron Lett.* **1996**, *37*, 8137. (m) Barton, D. H. R.; Hu, B.; Li, T.; MacKinnon, J. *Tetrahedron Lett.* **1996**, *37*, 8329. (n) Barton, D. H. R.; Hu, B.; Taylor, D. K.; Wahl, R. U. R. *J. Chem. Soc.,*

- Perkin Trans. 2* **1996**, 1031. (o) Barton, D. H. R.; Chabot, B. M. *Tetrahedron* **1996**, *52*, 10287. (p) Barton, D. H. R.; Chabot, B. M.; Hu, B. *Tetrahedron* **1996**, *31*, 10301. (q) Barton, D. H. R.; Hu, B. *Tetrahedron* **1996**, *31*, 10313. (r) Barton, D. H. R.; Li, T.; MacKinnon, J. *Chem. Comm.* **1997**, 557. (s) Barton, D. H. R.; Delanghe, N. C. *Tetrahedron* **1998**, *54*, 4471. (t) Barton, D. H. R.; Li, T. *Chem. Comm.* **1998**, 821.
53. (a) Schuchardt, U.; Mano, V. In *New Developments in Selective Oxidation*; Centi, G., Trifiro, F., Eds.; Elsevier: Amsterdam, 1990, p. 185. (b) Schuchardt, U.; Krahembuhl, C. E. Z.; Carvalho, W. A. *New J. Chem.* **1991**, *15*, 955. (c) Shul'pin, G. B.; Kitaygorodskiy, A. N. *J. Gen. Chem. USSR* **1990**, *60*, 920. (d) Knight, C.; Perkins, M. J. *J. Chem. Soc., Chem. Commun.* **1991**, 925. (e) Schuchardt, U.; Carvalho, W. A.; Spinace, E. V. *Synlett* **1993**, 713. (f) Minisci, F.; Fontana, F.; Araneo, S.; Recupero, F. *J. Chem. Soc., Chem. Commun.* **1994**, 1823. (g) Minisci, F.; Fontana, F. *Tetrahedron Lett.* **1994**, *35*, 1427. (h) Minisci, F.; Fontana, F.; Zhao, L.; Banfi, S.; Quici, S. *Tetrahedron Lett.* **1994**, *35*, 8033. (i) Newcomb, M.; Simakov, P.A.; Park, S.-U. *Tetrahedron Lett.* **1996**, *37*, 819. (j) Sobolev, A. P.; Babushkin, D. E.; Shubin, A. A.; Talsi, E. P. *J. Mol. Catal. A: Chem.* **1996**, *112*, 253. (k) Singh, B.; Long, J. R.; Papaefthymiou, G. C.; Stavropoulos, P. *J. Am. Chem. Soc.* **1996**, *118*, 5824.
54. Mukaiyama, T.; Yamada, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 17.
55. (a) Murahashi, S.; Oda, Y.; Naota, T. *J. Am. Chem. Soc.* **1992**, *114*, 7913. (b) Murahashi, S.; Oda, Y.; Naota, T.; Komiya, N. *J. Chem. Soc., Chem. Commun.* **1993**, 139. (c) Hata, E.; Takai, T.; Yamada, T.; Mukaiyama, T. *Chemistry Lett.* **1994**, 1849. (d) Murahashi, S.; Naota, T.; Komiya, N. *Tetrahedron Lett.* **1995**, *36*, 8059. (e) Punniyamurthy, T.; Karla, S. J. S.; Iqbal, J. *Tetrahedron Lett.* **1995**, *36*, 8497. (f) Battioni, P.; Iwanejko, R.; Mansuy, D.; Mlodnicka, T.; Poltowicz, J.; Sanches, F. *J. Mol. Catal. A: Chem.* **1996**, *109*, 91. (g) Komiya, N.; Naota, T.; Murahashi, S.; *Tetrahedron Lett.* **1996**, *37*, 1633. (h) Fujibayashi, S.; Nakayama, K.; Hamamoto, M.; Sakaguchi, S.; Nishiyama, Y.; Ishii, Y. *J. Mol. Catal. A: Chem.* **1996**, *110*, 105. (i) Komiya, N.; Naota, T.; Oda, Y.; Murahashi, S. *J. Mol. Catal. A: Chem.* **1997**, *117*, 21. (j) Chand, D. K.; Bharadwaj, P. K. *Inorg. Chem.* **1997**, *36*, 5658. (k) Dell'Anna, M. M.; Mastrorilli, P.; Nobile, C. F. *J. Mol. Catal. A: Chem.* **1998**, *130*, 65. (l) Lindsay Smith, J. R.; Shul'pin, G. B. *Russ. Chem. Bull.* **1998**, *47*, 2313. (m) Kaneda, K.; Haruna, S.; Imanaka, T.; Kawamoto, K. *J. Chem. Soc., Chem. Commun.* **1990**, 1467.

56. (a) Duprat, A. F.; Capdevielle, P.; Maumy, M. *J. Chem. Soc., Chem. Commun.* **1991**, 464. (b) Kurusu, Y.; Neckers, D. C. *J. Org. Chem.* **1991**, *56*, 1981. (c) Kitajima, N.; Ito, M.; Fukui, H.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 102. (d) Belova, V. S.; Gimanova, I. M.; Stepanova, M. L.; Khenkin, A. M.; Shilov, A. E. *Dokl. Akad. Nauk SSSR* **1991**, *316*, 653 (in Russian). (e) Belova, V. S.; Khenkin, A. M.; Postnov, V. N.; Prusakov, V. E.; Shilov, A. E.; Stepanova, M. L. *Mendeleev Commun.* **1992**, *7*. (f) Lu, W. Y.; Bartoli, J. F.; Battioni, P.; Mansuy, D. *New J. Chem.* **1992**, *16*, 621. (g) Yamanaka, I.; Otsuka, K. *J. Mol. Catal.* **1993**, *83*, L15. (h) Yamanaka, I.; Otsuka, K. *J. Mol. Catal. A: Chem.* **1995**, *95*, 115. (i) Yamanaka, I.; Akimoto, T.; Otsuka, K. *Chemistry Lett.* **1994**, 1511. (j) Yamanaka, I.; Akimoto, T.; Nakagaki, K.; Otsuka, K. *J. Mol. Catal. A: Chem.* **1996**, *110*, 119. (k) Yamanaka, I.; Nakagaki, K.; Akimoto, T.; Otsuka, K. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2511. (l) Yamanaka, I.; Soma, M.; Otsuka, K. *J. Chem. Soc., Chem. Commun.* **1995**, 2235. (m) Yamanaka, I.; Morimoto, K.; Soma, M.; Otsuka, K. *J. Mol. Catal. A: Chem.* **1998**, *133*, 251.
57. (a) Davis, R.; Durrant, J. L. A.; Khan, M. A. *Polyhedron* **1988**, *7*, 425. (b) Funabiki, T.; Tsujimoto, M.; Ozawa, S.; Yoshida, S. *Chemistry Lett.* **1989**, 1267. (c) Funabiki, T.; Toyoda, T.; Yoshida, S. *Chemistry Lett.* **1992**, 1279. (d) Tatsumi, T.; Yuasa, K.; Tominaga, H. *J. Chem. Soc., Chem. Commun.* **1992**, 1446. (e) Wang, Z.; Martell, A. E.; Motekaitis, R. J. *Chem. Comm.* **1998**, 1523. (f) Lin, M.; Sen, A. *J. Am. Chem. Soc.* **1992**, *114*, 7307.
58. (a) Otsuka, K.; Ishizuka, K.; Yamanaka, I. *Chemistry Lett.* **1992**, 773. (b) Otsuka, K.; Yamanaka, I.; Hagiwara, M. *Chemistry Lett.* **1994**, 1861. (c) Maki, S.; Konno, K.; Takayama, H. *Tetrahedron Lett.* **1997**, *38*, 7067.
59. Shul'pin, G. B.; Kats, M. M.; Lederer, P. *J. Gen. Chem. USSR* **1989**, *59*, 2450.
60. (a) Shul'pin, G. B.; Kats, M. M. *React. Kinet. Catal. Lett.* **1990**, *41*, 239. (b) Shul'pin, G. B.; Nizova, G. V.; Kats, M. M. *J. Gen. Chem. USSR* **1990**, *60*, 2447. (c) Shul'pin, G. B.; Kats, M. M. *Neftekhimiya* **1991**, *31*, 648 (in Russian); *Petrol. Chem.* **1991**, *31*, 647. (d) Lederer, P.; Nizova, G. V.; Kats, M. M.; Shul'pin, G. B. *Coll. Czech. Chem. Commun.* **1992**, *57*, 107. (e) Shul'pin, G. B.; Druzhinina, A. N. *Mendeleev Commun.* **1992**, 36. (f) Shul'pin, G. B.; Druzhinina, A. N. *Bull. Russ. Acad. Sci., Div. Chem. Sci.* **1992**, *41*, 346. (g) Shul'pin, G. B.; Nizova, G. V. *Neftekhimiya* **1993**, *33*, 118 (in Russian); *Petrol. Chem.* **1993**, *33*, 107. (h) Shul'pin, G. B.; Nizova, G. V.; Kozlov, Yu. N. *New J. Chem.* **1996**, *20*, 1243.

61. (a) Nizova, G. V.; Kats, M. M.; Shul'pin, G. B. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1990**, *39*, 618. (b) Shul'pin, G. B.; Nizova, G. V.; Kats, M. M. *Neftekhimiya* **1991**, *31*, 658 (in Russian); *Petrol. Chem.* **1991**, *31*, 657. (c) Nizova, G. V.; Shul'pin, G. B. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1989**, *38*, 2205. (d) Shul'pin, G. B.; Nizova, G. V. *J. Gen. Chem. USSR* **1990**, *60*, 1892. (e) Nizova, G. V.; Shul'pin, G. B. *Neftekhimiya* **1991**, *31*, 822 (in Russian); *Petrol. Chem.* **1991**, *31*, 829. (f) Nizova, G. V.; Losenkova, G. V.; Shul'pin, G. B. *React. Kinet. Catal. Lett.* **1991**, *45*, 27.
62. (a) Druzhinina, A. N.; Shul'pina, L. S.; Shul'pin, G. B. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1991**, *40*, 1492. (b) Shul'pin, G. B.; Druzhinina, A. N.; Shul'pina, L. S. *Neftekhimiya* **1993**, *33*, 335 (in Russian); *Petrol. Chem.* **1993**, *33*, 321.
63. (a) Shul'pin, G. B.; Nizova, G. V. *Mendeleev Commun.* **1995**, 143. (b) Maldotti, A.; Bartocci, C.; Amadelli, R.; Polo, E.; Battioni, P.; Mansuy, D. *J. Chem. Soc., Chem. Commun.* **1991**, 1487. (c) Shelnut, J. A.; Trudell, D. E. *Tetrahedron Lett.* **1989**, *30*, 5231. (d) Weber, L.; Hommel, R.; Behling, J.; Haufe, G.; Hennig, H. *J. Am. Chem. Soc.* **1994**, *116*, 2400. (e) Maldotti, A.; Bartocci, C.; Amadelli, R.; Varani, G.; Pietrogrande, M. C.; Carassiti, V. *Gazz. Chim. Ital.* **1994**, *124*, 411. (f) Maldotti, A.; Mollinari, A.; Andreotti, M.; Fogagnolo, R.; Amadelli, M. *Chem. Commun.* **1998**, 507.
64. (a) Muzart, J.; Henin, F. *C. R. Acad. Sci. Paris, Part II* **1988**, *307*, 479. (b) Monaci, A.; Dal Zotto, R.; Tarli, F. *J. Photochem. Photobiol. A: Chem.* **1990**, *52*, 327. (c) Shul'pin, G. B.; Druzhinina, A. N. *React. Kinet. Catal. Lett.* **1992**, *47*, 207. (d) Shul'pin, G. B.; Bochkova, M. M.; Nizova, G. V. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1465.
65. (a) Shul'pin, G. B.; Kats, M. M. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1989**, *38*, 2202. (b) Shul'pin, G. B.; Kats, M. M. *J. Gen. Chem. USSR* **1989**, *59*, 2447. (c) Attanasio, D.; Suber, L. *Inorg. Chem.* **1989**, *28*, 3779. (d) Chambers, R. C.; Hill, C. L. *Inorg. Chem.* **1989**, *28*, 2509. (e) Zakrzewski, J.; Chauveau, F.; Giannotti, C. *C. R. Acad. Sci. Paris, Part II* **1989**, *309*, 809. (f) Maldotti, A.; Amadelli, R.; Carassiti, V.; Molinari, A. *Inorg. Chim. Acta* **1997**, *256*, 309. (g) Muradov, N. Z.; Rustamov, M. I. *Kinet. Katal.* **1989**, *30*, 248 (in Russian).
66. (a) Shul'pin, G. B.; Kats, M. M. *J. Gen. Chem. USSR* **1989**, *59*, 2338. (b) Shul'pin, G. B.; Druzhinina, A. N.; Nizova, G. V. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1991**, *40*, 2145. (c) Nizova, G. V.; Shul'pin, G. B. *J. Gen. Chem. USSR* **1990**, *60*, 1895. (d) Shul'pin, G. B.; Druzhinina, A. N. *React. Kinet.*

- Catal. Lett.* **1991**, *44*, 387. (e) Shul'pin, G. B.; Druzhinina, A. N. *Neftekhimiya* **1993**, *33*, 256 (in Russian); *Petrol. Chem.* **1993**, *33*, 247. (f) Shul'pin, G. B.; Nizova, G. V. *React. Kinet. Catal. Lett.* **1991**, *45*, 7. (g) G. V. Nizova, G. V.; Muzart, I.; Shul'pin, G. B. *React. Kinet. Catal. Lett.* **1991**, *45*, 173. (h) Muzart, J.; Druzhinina, A. N.; Shul'pin, G. B. *Neftekhimiya* **1993**, *33*, 124 (in Russian); *Petrol. Chem.* **1993**, *33*, 113. (i) Nizova, G. V.; Shul'pin, G. B. *Neftekhimiya* **1994**, *34*, 364 (in Russian); *Petrol. Chem.* **1994**, *34*, 353. (j) Shul'pin, G. B.; Druzhinina, A. N.; Nizova, G. V. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1990**, *39*, 195. (k) Ermolenko, L. P.; Giannotti, C. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1205. (l) Zakrzewski, J.; Giannotti, C. *J. Photochem. Photobiol. A: Chem.* **1992**, *63*, 173. (m) Ermolenko, L. P.; Delaire, J. A.; Giannotti, C. *J. Chem. Soc., Perkin Trans. 2* **1997**, 25.
67. (a) Farinas, E. T.; Nguyen, C. V.; Mascharak, P. K. *Inorg. Chim. Acta* **1997**, *263*, 17. (b) Hikichi, S.; Komatsuzaki, H.; Akita, M.; Moro-oka, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4699.
68. Vicente, J.; Areas, A.; Bautista, D.; Shul'pin, G. B. *J. Chem. Soc., Dalton Trans.* **1994**, 1505.