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# C–H functionalization: thoroughly tuning ligands at a metal ion, a chemist can greatly enhance catalyst's activity and selectivity

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This brief essay consists of a few "exciting stories" devoted to relations within a metal-complex catalyst between a metal ion and a coordinated ligand. When, as in the case of a human couple, the rapport of the partners is cordial and a love cements these relations, a chemist finds an ideal married couple, in other words he obtains a catalyst of choice which allows him to functionalize C-H bonds very efficiently and selectively. Examples of such lucky marriages in the catalytic world of ions and ligands are discussed here. Activity of the catalyst is characterized by turnover number (TON) or turnover frequency (TOF) as well as by yield of a target product. Introducing a chelating N,N- or N,O-ligand to the catalyst molecule (this can be an iron or manganese derivative) sharply enhances its activity. However, the activity of vanadium derivatives (with additionally added to the solution pyrazinecarboxylic acid, PCA) as well as of various osmium complexes does not dramatically depend on the nature of ligands surrounding metal ions. Complexes of these metals are very efficient catalysts in oxidations with H<sub>2</sub>O<sub>2</sub>. Osmium derivatives are record-holders exhibiting extremely high TONs whereas vanadium complexes are on the second position. Finally, elegant examples of alkane functionalization on the jons of non-transition metals (aluminium, gallium etc.) are described when one ligand within the metal complex (namely, hydroperoxyl ligand HOO<sup>-</sup>) helps other ligand of this complex (H<sub>2</sub>O<sub>2</sub> molecule coordinated to the metal) to disintegrate into two species, generating very reactive hydroxyl radical. Hydrogen peroxide molecule, even ligated to the metal ion, is perfectly stable without the assistance of the neighboring HOO<sup>-</sup> ligand. This ligand can be easily oxidized donating an electron to its partner ligand (H<sub>2</sub>O<sub>2</sub>). In an analogous case, when the central ion in the catalyst is a transition metal, this ion changing its oxidation state can donate an electron to the coordinated  $H_2O_2$  fragment. This provokes the O–O bond rupture in the hydrogen peroxide molecule as is assumed for the role of Fe<sup>2+</sup> ions in the Fenton system.

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#### 1. Introduction

Activation and functionalization of C–H bonds in organic compounds<sup>1</sup> is a very important process both from academic and practical point of view because splitting C–H bonds transforms inert hydrocarbons (particularly alkanes, which are 'noble gases of organic chemistry'<sup>1b</sup>) into valuable products. Earlier we proposed the following classification which is based on types of interaction between the C–H compound and a metal complex.<sup>1b</sup> We assigned to the first type ('true' or organometallic activation) processes in which organometallic derivatives (*i.e.*, compounds containing a metal–carbon bond) are formed either as intermediates or as final products. In this case, the

closest contact between metal ion and the C-H bond is realized. In the present brief review catalytic processes which include 'true' activation are discussed in Section 3. We included into the second group reactions in which the contact between the complex and the C-H bond is realized only via a complex' ligand during the process of the C-H bond cleavage. In the course of this process the  $\sigma$ -C–M bond is not generated directly at any stage. The metal complex under these conditions usually abstracts an electron or a hydrogen atom from the hydrocarbon. In the processes belonging to the third type, the complex activates initially not the hydrocarbon but the other reactant, for example, green oxidants: molecular oxygen or hydrogen peroxide. The reactive species formed (e.g., hydroxyl radical) attacks then the hydrocarbon molecule without the participation of the metal complex. The reactions which proceed with the participation either of high-valent metal derivatives or/and with the generation of free radicals are discussed in

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Sections 4–7. For alternative definitions of C–H bond activation (functionalization) proposed in the literature, see ref. 2.

Some metal ions are known to catalyze various oxidation reactions. In many cases, the catalyst is greatly improved if the chemist 'arrays' this metal ion in wear of ligands. This essay describes a few examples when the chemist, tuning ligands which surround the metal reaction center, can enhance the activity and/or selectivity of the catalytic system. The rational matching ligands and their architecture can lead to breathtaking results: the catalytic reaction becomes very efficient and/or selective. Here a crucial question arises: how to invent a "good" catalyst? In preface to a very recent book "Inventing Reactions" (Springer-Verlag, Berlin, Heidelberg, 2013) the editor L. J. Gooßen wrote: "In popular media, chemists are often portrayed as characters aimlessly throwing together concoctions of random ingredients in the hope of spectacular discoveries. As exaggerated as this may appear, the grain of truth behind this image is that some prominent chemical processes have indeed been found by serendipity rather than through rational thought processes. However, even in these cases, a substantial intellectual contribution was made by the discovering scientists, who grasped the significance of their experimental results and readjusted the focus of their research activity. I am convinced that it has meanwhile become the rule rather than the exception for the discovery of a chemical reaction to result from an intentional invention process with a clearly defined target".<sup>3</sup>

It is not surprising that metal-catalyzed reactions depend on the nature and architecture of ligands surrounding the central ion (for a theoretical description of metal-ligand



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Georgiy Borisovich Shul'pin is currently a Leading Scientific Researcher at the Semenov Institute of Chemical Physics, Russian Academy of Sciences (Moscow, Russia). His research activities concern catalysis, functionalization of hydrocarapplied organometallic bons, chemistry. Main achievements: the electrophilic platination of arenes, the oxidizing reagent "hydrogen peroxide-vanadium derivative-pyrazinecarboxylic

acid", aerobic photooxidation of alkanes catalyzed by chloride and oxo complexes of transition metals, oxygenation by hydrogen peroxide catalyzed by a manganese complex in the presence of a carboxylic acid, a chromatographic method for determination of alkyl hydroperoxides. He has published a number of monographs and 250 original papers. Shul'pin is the Editor and member of Editorial Boards of journals "Catal. Commun.", "J. Engineering", "Am. Chem. Sci. J.", "Catalysts", "Adv. Chem. Eng. Sci.", "Modern Chem.". bonds, see a recent review<sup>4</sup>). Oxidation reactions catalyzed by nanoparticles in which neighboring metal atoms play the role of surrounding ligands have become especially popular.<sup>5</sup> Pronounced ligand effects have been described for the C-H activation in the gas phase.<sup>6</sup> Metal catalysts bearing chiral ligands are necessary for the asymmetric reactions.<sup>7</sup> Hydrogen bonds play an important role because they can stabilize unusual coordination geometries, or reactive species.8 In recent decades, new terms and concepts have been introduced into coordination chemistry and metal-complex catalysis. We will briefly mention them here. Tridentate pincer-type ligands form complexes with metal ions<sup>9</sup> which can be active catalysts. Metallated cavitands (calixarenes, resorcinarenes, cyclodextrins etc.) with internal coordination sites,<sup>10a</sup> metal-organic frameworks (MOFs),<sup>10b,c</sup> scorpionates<sup>10d-g</sup> and inorganic polymers<sup>10h</sup> as ligand surroundings are in some cases efficient catalysts of oxidation reactions. A very interesting and important for a catalysis concept of redox-active or "non-innocent" ligands has been developed.<sup>11</sup>

What do we mean when say "improving the metal-complex catalyst by adding proper ligands to proper positions"? A few criteria can be stated: (i) we can enhance the activity of the catalyst, *i.e.*, increase the rate of the reaction, the turnover number (moles of products per one mole of the catalyst, TON), turnover frequency (moles of products per one mole of the catalyst in the time unity, TOF) and yield of the products; (ii) we can make the reaction conditions milder, that is decrease the temperature and pressure; (iii) the selectivity of the reaction (substrate, product, regio-, stereo-, enantio-selectivity) can be enhanced; (iv) a catalyst may be supported on the solid material without leaching, and this facilitates the separation of the catalyst and its reusing; (v) a catalytically active species can be created in situ by mixing a metal ion and ligands which simplifies the catalytic procedure and makes it cheaper. We will describe here some random examples of recently discovered catalytic systems when a lucky marriage of metal ion and ligand leads to the fantastic results (namely, high efficiency and selectivity).

The survey includes a few short "stories" devoted to various important roles of ligands which these ligands play in oxidation catalysis. The author's original works are emphasized. We will describe our own catalytic combinations in more detail. In the last decades, we invented and developed a few very efficient systems for oxidation of hydrocarbons and other organic compounds with peroxides. These systems consist of metal ions (in some cases surrounded by N-ligands) and "co-catalysts" which are in reality the ligands for catalysts: "vanadium derivative–pyrazinecarboxylic acid (PCA)–H<sub>2</sub>O<sub>2</sub>" (Section 5), "complex  $[Mn_2L_2O_3]^{2+}$  (L = 1,4,7-trimethyl-1,4,7-triazacyclononane)–carboxylic acid–H<sub>2</sub>O<sub>2</sub>" (Section 4), "osmium derivative–pyridine–H<sub>2</sub>O<sub>2</sub>" (Section 6).

#### 2. Activity and selectivity

To characterize the efficiency of a catalyst or catalytic reaction the parameter "turnover number" is widely used in the

catalytic studies. Turnover number (TON) is the number of moles of substrate that can be converted by one mol of catalyst before this catalyst becomes inactive. Often chemists do not determine the moment of complete catalyst's inactivation but simply measure the concentration of product(s) when "the reaction is over". In many cases we can find in publications the information on how many TONs have been attained after the arbitrary time. TON does not give us any notion of how fast the reaction is. To characterize simultaneously the activity of catalyst and "speed" of its work the parameter "turnover frequency" (TOF) is used in catalytic publications to refer the turnover per unit time (hour, min or s). It is clear that TON is a dimensionless value whereas TOF is presented in h<sup>-1</sup>, min<sup>-1</sup> or s<sup>-1</sup>. As TOF reflects the reaction rate it is reasonable to consider initial (TOF<sub>0</sub>) or maximum (TOF<sub>max</sub>) turnover frequency when the TON value is measured either at the initial period of the reaction or at the period when the rate is highest. Naturally, the TOF value depends on the reaction conditions: concentrations of the reactants, temperature etc.

Kozuch and Martin<sup>12</sup> proposed a standard TOF° where the reactants and products concentrations are set to 1 M, or  $10^5$  Pa (1 bar) for gases. The temperature should be set at 273.15 K. Similarly, to define a TON° the concentrations should be maintained at 1 M (or  $10^5$  Pa), at a steady state regime and at 273.15 K. "For development and small scale synthesis, a TON of 100 may be enough. For industrial applications, a high turnover catalyst should have a TON of no less than 1000 (and ideally over  $10^5$ ) to minimize the recovery of the active species, to avoid preactivation steps and the contamination of the product, and from economic reasons. TONs as high as  $10^8$  have only been reached for very specific reactions".<sup>12a</sup> In the case of catalysts that contain many reactive ions both TONs and TOFs may be calculated either considering the catalyst as one molecule or per one metal ion.

In addition to efficiency, there is the second parameter which is very important: selectivity.<sup>13</sup> The reaction occurs selectively if either only one substrate from a mixture of potential substrates preferably enters into the transformation or only one product is predominantly formed. In the first case we deal with the substrate selectivity, in the second case we discuss the product selectivity. The higher the selectivity the higher will be yield of the target product. Reactions that exhibit 100% selectivity (specific reactions) can produce the target product(s) in quantitative yield. The substrate selectivity is very important for living systems because the cell contains a myriad of various compounds that might be potential substrates. Usually an enzyme transforms mainly (selectively) or exclusively (specifically) only one or a few substances. These substrates can differ by functional groups or be isomers of one organic compound. The regio-selectivity in oxidation of alkanes can be enhanced by using the principles of supramolecular control.<sup>13</sup>

A very important problem in functionalization of inert hydrocarbons is a competition between the hydrocarbon and a solvent. This is why the most commonly used solvents in alkane functionalizations are acetic and trifluoroacetic acid, acetonitrile and water, *i.e.*, relatively inert compounds. In some cases we can enhance selectivity of the reaction using very reactive species which "non-selectively" react with all compounds present in the reactions solution. Thus, alcohols are usually more easily oxidizable compounds in comparison with alkanes. It is noteworthy, however, that in the systems developed by us, alcohols can be used as solvents for aerobic oxidation of alkanes catalyzed by FeCl<sub>3</sub> under visible light irradiation.<sup>14*a*</sup> Photohomolysis of the Fe<sup>III</sup>–Cl bonds in the initial stage of the reaction affords very reactive Cl<sup>-</sup> radicals<sup>14*b*</sup> that attack both the alkane and the alcohol used as a solvent with comparable rates. As a result, oxygenation products are formed from the alkanes in quite high yield.

Another important problem of hydrocarbon functionalization is over-oxidation because usually the products are more reactive than the parent hydrocarbons. Let us consider a simple case when the substrate Sub is transformed into a target valuable product Prod, which is in turn transformed further into the unwanted needless product Unw:

$$\text{Sub} \to \text{Prod}; \ k_{\text{Sub} \to \text{Prod}}$$
 (1)

$$Prod \to Unw; \ k_{Prod \to Unw}$$
(2)

An example of such type of reaction is the oxidation of methane to valuable target methanol (or the deeper oxidation to formaldehyde) which can be easily over-oxidized to produce waste  $CO_2$ . Fig. 1 demonstrates the kinetic curves of the Sub consumption as well as the accumulation and consumption of Prod and the accumulation of Unw. The accumulation rate of intermediate product Prod is the difference between the rates *W* of its formation and consumption:

$$\frac{\mathrm{d}[\mathrm{Prod}]}{\mathrm{d}t} = W_{\mathrm{Sub}\to\mathrm{Prod}} - W_{\mathrm{Prod}\to\mathrm{Unw}}$$
$$= -\frac{\mathrm{d}[\mathrm{Sub}]}{\mathrm{d}t} - k_{\mathrm{Prod}\to\mathrm{Unw}}[\mathrm{Prod}] \tag{3}$$



Fig. 1 Kinetic curves for the accumulation and consumption of compounds in the consecutive reactions Sub  $\rightarrow$  Prod  $\rightarrow$  Unw.

If the transformations of our substrate Sub occur under the action of the reagent X we can consider<sup>14c</sup> two stages:

$$\operatorname{Sub} + X \xrightarrow{\kappa_1} \operatorname{Prod}$$
(4)

$$\operatorname{Prod} + X \xrightarrow{\kappa_2} \operatorname{Unw}$$
(5)

The analysis of scheme (4)–(5) for the maximum attained yield of Prod gives the following expression:

$$\frac{[\text{Prod}]_{\text{max}}}{[\text{Sub}]_0} = (k_2/k_1)^{\frac{k_2/k_1}{1-(k_2/k_1)}}$$
(6)

Alkanes and other organic compounds usually substitute their C-H bonds non-selectively and comparable amounts of various position isomers are produced in the reaction. However, some catalytic systems are able to direct the substituent predominantly to only one position (region). Such reactions are regioselective or regiospecific. In another words, regioselectivity is the preferential formation of one constitutional isomer over another (constitutional isomers of the same molecular formula differ in how their atoms are connected). Usually parameter C(1): C(2): C(3): C(4) is used which is relative normalized (calculated taking into account the number of hydrogen atoms at each carbon) reactivities of hydrogen atoms at carbons 1, 2, 3 and 4 of the chain of normal alkane. For example, n-heptane contains six methyl C-H bonds, and the concentration of heptanol-1 should be divided by 6 to measure the reactivity of one methyl C-H bond. Analogously, reactivities of methylene C-H bonds in positions 2 and 3 can be calculated dividing concentration of heptan-2-ol or heptan-3-ol primarily by 4 (the number of methylene groups at these positions) and after that dividing by the reactivity of one methyl C-H bond. We should divide the relative concentration of heptanol-4 by 2 because only two hydrogens are situated in this position. In functionalizations of branched alkanes, the bond selectivity parameter 1°: 2°: 3° is widely used which combines relative normalized reactivities of hydrogen atoms at primary, secondary and tertiary carbons of a branched alkane, for example, methylcyclohexane. The oxidations with the participation of very reactive radicals (Cl., HO') exhibit low selectivity,  $1^\circ: 2^\circ: 3^\circ \approx 1:5: 20$ . The nonradical oxygenations occur with much higher selectivities. For example, peroxyacids do not oxidize primary C-H bonds and relative rates of attack at tertiary and secondary C-H bonds (after statistical correction) are in the interval between 90 and 500, which can be conventionally presented as  $1^\circ: 2^\circ: 3^\circ \approx$ 0:1:90-500.

Stereoselective (stereospecific) functionalization of C–H compounds is a very important goal of metal-complex catalysis. Stereoselectivity is the preferential formation in a chemical reaction of one stereoisomer over another. Stereoisomers are isomers that possess identical constitution, but which differ in the arrangement of their atoms in space. In a diastereoselective reaction, one diastereoisomer is preferentially formed over another. When a reaction gives preferentially one enantiomer over another, the phenomenon is called enantioselectivity. A study of stereoselectivity of a reaction helps to understand the mechanism of the interaction between the active species and C–H bonds.

# 3. Versatile platinum in hydrocarbon functionalizations

In this Section we will concern roles of ligands in functionalization of alkanes and arenes with the participation of platinum complexes (for comprehensive reviews of this field, see ref. 15).

#### 3.1. Shilov reaction: platinum complexes in alkane transformations

In 1969-1972 Shilov and co-workers reported the first examples of a "true" metal-catalyzed functionalization of C-H bonds in alkanes (see reviews<sup>15</sup>). These authors demonstrated that complex Pt<sup>II</sup>Cl<sub>4</sub><sup>2-</sup> can catalyze H/D exchange in methane in a D<sub>2</sub>O-CD<sub>3</sub>COOD solution and, if Pt<sup>IV</sup>Cl<sub>6</sub><sup>2-</sup> is added, the latter oxidizes methane to methanol (Shilov chemistry). The reaction proceeds with the participation of organometallic compounds. The catalytic cycle in which  $\sigma$ -methyl complexes of platinum( $\pi$ ) and platinum( $\pi$ ) are involved is shown in Fig. 2. A great number of experimental (Zamaschikov, Rudakov, Labinger, Bercaw, Sen, Goldberg, Vedernikov) and theoretical (Shestakov, Cundari, Crabtree, Eisenstein) works was devoted to both stages of this reaction. The first stage is the interaction of platinum(II) derivative with C-H bonds of the alkane which can lead to the formation of the corresponding deuterated alkane if the reaction solution contains ions D<sup>+</sup> in the form of CH<sub>3</sub>COOD and D<sub>2</sub>O. The second stage is the oxidation of the Pt(n)-containing intermediates, for example,  $CH_3$ -Pt(n), with Pt(w) to produce finally stable  $CH_3Cl$  and  $CH_3OH$ .

It has been shown that in aqueous solution,  $PtCl_4^{2-}$  ions undergo dissociation when chloride anions are replaced by



Fig. 2 Methane functionalization in Shilov system with the participation of Pt(n) (first stage) and Pt(n) second stage.

solvent molecules (S):  $PtCl_4^{2-} + S \Rightarrow PtSCl_3^{-} + Cl^{-}$  and  $PtSCl_3^{-}$ + S  $\Rightarrow$  PtS<sub>2</sub>Cl<sub>2</sub> + Cl<sup>-</sup>. The rate constants of H/D exchange in alkanes catalyzed by the complexes containing ligands L  $(PtCl_2S_2 + 2L^- \Rightarrow PtCl_2L_2^{2-} + 2S)$  decrease in the following order of ligands L<sup>-</sup>:  $F > SO_4^- > Cl > Br > I > NO_2 > CN$ . The rate constant of the H/D exchange catalyzed by complexes PtCl<sub>3</sub>L<sup>-</sup>  $(L = H_2O, Cl^-, NO_2^-, DMSO, NH_3, py)$  and  $PtCl_2L_2^{2-}$   $(L = H_2O, Cl^-, NO_2^-, DMSO, NH_3, py)$ Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, CN<sup>-</sup>, PPh<sub>3</sub>) changes by three orders of magnitude. Experimental and theoretical studies demonstrated that there is acceleration of the H/D exchange when catalysts  $PtCl_4^{2-}$  or  $Pt(H_2O)_4^{2+}$  are replaced by the neutral complex PtCl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>. A  $\sigma$ -alkyl complex of platinum(II) can be converted in the presence in the solution of  $PtCl_6^{2-}$  into a  $\sigma$ -alkyl platinum(IV) derivative. This stage involves<sup>16a,b</sup> electron transfer  $\sigma\text{-}R\text{-}Pt^{II}C{l_3}^{2-} + \text{*}Pt^{IV}C{l_6}^{2-} \rightarrow \sigma\text{-}R\text{-}Pt^{IV}C{l_5}^{2-} + \text{*}Pt^{II}C{l_4}^{2-} \text{ rather}$ than alkyl transfer:  $\sigma$ -R-Pt<sup>II</sup>Cl<sub>3</sub><sup>2-</sup> + \*Pt<sup>IV</sup>Cl<sub>6</sub><sup>2-</sup> -×→  $\sigma$ -R-\* $Pt^{IV}Cl_3^{2-}$  +  $Pt^{IV}Cl_6^{2-}$ . See also other mechanistic studies of alkane functionalization by Shilov system including ligand effects.<sup>16c,d</sup> Many platinum complexes with various ligands have been studied which are models of certain intermediates in the Shilov system.<sup>16e-n</sup> Prince and Cundari<sup>16o</sup> showed by calculations "the importance of designing C-H activation catalysts where the ground state active species is already structurally 'prepared' and which either does not need to undergo any geometric perturbations to access the methane C-H activation transition state or is not energetically prohibited from such perturbations". We can note here that the subtitle of that paper is: "The importance of having the ligands in the right place at the right time".

## 3.2. Periana system: the incredibly stable N-ligand and long-living catalyst

In the original Shilov system expensive  $PtCl_6^{2-}$  ion is an oxidizing reagent which transforms methane (and other alkanes) to methanol and methyl chloride. It is clear that platinum compounds as stoichiometric oxidants are very expensive. Classical Shilov reaction attains relatively low TONs. Periana and coworkers decided to use in platinum-catalyzed reaction concentrated sulfuric acid as both solvent and oxidizing reagent. Simple salts were not effective under these conditions due to poor solubility, stability and selectivity. Complex (NH<sub>3</sub>)<sub>2</sub>PtCl<sub>2</sub> was soluble in sulfuric acid and active in the functionalization of methane. However, unfortunately, this catalyst was unstable and gave less than 20 turnovers before catalysis stopped due to precipitation of platinum chloride. The replacement of ammonia by chelating bidentate ligand 2,2'-bipyrimidyl led to (2,2'-bipyrimidyl)platinum(II) dichloride as an efficient and stable catalyst for the selective, high-yield oxidation of methane to 1 M methanol in sulfuric acid at 220 °C.<sup>17</sup> Fuming sulfuric acid is the oxidant in this case. "Periana (Catalytica) system" demonstrates a possible approach to industrial alkane functionalization. A simplified scheme of the catalytic cycle is shown in Fig. 3. As in Shilov system, some intermediates contain σ-methyl-platinum bonds. "Remarkably, stability was the result of oxidative dissolution of Pt<sup>0</sup> by H<sub>2</sub>SO<sub>4</sub> facilitated by the bipyrimidine ligand."<sup>17a</sup> The Periana system gives us a rare



**Fig. 3** Methane oxygenation in Periana system in fuming sulfuric acid with the participation of (2,2'-bipyrimidyl)platinum(n) dichloride as catalyst.

example of both an incredibly stable N-ligand and metalcomplex catalyst bearing this ligand.

### 3.3. Platinum(rv) and arenes, plus ammonia as a ligand: an easy route to stable aryl Pt(rv) complexes

In the early 1980s, we found that acid H<sub>2</sub>PtCl<sub>6</sub> reacts in aqueous CF<sub>3</sub>COOH with benzene and substituted benzenes to form stable  $\sigma$ -aryl platinum(w) complexes.<sup>18</sup> The reaction proceeds at elevated temperature (40-70 °C) and affords a mixture of para- and meta-isomers when monosubstituted benzenes are used. There is mutual interconversion of isomers para  $\rightleftharpoons$ meta which occurs in the course of complex accumulation; ortho-Platinated compounds are not formed due to steric reasons. This reaction ("the Shul'pin reaction"<sup>19</sup>) is a convenient synthetic route to  $\sigma$ -aryl platinum(IV) complexes. The complexes are formed in high yields and can be isolated as solids if... a serendipitously found "know-how" is used. This "know-how" is the ligand exchange in the course of the chromatographic separation. In order to isolate the complex<sup>18</sup> we evaporated trifluoroacetic acid and chromatographed the residue on columns or plates with silica gel containing adsorbed ammonia (ca. 1 mg NH<sub>3</sub> per 1 g SiO<sub>2</sub>; this solid product can be easily obtained by exposure of silica gel to the atmosphere containing ammonia). The elution with a hexaneacetone mixture gives the orange band of complex. The unreacted hexachloplatinic acid in the form of adduct with ammonia can be further eluted with water. The σ-aryl derivative can be obtained in the form of ammonium salt of the complex containing ammonia ligand:

$$\operatorname{ArH}_{+} H_2 \operatorname{PtCl}_6 \rightarrow \sigma \operatorname{ArPtCl}_5^{2-} \rightleftharpoons \sigma \operatorname{ArPtCl}_4 (H_2 O)^{-}$$

Direct addition of aqueous ammonia to the reaction mixture did not give the complex in a form which can be easily isolated. Only chromatography on  $SiO_2 \cdot NH_3$  allowed us to



**Fig. 4** Mechanism proposed for the photoelectrophilic metalation of aromatic compounds with  $PtCl_6^{2-}$  ion.

prepare the complexes by gentle and convenient method in high yields.

Unlike functionalization of alkanes catalyzed by platinum(II) complexes in Shilov and Periana systems, the reaction between  $PtCl_6^{2-}$  and arenes proceeds as typical electrophilic substitution. It is noteworthy that the same reaction can be stimulated not only by heating but also by irradiation by visible light<sup>18c,20a</sup> or by gamma-irradiation.<sup>20b</sup> In contrast to the thermally induced reaction, the photochemical process occurs without *para-meta* isomerisation, and gives only pure *para*-isomer in the case of benzenes bearing electronreleasing substituents. The proposed mechanism<sup>18c</sup> which includes electron transfer from the arene to Pt(rv) ion is shown in Fig. 4.

Another interesting peculiarity of the photoelectrophilic substitution is that the reaction does not require acidic media: trifluoroacetic acid can be replaced by methylene chloride.<sup>20a</sup> Thus, the interaction of (NBu<sub>4</sub>)<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O with an arene in CH<sub>2</sub>Cl<sub>2</sub> under irradiation by full light of a medium-pressure mercury lamp gave  $\sigma$ -complexes of (yield is in parentheses): anisole (87%), phenethol (50%), diphenyl oxide (40%) and benzene (10%). The solvent was evaporated and the residue dissolved in acetone. Addition of aqueous ammonia and NH<sub>4</sub>Cl led to the ligand exchange and afforded the complexes which were purified by usual chromatography on silica gel. Besides being carefully studied by us in thermally and photochemically induced reactions18,20a Mitchenko, Beletskaya and co-workers<sup>20c</sup> more recently reported the formation of  $\sigma$ -aryl platinum(IV) complexes in the mechanically activated reaction of K<sub>2</sub>PtCl<sub>6</sub> with gaseous benzene and toluene. In that work the complexes were not isolated in pure solid form but were quantified by NMR and IR spectroscopy.

# 4. Efficient metal-based catalysts which contain chelating ligands

Transition-metal complexes are known to catalyze oxidation of hydrocarbons and other C–H compounds by molecular oxygen, hydrogen peroxide, organic peroxides and peroxoacids<sup>1b,h,15,21</sup> Such complexes often bear various chelating ligands and can be considered as models of the reaction centers of oxidizing enzymes.

#### 4.1. Iron complexes

Iron ions play an extremely important role in living nature.<sup>22</sup> They in particular are main components of certain oxidizing enzymes.<sup>22c,d</sup> Enzyme cytochrome P450 is a porphyrin complex in which iron atom is surrounded by various ligands.<sup>22e-j</sup> Porphyrin and phthalocyanine complexes of iron and manganese are models of heme monooxygenase enzymes (for selected examples, see ref. 23). Many works devoted to nonheme iron complexes<sup>24</sup> which play the roles of models of some hydrocarbon-oxidizing enzymes were published,<sup>25</sup> particularly, by Beller,<sup>24d</sup> Que,<sup>25b,c</sup> Pombeiro,<sup>25d</sup> Norlander,<sup>25e</sup> Hutchings,<sup>25f</sup> Mandon,<sup>25g</sup> Reedijk,<sup>25h</sup> Costas,<sup>25i,j</sup> Shteinman,<sup>25k</sup> Britovsek,<sup>25l,m</sup> White,<sup>25n</sup> Nam,<sup>25o</sup> Talsi.<sup>25p</sup> Usually these complexes contain polydentate N-ligands and catalyze the oxidation reactions by hydrogen peroxide and organic peroxides. Almost in all cases, the authors reported the direct transformation of alkanes into a mixture of corresponding alcohol (hydroxylation) and ketone (ketonization) and typically did not discuss a possible formation of alkyl peroxides. Meanwhile the formation of alkyl hydroperoxides and also a lack of stereoselectivity can indicate that the reaction proceeds with the participation of free radicals (see below, Subsection 4.2). An absence of alkyl hydroperoxides can testify that the system under consideration operates via a metal-based mechanism without involvement of free diffusing radicals. Such reactions occur often stereoselectively.

Replacing "usual" inorganic ligands (Cl<sup>-</sup>, H<sub>2</sub>O, HO<sup>-</sup> *etc.*) in the catalyst by macrocyclic chelating N-ligands often leads to the enhancing catalyst stability, its efficiency and – what is very important – stereoselectivity. Thus, complex [Fe<sup>II</sup>(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>-(<sup>Me2</sup>PyTACN)] (1) converts cyclohexane under the action of H<sub>2</sub>O<sub>2</sub> to cyclohexanol and cyclohexanone with TONs 6 and 0.5, respectively, and yields 65% based on the oxidant (as measured by direct injection of the samples to the chromatograph).<sup>26a</sup> The oxidation of *cis*-1,2-dimethylcyclohexane afforded the tertiary alcohol product with 93% retention of configuration. We have found<sup>26b</sup> that similar binuclear complex 2 (in combination with a catalytic amount of pyrazinecarboxylic acid, PCA; see Section 5) oxidizes cyclohexane by H<sub>2</sub>O<sub>2</sub> at room temperature to cyclohexyl hydroperoxide with TON = 240 after 24 h.



Goldsmith and co-workers in the paper entitled "Steric modifications tune the regioselectivity of the alkane oxidation

catalyzed by non-heme iron complexes"26c described the alkane oxidation with H<sub>2</sub>O<sub>2</sub> catalyzed by iron complexes with the tetradentate N-donor ligand N,N'-di(phenylmethyl)-N,N'bis(2-pyridinylmethyl)-1,2-cyclohexanediamine (bbpc, 3). The catalysts bearing this more sterically encumbered analog of previously reported tetradentate N-donor ligands direct oxidation toward the secondary carbons to a greater degree than other previously reported iron-containing catalysts. White and co-workers<sup>26d</sup> demonstrated that by acting as ligands for the metal, carboxylic acids overcome a range of substrate biases (electronic, steric and stereoelectronic) in C-H hydroxylation reactions which are catalyzed by the non-heme iron complex Fe(pdp) (4). Costas and co-workers<sup>26e</sup> used various similar iron catalysts with tetradentate N-ligands for the oxidation of complex organic molecules where oxidation of multiple C-H sites is competitive. They concluded that "the highly elaborate structure of the catalysts allows modulation of C-H regioselectivity between the oxidation of tertiary and secondary C-H groups and also among multiple methylene sites, providing oxidation products in synthetically valuable yields". The authors did not find alkyl hydroperoxides in the reaction mixture and concluded that their reaction is a metal-centered transformation where long-lived carbon-centered radicals are not involved. Interestingly, the DFT calculations<sup>26f</sup> of complex 5 showed that this high-valent oxo intermediate is a more powerful oxidant than P450.



## 4.2. Oxidation with dioxygen or peroxides often affords alkyl hydroperoxides: how to detect them?

Reactions of C-H compounds with molecular oxygen or/and peroxides (H<sub>2</sub>O<sub>2</sub>, *tert*-BuOOH, peroxy acids)<sup>27*a*-*d*</sup> often afford as primary product alkyl peroxides: R'R"R'"CH  $\rightarrow$  R'R"R'"CH-OOH. Hydroperoxides are easily formed from compounds with activated weak C-H bonds (cumene, ethylbenzene, cyclohexene). In these cases, the peroxides are relatively stable and can be detected and isolated (for stable hydroperoxides obtained by other methods, see ref. 27*e*,*f*). Oxidation of lower alkanes gives less stable peroxides. Under the action of catalyst which is present in the reaction mixture, the peroxides in the course

of the oxidation reaction can be partly or completely decomposed to give a mixture of the corresponding alcohol and ketone. In the Gif systems operating in pyridine solution,<sup>27g</sup> the alkane oxidation with  $H_2O_2$  leads to the formation of alkyl hydroperoxides which are transformed into a mixture of the corresponding ketone and alcohols with the ketone being prevalent ("the ketonisation").

Usually researchers measure the concentrations of the products formed in the oxidation of C-H compounds with O2 or peroxides directly injecting a sample of the reaction solution to the gas chromatograph (GC; see, for example, ref. 28). In some works, the reaction solution was filtered through a short plug of silica gel or basic alumina to remove the metal complexes. Generally speaking this procedure can lead to the transformation of the formed alkyl hydroperoxide into the corresponding alcohol and ketone. Alkyl hydroperoxides decompose further in the injector and columns of a gas chromatograph to produce the corresponding alcohols and ketones (aldehydes). The decomposition in the GC, for example, of cyclohexyl hydroperoxide gives cyclohexanol and cyclohexanone in the ratio around 1:1. It should be noted here that under mild conditions the alkyl hydroperoxide, ROOH, can be easily transformed into the corresponding ketone (or aldehyde), R'COR", via dehydration without formation of the alcohol, ROH. However, at elevated temperature ROOH decomposes via a multistep radical-chain mechanism. Some stages of this process afford both products, the ketone and alcohol in 1:1 ratio (ROOH = RO' + HO'; 2ROOH = RO' + ROO' +  $H_2O$ ;  $ROO' + ROO' = ROH + R'COR'' + O_2$  (see ref. 15b, p. 41, 47).

Since the alcohol and ketone are not the primary products but are formed in the subsequent decay in the GC, concentrations of these secondary products and their ratio cannot give any information about the real composition of the primary products (isomeric alkyl hydroperoxides that partly or completely transformed in the course of the reaction into the alcohol and ketone). The estimation of real concentrations of all three products formed in the reaction (and not in GC) can be performed by a simple method which we developed in the early 1990s and used in all our further works.<sup>29</sup> According to this method (the Shul'pin method), an excess of solid PPh<sub>3</sub> is added to a sample of the reaction solution ca. 10 min before GC analysis. The alkyl hydroperoxide, ROOH, present in the reaction mixture is completely reduced to the corresponding alcohol. As a result, the chromatogram differs from that of a sample not subjected to the reduction (the alcohol peak rises, while the intensity of the ketone peak decreases). The determination of a sum of concentrations alcohols + ketone (aldehyde) after reduction with PPh<sub>3</sub> gives us precise value of total concentration of the three products (that is of alkyl hydroperoxide, alcohol and ketone). The comparison of this value with concentrations of the alcohol and ketone (aldehyde) before reduction with PPh3 allows us to estimate the real concentrations of the alkyl hydroperoxide, alcohol and ketone (aldehyde) in the reaction solution. Obtaining the chromatogram of the reaction solution after the addition of pyridine we can also estimate the real concentration of the alkyl hydroperoxide:

indeed, concentration of the ketone after  $PPh_3$  corresponds to real concentration of the ketone in the reaction mixture whereas concentration of the ketone after treating with pyridine approximately equals to the sum of the ketone and alkyl hydroperoxide in the solution.

One more advantage of our method is the simultaneous removing the oxidizing reagent ( $H_2O_2$ , peroxy acid) from the sample prior to the GC analysis. This procedure prevents a possible additional oxidation of substrate in the GC (for example, *m*-chloroperoxybenzoic acid efficiently oxidizes alkanes in the GC; whereas this oxidant performs the alkane oxidation in the solution only in the presence of certain metal catalysts). In recent years, our method was successfully used by other chemists in order to detect qualitatively the presence or absence of an alkyl hydroperoxide<sup>23c,25g,l,30</sup> and even to estimate concentrations of all C–H oxygenation products (namely, alkyl hydroperoxide, ketone and alcohol; see, for example, ref. 31).

In summary of this subsection we can say that data on the existence or non-existence of peroxides in hydrocarbon oxidation reactions are very important because this information helps to propose a mechanism of the process. Our method which uses GC analysis before and after reduction with triphenylphosphine allows us to detect and even quantify peroxides in the reaction mixtures.

## 4.3. To oxidize efficiently, manganese catalysts require addition of a carboxylic acid

Manganese complexes containing polydentate N-ligands and chelating Schiff bases as ligands are known to catalyze certain oxidation reactions with peroxides.<sup>32</sup>

In 1988, Wieghardt and co-workers<sup>33a</sup> described the synthesis of a binuclear manganese(IV) complex bearing 1,4,7-trimethyl-1,4,7-triazacyclononane (TMTACN) as ligands (compound 6). A few years later Hage and co-workers applied this compound as catalyst for oxidation of olefins and phenols as well as for bleaching with hydrogen peroxide (see recent review<sup>32e</sup>). In 1998, Shul'pin and Lindsay Smith<sup>33b,c</sup> discovered that compound 6 catalyzes the oxidation by hydrogen peroxide much more efficiently if a small amount of a carboxylic acid is added to the reaction solution. During following years, we demonstrated<sup>33d-r</sup> that the '6/carboxylic acid/H<sub>2</sub>O<sub>2</sub>' combination in acetonitrile solution very efficiently (TONs attained 3300) oxidizes inert alkanes to afford primarily the corresponding alkyl hydroperoxides which are gradually transformed into the more stable ketones (aldehydes) and alcohols. The reaction with alkanes proceeds stereoselectively. It turned out that our system oxidizes not only alkanes but also epoxidizes olefins, transforms alcohols into ketones (aldehydes), sulfides into sulfoxides and decolorizes dyes. The reaction with olefins gave rise to the products of dihydroxylation in addition to the corresponding epoxides. Alkanes, olefins and alcohols were oxidized also in the absence of acetonitrile.<sup>34a</sup> A relevant soluble polymer-bound Mn(IV) complex with N-alkylated 1,4,7-triazacyclononane was used as a catalyst in the  $H_2O_2$ oxygenation of alkanes.<sup>34b</sup> Complex 6 catalyzed the alkane oxidation with other peroxides (*tert*-BuOOH, peroxyacetic acid, Oxone).<sup>33b,c,34c-g</sup>



Complex 6, due to the presence of TMCN ligands, is a remarkable efficient catalyst among all known manganese compounds that catalyze oxidation reactions with peroxides. It is necessary to emphasize that the crucial peculiarity of our system is the presence of a carboxylic acid in a small concentration. Usually we used acetic or oxalic acids. More recently Kilic, Adam and Alsters<sup>35a</sup> used oxalic and ascorbic acids and their sodium salts in H2O2 oxidation of olefins and alcohols. Earlier we demonstrated<sup>33l,n</sup> that certain amino acids used in small amounts (10 catalyst equivalents) strongly accelerate the H<sub>2</sub>O<sub>2</sub> oxidation of cyclohexane catalyzed by complex 6. The efficiency of the co-catalyst dramatically depends on the nature and structure of the acid. Pyrazine-2,3dicarboxylic acid has been found<sup>35b</sup> to be the most efficient co-catalyst whereas picolinic acid is almost inactive in the oxidation of olefins.

Recently Talsi, Bryliakov and co-workers<sup>35*c*,*d*</sup> reported on the olefin oxidation with  $H_2O_2$  catalyzed by aminopyridine manganese complexes which requires the presence of a carboxylic acid. Ribas, Costas and co-workers<sup>35*e*</sup> used complexes containing N<sub>4</sub>-tetradentate ligands derived from chiral bipyrrolidinediamines (for example, compounds **7**, **8**). Addition of acetic acid significantly improves the epoxidation: yields attain almost 100% and ee (in the case of chiral ligands) are up to 54% whereas in the absence of acetic acid the reactions proceeded with conversion <5% and yields <5%.<sup>35*e*</sup>



Neier and co-workers<sup>35*f*</sup> studied alkene epoxidation catalyzed by the manganese complex of a reduced porphyrinogen

macrocycle (9). Addition of acetic acid also improved the yield of styrene epoxide.



Bryliakov, Talsi and co-workers<sup>35g</sup> reported an efficient oxygenation of aliphatic C–H bonds with  $H_2O_2$  catalyzed by the manganese(II) complex **10**. The reaction proceeds in the presence of acetic acid, demonstrates high efficiency (TONs up to 970) and stereoselectivity (up to >99%). The oxidation of bromoalkane **11** gives isomers **12** and **13** with 97:1 ratio.



## 4.4. Efficient catalysts containing copper ions surrounded with globules formed by multidentate ligands

Simple copper salts are typically not powerful catalysts in C–H oxidation with hydrogen peroxide.<sup>30k,36a</sup> Coordination of copper ions with ligands such as pyrazol,<sup>30j</sup> 2,2'-dipyridyl or poly(4-vinylpyridine),<sup>36b</sup> arylhydrazones of  $\beta$ -diketones,<sup>36c-f</sup> 3,3'-(1,4-diazepane-1,4-diyl)bis(1-(bis(pyridin-2-yl)methyl)-amino)propan-2-ol or 3,3'-(1,4-diazepane-1,4-diyl)bis(1-thiomorpholinopropan-2-ol),<sup>36g</sup> hemicryptophane,<sup>36h</sup> Schiff bases,<sup>36i</sup> L-prolinate,<sup>36j</sup> polymers obtained from the reaction of chloromethylated polystyrene with 2-thiomethylbenzimidazole<sup>36k</sup> and scorpionates<sup>36l</sup> give efficient catalysts for oxidation with peroxides.

Simple copper salts and various complexes usually work much better in the oxidation of C–H compounds with other peroxides (TBHP, dialkyl peroxides, peroxyacetic acid).<sup>37</sup> Thus, the salt Cu(MeCN)<sub>4</sub>BF<sub>4</sub> catalyzed the cyclohexane oxidation by TBHP with TON =  $2200.^{37a}$  Under the same conditions, complex 14 containing a chelating N,O-ligand gave 1760 cycles after 5 h. It is noteworthy that complexes 14, 15 and 16 bearing similar N,O-ligands containing also sulfur (which can be considered as models of copper derivatives of certain amino acids) exhibited different activities in cyclohexane oxidation with peroxyacetic acid. The activity dramatically depends on the ligand structure. Complex 14 containing copper( $\pi$ ) ion coordinated to three nitrogens and only one oxygen efficiently catalyzes the oxidation with TON = 480. Compound **15** which contains a ligand with two nitrogens and two oxygens surrounding copper symmetrically gave a relatively lower TON (126). Surprisingly, similar complex **16** (which, however, differs from **15** by its geometry) exhibited only moderate activity (TON = 30).



In recent decades, Pombeiro, Kirillov and co-workers developed multicopper catalysts with an N,O-environment for mild oxidation of alkanes and alcohols by peroxides (see reviews<sup>38a,b</sup>). The tetracopper(II) triethanolaminate catalyst  $[O \subset Cu_4 - \{N(CH_2CH_2O)_3\}_4 (BOH)_4] [BF_4]_2$  (17) exhibited the highest activity in the alkane oxidation with H<sub>2</sub>O<sub>2</sub> in acetonitrile in the presence of an acid.<sup>38c</sup> The nature of the acid promoter (hydrochloric, sulfuric, nitric and trifluoroacetic acid were tested) is a key factor affecting significantly the rate of alkane oxidation. In the presence of HCl the reaction proceeds very rapidly, being one order of magnitude faster (TOF = *ca.* 600  $h^{-1}$ ) than those promoted by the other acids. A mechanism was proposed which involves the formation of hydroxyl radicals via the interaction between H2O2 and catalytically active Cu(1) species, the latter being reversibly generated from 17 under the action of an acid, H<sub>2</sub>O<sub>2</sub> and water. Complex  $17^{38d}$  and relevant mono- (18) and dicopper(II) (19) aminopolyalcoholates<sup>38e</sup> turned out to be good catalysts in oxidation of alkanes and alcohols with TBHP in the absence of any acid. It is interesting that compound 18 was significantly more active than 19 in the oxidation of both alkanes and alcohols.





Very recently, Levitsky, Bilyachenko and co-workers<sup>38/</sup> synthesized a cage-like metallasilsesquioxane with unusual structure in which two copper(II) ions are surrounded by a siloxane globule (compound **20**, where  $\phi$  is phenyl ring). This compound is an excellent catalyst for the oxygenation of benzene to phenol with H<sub>2</sub>O<sub>2</sub> in the presence of nitric or trifluoroacetic acid as well as oxidation of alcohols to the corresponding ketones or aldehydes with TBHP in the absence of an acid.<sup>38/</sup> Analogous globules containing four (for example, compound **21**; for the method of its preparation, see ref. 38*g*) or six copper ions are also active in oxidation catalysis. The oxidation of 1-phenylethanol catalyzed by **21** occurs with the formation of acetophenone in 90% yield.<sup>38*h*</sup>



solution, and nitric acid in low concentration is a necessary component of the reaction mixture. The acid apparently promotes partial decoordination of some ligands, and as a result a substrate and oxidant can more easily approach the metal center. We can compare the acid with an oyster knife which opens the valves of the mollusk shell.

#### A magic co-catalyst: pyrazinecarboxylic acid (PCA)

It is known long ago that the interaction of metal derivatives of  $\alpha$ -pyridinecarboxylic (picolinic) acid, pyrazinecarboxylic acid and relevant amino acids with hydrogen peroxide affords stable peroxo complexes.<sup>39a</sup> For example, in the 1980s Mimoun and co-workers described the synthesis of such complexes of vanadium.<sup>39b</sup> It was shown that these compounds are able to *stoichiometrically* oxygenize hydrocarbons. Later we demonstrated that pyrazinecarboxylic acid (see reviews on accelerating effect of PCA<sup>39c,d</sup>) as well as certain relevant compounds<sup>39e,f</sup> are very efficient co-catalysts in oxidation reactions with hydrogen peroxide.

#### 5.1. The efficient reagent: "H<sub>2</sub>O<sub>2</sub>-vanadium complex-PCA"

In 1993, we discovered that the vanadate anion 22 (*n*-Bu<sub>4</sub>N)-[VO<sub>3</sub>] (as well as various other vanadium-containing derivatives; for example, compounds 23, 24, see below) efficiently catalyzes the oxidation of organic compounds (alkanes, olefins, aromatic hydrocarbons and alcohols) by  $H_2O_2$  in acetonitrile solution in the presence of a small amount of pyrazine-2-carboxylic acid (PCA  $\equiv$  pcaH, where pca<sup>-</sup> is the anion of PCA) as the co-catalyst and then investigated this convenient reagent in detail.<sup>14c,40</sup>



Catalysis by polynuclear metal complexes of oxidation processes often requires addition of a strong acid. Examples based on copper derivatives have been described above. Another representative of such compounds consists of cobalt and iron ions  $[Co_4Fe_2OSae_8]$  (H<sub>2</sub>Sae is salicylidene-2-ethanolamine) and is an efficient catalyst for alkane oxidation with hydrogen peroxide.<sup>38i</sup> The reaction occurs in acetonitrile Only negligible amounts of products were obtained in these reactions in the absence of PCA. For the maximum reaction rate some access of PCA over vanadium compound should be used. It is noteworthy that isolated vanadium complexes bearing pca ligands 25 and  $26^{41a}$  are less efficient catalysts in comparison with the "22–PCA" combination at a 22 : PCA ratio around 1:4. Addition of a few equivalents of PCA to the

solution of catalysts **25** or **26** significantly improves the oxidation.



We found two examples which demonstrate the accelerating role of PCA in the transformations of isoeugenol into vanillin catalyzed by monovanadate  $(n-Bu_4N)[VO_3]$  (Fig. 5)<sup>14c</sup> and cyclohexane into oxygenates catalyzed by the divanadium complex **24** (Fig. 6).<sup>41b</sup> The dependence of  $W_0$  on [PCA]<sub>0</sub> shown in Fig. 6 is described by the following formula

$$W_0 = \frac{\alpha [\text{PCA}]_0}{1 + \beta [\text{PCA}]_0 + \gamma [\text{PCA}]_0^2}$$
(7)

where  $\alpha = 5.3 \times 10^{-2} \text{ s}^{-1}$ ,  $\beta = 0$ ,  $\gamma = 1.1 \times 10^7 \text{ M}^{-2}$  and is presented in Fig. 6 by a dotted curve 1a.<sup>41b</sup>

It can be seen in Fig. 7 that the activity of complex 24 is two times higher than the activity of mononuclear vanadium(v) complexes such as vanadate (22) or vanadatrane (23). Thus, the activity of complex 24 per vanadium(v) ion is equal to those of mononuclear complexes: the TON values per vanadium ion are 5350, 5000 and 5700 for complexes 24, 22 and 23, respectively, after 360 min at a catalyst concentration of  $1.0 \times 10^{-5}$  M (Fig. 7). At a lower concentration of each catalyst ( $1.0 \times 10^{-6}$  M) the corresponding TONs per vanadium ion for the same complexes 24, 22 and 23 are extremely high for the oxidation of an inert saturated hydrocarbon: 19 000, 20 000 and 19 000, respectively,



**Fig. 5** Dependences of the initial rates of the isoeugenol (initial concentration 0.2 M) consumption and vanillin accumulation in the oxidation of isoeugenol with  $H_2O_2$  (initial concentration 0.4 M) catalyzed by (*n*-Bu<sub>4</sub>N)[VO<sub>3</sub>] (1 × 10<sup>-4</sup> M). Solvent was MeCN, temperature 40 °C. The Figure is based on the material from ref. 14c.



**Fig. 6** Dependence of the initial oxidation rate  $W_0$  on initial concentration of PCA (curve 1) in the cyclohexane (0.40 M) oxidation with  $H_2O_2$  (0.40 M) catalyzed by complex **24** ( $2.0 \times 10^{-5}$  M) in acetonitrile at 50 °C. Concentrations of oxygenates (sum of cyclohexanol and cyclohexanone) were measured after reduction with PPh<sub>3</sub>. The dotted curve 1a corresponds to the calculated dependence in accordance with eqn (7). Adapted from ref. 41b with permission of The Royal Society of Chemistry.



**Fig. 7** Kinetic curves of product accumulation in the cyclohexane oxidation catalyzed by various vanadium-containing systems: complex **24**, vanadate anion (*n*-Bu<sub>4</sub>N)[VO<sub>3</sub>] **(22)** and oxovanadium(v) triethanolaminate (vanadatrane, compound **23**). *Conditions*: [catalyst]<sub>0</sub> =  $1.0 \times 10^{-5}$  M; [PCA] =  $6 \times 10^{-4}$  M; [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 0.4 M, [H<sub>2</sub>O]<sub>total</sub> = 0.76 M; [cyclohexane]<sub>0</sub> = 0.40 M; solvent MeCN; 50 °C. Adapted from ref. 41*b* with permission of The Royal Society of Chemistry.

after 1000 min. Under these conditions, for the catalysis by complex 22 the initial TOF =  $2100 \text{ h}^{-1}$ .

The bis(maltolato)oxo vanadium complex both in a soluble form 27a and anchored to chemically modified silica gel (27b; Fig. 8), when used in combination with PCA, catalyzes the oxidation of benzene to phenol and alkanes to the corresponding alkyl hydroperoxides with  $H_2O_2$  at 40–50 °C.<sup>41c</sup> A comparison of selectivity parameters obtained for isooctane (2,2,4-trimethylpentane) in the oxidation reactions catalyzed by the soluble vanadium complex and by the heterogenized catalyst revealed noticeable difference. Thus, parameter 1°:2°:3° (relative normalized reactivities of hydrogen atoms at primary,



Fig. 8 Oxidation of isooctane by the  $27\mathchar`-PCA\mathchar`-H_2O_2$  reagent. The Figure is based on material from ref. 41c.

secondary and tertiary carbons) in the case of soluble complex was equal to 1:4.6:4.2, whereas complex 27b surrounded by a silica surface gave a different distribution: 1:2.8:5.6 (Fig. 8). The change in selectivity can be explained by steric hindrance around the vanadium reaction center in the anchored compound 27b.

The proposed mechanism of the oxidation by the "H<sub>2</sub>O<sub>2</sub>vanadium derivative-PCA" reagent<sup>40m,n,42</sup> involves the V(v)-V(IV) manifold in two crucial steps: the decomposition of a transient peroxovanadium(v) complex to produce a peroxyl radical HOO' and a V(w) species and further interaction of this V(w)complex with a second hydrogen peroxide molecule to afford a hydroxyl radical HO' which then attacks the hydrocarbon substrate. We assumed<sup>40m</sup> that PCA coordinated to the vanadium center in the form of the pca<sup>-</sup> ligand (PCA =  $H^+pca^-$ ) facilitates the proton transfer between the hydrogen peroxide molecule coordinated to vanadium and oxo or hydroxy ligands of the vanadium complex: " $H_2O_2\cdots O=V$ "  $\rightarrow$  "HOO-V-OH". This "robot's arm mechanism" (Fig. 9)<sup>40m</sup> may have analogies in enzyme catalysis (vanadium is known to promote hydroxyl radical formation in living organisms). It is found that a vanadium complex with one pca (or pca- or PCA) fragment and one H<sub>2</sub>O<sub>2</sub> ligand is the precursor to the species responsible for the radical HOO' generation. Studies of the mechanism of radicals generation and particularly of the "robot's arm mechanism" by the DFT method led Khaliullin,



**Fig. 9** Schematically depicted idea of the "robot's arm mechanism" for proton transfer between ligands at vanadium ion. Adapted from ref. 40*m* with permission of The Royal Society of Chemistry.

Bell and Head-Gordon<sup>42d</sup> to the conclusion that "the generation of HOO' radicals cannot occur via cleavage of a V-OOH bond in the complex formed directly from the precursors" because the activation barrier for this process is too high. Instead, peroxyl radicals are formed via a sequence of additional steps and diperoxo complexes are involved in this transformation. Besides, the conversion of the precursors requires hydrogen transfer from H<sub>2</sub>O<sub>2</sub> to a vanadyl group, and the calculations by Bell and co-workers showed "that direct transfer has a higher barrier than pca-assisted indirect transfer. Indirect transfer occurs by migration of hydrogen from coordinated  $H_2O_2$  to the oxygen of a pca ligand connected to the vanadium atom" (Fig. 9). In Bell's variant of our mechanism, the hydrogen transfer from a coordinated hydrogen peroxide molecule to a vanadyl group becomes the rate-determining step. The experimentally measured<sup>40m</sup> activation energy (63-80 kJ mol<sup>-1</sup>) agreed very well with calculated<sup>42d</sup> values  $(67-81 \text{ kJ mol}^{-1})$ . It is important to note that the theoretical calculation suggested that it might not be possible to find a better co-catalyst than PCA.

An alternative "water-assisted mechanism" for proton migration in the vanadium complex has been proposed more recently by Kuznetsov and co-workers42h on the basis of DFT calculations. This pathway includes the molecule H<sub>2</sub>O as a part of a six-membered transition state.42j A water-assisted mechanism of proton transfer turned out to be even more effective than the robot's arm mechanism. In the waterassisted mechanism the rate limiting step is the H-transfer from ligated H<sub>2</sub>O<sub>2</sub> to an oxygen-containing ligand. The pca ligand plays in this case a key role as a stabilizer of transitionstate V(v) species involved into the rate-limiting stage. The presence of PCA dramatically accelerates the reaction of the H<sub>2</sub>O<sub>2</sub> decomposition as confirmed by DFT calculations: the activation barrier of the HO' formation in the presence of PCA is by 9.6 kcal mol<sup>-1</sup> lower than that in the absence of PCA.42h,i

Soluble and supported vanadium complexes have been reported to catalyze the oxidation of saturated hydrocarbons with molecular oxygen at relatively high temperatures and PCA improves the yields of oxygenates.<sup>30l,43*a*-*d*</sup> It is noteworthy that the activity of the catalyst  $[VO(mal)_2]$  in cyclohexane oxidation is noticeably promoted by PCA while picolinic acid was an almost inactive co-catalyst.<sup>43*a*</sup> Similarly, the addition of PCA accelerates the alkane oxidation with molecular oxygen catalyzed by supported complexes of palladium<sup>43*e*</sup> and copper.<sup>43/g</sup>

## 5.2. PCA greatly improves oxidation reactions catalyzed by various other metal ions

After discovery of the remarkable accelerating role of PCA in vanadium-catalyzed oxidation with hydrogen peroxide we decided to explore the possibility of this additive to improve analogous reactions catalyzed by other metals. We found that certain iron complexes, for example, iron(m) diacetate hydroxide Fe(OAc)<sub>2</sub>(OH),<sup>26b</sup> compounds **28**,<sup>44a</sup> **29**<sup>44b</sup> and **30**<sup>44c</sup> require addition of PCA to catalyze efficiently hydrocarbon oxidation. Thus, products are not formed in the hydrocarbon oxidation catalyzed by ferrocene<sup>44d,e</sup> if PCA is absent (see Fig. 10). The kinetic analysis of the benzene oxygenation gave the equation for initial reaction rate:

$$W_{0} = \frac{\alpha [\text{PCA}]_{0}^{2}}{(1 + \beta [\text{PCA}]_{0}^{2})^{2}}$$
(8)



For conditions of experiments shown in Fig. 10 the values  $\alpha = 25 \text{ M}^{-1} \text{ s}^{-1}$  and  $\beta = 7.8 \times 10^4 \text{ M}^{-2}$ . It can be seen that the simulated curve coincides closely with the experimental curve.

It is noteworthy that in some cases PCA can play the role of inhibitor of oxidation reactions. For example, Reedijk and coworkers<sup>45a</sup> studied the functionalization of alkanes and olefins with  $H_2O_2$  catalyzed by the complex {[Fe(mebpa)Cl]<sub>2</sub>O}(ClO<sub>4</sub>)<sub>2</sub> [mebpa = *N*-(2-methoxyethyl)-*N*,*N*-bis(pyridin-2-yl-methyl)amine] and found that "addition of 2 equiv. of 2-pyrazinecarboxylic acid (Hpca) to the catalytic mixture results in the complete inhibition of the oxidation of alkanes". Analogously, the



**Fig. 10** Dependence of the initial rate  $W_0$  of oxygenates accumulation in the benzene oxidation with  $H_2O_2$  catalyzed by ferrocene in MeCN on the initial concentration of PCA [in the intervals  $(0-10) \times 10^{-3}$  M and  $(0-2) \times 10^{-3}$  M]. *Conditions*: [FeCp<sub>2</sub>]<sub>0</sub> = 5.0 × 10<sup>-4</sup> M, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 1.28 M, [benzene]<sub>0</sub> = 0.56 M, 50 °C. Dotted curves present the simulated dependence obtained using eqn (8). The Figure is based on the material from ref. 44e.

addition of 2 equiv. of PCA to the catalytic mixture resulted in a dramatically decreased catalytic activity in all alkene oxidation reactions. It has been shown that PCA binds readily to iron( $\Pi$ ) to form an inactive species, {[Fe(mebpa)]<sub>2</sub>O(pca)}- $(ClO_4)_3$  containing a (µ-oxido)(µ-carboxylato) diiron(m) core. The same group found<sup>45b</sup> that  $bis(\mu-alkoxo)$ -bridged dinuclear iron(III) complexes with the ligands 1-(2-hydroxyethyl)pyrazole (Hnhep) and 1-(2-hydroxyethyl)-3,5-dimethylpyrazole (Hnhed),  $[Fe(nhep)Cl_2(EtOH)]_2$  and  $[Fe(nhed)Cl_2]_2$  are inactive in cyclohexane hydroxylation. Addition of PCA (or other relevant compounds) did not improve the oxidation. Further, the complexes bearing pca ligands,  $[Fe(pca)_2(py)_2] \cdot py (31)$  and  $Na_2\{[Fe(pca_3)]_2O\}$ . 2H2O·CH3CN (32) have been isolated and their reaction with  $H_2O_2$  was studied.<sup>25h</sup> The complexes were active as catalysts in the alkane oxidation although the TON values were not high (around 20).



Pombeiro and co-workers<sup>46</sup> studied oxidation reactions of hydrocarbons and alcohols with  $H_2O_2$  or TBHP catalyzed by various new complexes of transition metals bearing chelating ligands **33–49**. Opposite effects were found for PCA additive in cyclohexane oxidation with  $H_2O_2$  catalyzed by the iron and copper complexes **33–37**.<sup>46b</sup> Thus, while the reactions in the

absence of PCA gave product yields 2.5, 8.3, 10.3, 12.2 and 8.6%, respectively, the addition of PCA led to the following yields: 17.5, 0.4, 0.2, 15.9 and 0.2%. It means that PCA is strong promoting co-catalyst in the cases of iron complex **33**. It does not practically affect the reaction when iron complex **36** is used. It is noteworthy that PCA turned out to be a strong inhibitor in the cases of copper complexes **34**, **35** and **37**. In the cyclohexane oxidation catalyzed by complexes **38–42** the same tendency was found as for compounds **33–37**: yields of oxygenates were 9.0, 12.3, 1.0, 3.1 and 9.5%, respectively, for complexes **38–42** in the absence of PCA and 0.2, 0.2, 20.5, 0.4 and 14.1% in the presence of 200 µmol of PCA per 20 µmol of the catalyst.<sup>46c</sup> Thus, it can be concluded that in such reactions PCA is a good co-catalyst in combination with iron

complexes and is a strong inhibitor in the case of catalysis by copper compounds. Comparison of the PCA effect on the yield of products for compounds **43–47**: in the absence of PCA: 9.8, 4.3, 4.8, 1.3 and 4.0; in the presence of 5 equivalents of PCA: 0.2, 0.5, 13.8, 17.1 and 11.0%.<sup>46d</sup> The oxidation of 1-phenylethanol catalyzed by complex **45** in the presence of PCA is very fast, giving the acetophenone product (TOF = 4470 h<sup>-1</sup>) in good yield (75%). Martins *et al.*<sup>46e</sup> found that the hydrotris(pyrazol-1-yl)methane iron(II) complex [FeCl<sub>2</sub>{ $\eta^3$ -HC-(pz)<sub>3</sub>}] (**48**, pz = pyrazol-1-yl) immobilized on commercial or desilicated zeolite, catalyzes the oxidation of cyclohexane with hydrogen peroxide. The reaction is greatly improved by addition of PCA. In the catalysis by the complex [Fe<sup>III</sup>(gma<sup>-</sup>)-(PBu<sub>3</sub>)] (**49**) containing the non-innocent ligand glyoxal-bis-





 $(2\text{-mercaptoanil})^{47a}$  the yield of cyclopentane oxygenates was increased from 0.7 to 13.0% when PCA (0.05 mmol per 0.01 mmol of **49**) was introduced into the reaction solution.<sup>46a</sup>

Oxidation of C-H compounds with peroxides catalyzed by derivatives of certain other metals also can be improved by addition of PCA. We demonstrated<sup>331</sup> that 2,3-pyrazinedicarboxylic acid is a unique co-catalyst in the catalyzed by complex 6 oxidation of cyclohexane by H<sub>2</sub>O<sub>2</sub>, while pyrazinecarboxylic acid is less efficient. It is noteworthy that picolinic acid is almost inactive. Thus, only a heteroaromatic carboxylic acid with a specific structure can interact with the catalyst reaction center enhancing its activity. Methyltrioxorhenium (MTO) in combination with PCA and anhydrous H<sub>2</sub>O<sub>2</sub> forms a versatile system for the oxidation of alkanes and arenes.47b The mononuclear complex  $[Cu(pca)_2]$  and supported materials therefrom catalyze the oxidation of cyclohexene by H<sub>2</sub>O<sub>2</sub> in acetone to give cyclohexene oxide, 2-cyclohexen-1-ol, 2-cyclohexen-1-one, and 1,2-cyclohexanediol.<sup>47c</sup> The analogous Co(II)pca derivatives have been synthesized and show similar features in cyclohexene oxidation. The effect of PCA addition has been studied in the oxidation of cycloheptane<sup>47d,e</sup> by the OsCl<sub>3</sub>-H<sub>2</sub>O<sub>2</sub> system. As in some other cases, in this reaction the addition of PCA has a negative effect, reducing the total yield of cycloheptanol and cycloheptanone from 15 to 7%.

# 6. Osmium is a record-holder, vanadium is in second place

Some time ago in the course of our systematic studies of hydrocarbon oxygenations with peroxides we decided to test osmium complexes as catalysts. We found that simple osmium salts (OsCl<sub>3</sub>, Na<sub>2</sub>OsCl<sub>6</sub>) are good catalysts for the alkane oxidation with hydrogen peroxide. The oxidation of cycloheptane (0.4 M) in MeCN with  $H_2O_2$  (1.0 M) in the presence of OsCl<sub>3</sub>  $(1.0 \times 10^{-3} \text{ M})$  gave after 3 h cycloheptanol (0.05 M) and cycloheptanone (0.013 M), the total TON being 63. Comparison of the chromatograms of the reaction samples before and after their treatment with  $PPh_3$  (for this method, see subsection 4.2) demonstrated that concentrations of alkyl hydroperoxides were very low. Thus, under these conditions all cycloheptyl hydroperoxide decomposed in the course of the oxidation reaction. Addition of a small amount of pyridine (0.125 M) gave rise to a noticeable increase in the yield and to the predominant formation of the ketone (after 90 min: cycloheptanol, 0.020 M; cycloheptanone, 0.092 M; TON, 112).47d,e The simple chloride OsCl<sub>3</sub> catalyzes the oxidation of alcohols. Thus, the oxidation of 2-cyanoethanol with hydrogen peroxide produces the corresponding aldehyde and acid in yield of products up to 90% and TON up to 1500.<sup>47f,g</sup> Introduction of a  $\pi$ -coordinated olefin to a carbonyl osmium(0) complex led to noticeable enhancement of activity: (2,3-ŋ-1,4-diphenylbut-2-en-1,4-dione)undecacarbonyl triangulo-triosmium (50) was a powerful catalyst for the

alkane oxidation with hydrogen peroxide (TONs were up to 2400).  $^{47h,i}$ 



A bit later we discovered a great efficiency of other osmium catalysts in alkane oxidation with H<sub>2</sub>O<sub>2</sub>. Addition of pyridine sufficiently improved the reactions. Organometallic osmium derivatives of different structures 51-56 were used as catalysts. In the alkane oxidation osmium carbonyl 51 gave<sup>29e</sup> very high TON = 60 000 and TOF = 24 000  $h^{-1}$ . The carbonyl hydride 52 with the similar structure was less efficient (TON = 1400 and TOF = 480 h<sup>-1</sup>).<sup>29f</sup> Decamethylosmocene 53 exhibited a very high activity calculated per metal ion (TON = 51 000 and TOF = 6000  $h^{-1}$ ).<sup>47j</sup> Finally, we found that the *p*-cymene osmium complexes are very efficient catalysts of hydrocarbon oxidation. Under identical conditions (concentration of the catalyst was 5  $\times$  10<sup>-5</sup> M) TON values for compounds 54, 55 and 56 after 5.5 h were 11 100, 980 and 7500, respectively.47k At a very low concentration of the catalyst 54 ( $1 \times 10^{-7}$  M; entry 1 in Table 1) the TON (after subtracting the concentration of products formed in the reaction in the absence of 54) was 200 200. The dinuclear p-cymene chloride complex 54 turned out to be the recordholder47k among all studied homogeneous catalysts. The activity of the mononuclear p-cymene chloride complex 57 is of the same order of magnitude because at its concentration 2  $\times 10^{-7}$  M the TON value was 90 000 (see Table 1, entry 2). The initial TOF for compound 57 (9200) was even higher than this value per Os ion for 54 (7000). Table 1 (entries 1-4) shows that osmium complexes 54, 57, 51 and 53 bearing different ligands catalyze the alkane oxygenation with almost the same TOF value (6000-9200). Thus, we can conclude that the nature of ligands surrounding the osmium ion does not dramatically affect the catalyst power.



**Dalton Transactions** 



It is necessary to emphasize that activities (TON and TOF values; see section 2 and ref. 12) of different soluble catalysts can be compared only roughly, using the orders of magnitude. Indeed, for precise comparison of TONs and TOFs all experiments with various catalysts must be carried out under the same conditions (catalyst concentration, concentrations of all reactants, temperature, the reaction time). For example, Table 1 can give only a rough estimate of relative activities for complexes 54, 57, 51 and 53 because TON and TOF parameters were measured for slightly different conditions. Nevertheless, the data of Table 1 unambiguously demonstrate that osmium and vanadium complexes are the most active catalysts in hydrogen peroxide oxidation of alkanes if pyridine and PCA, respectively, are present in the reaction solution. Vanadium compounds in combination with PCA give also very efficient catalytic systems for the oxidation reactions with hydrogen peroxide (see subsection 5.1). However, TONs and TOFs in this case are a bit lower (compare entries 5-7 and entries 1-4 in Table 1). It is noteworthy that initial TOFs for the oxidation by the "H<sub>2</sub>O<sub>2</sub>-vanadium derivative-PCA" reagent (Table 1, entries 5-7) are comparable. Due to this we can conclude that, like Os-catalyzed oxidations, the alkane oxygenation by the "H<sub>2</sub>O<sub>2</sub>vanadium derivative-PCA" reagent is not very sensitive to the nature of ligands at the vanadium ion. It should be also noted that in the dinuclear vanadium complex 24 both vanadium reaction centers work independently one from another because TONs and TOFs per ion are approximately equal for (n-Bu<sub>4</sub>N)[VO<sub>3</sub>] and 24 (Table 1, entries 6 and 7). Complexes of other transition metals (Table 1, entries 8-14) are noticeably less efficient catalysts in comparison with compounds of vanadium and especially osmium. The polynuclear bimetallic complex [Co<sub>4</sub>Fe<sub>2</sub>OSae<sub>8</sub>]·4DMF·H<sub>2</sub>O, where H<sub>2</sub>Sae is salicylidene-2-ethanolamine in the presence of nitric acid (Table 1, entry 12) gave moderate TONs but very high TOFs.

In contrast to certain osmium or vanadium complexes, organometallic derivatives of rhodium turned out to be very sensitive to the nature of the ligands in the catalyst.<sup>47m</sup> We found that hexanuclear rhodium carbonyl cluster **58** catalyzes

benzene hydroxylation with hydrogen peroxide in acetonitrile solution. Phenol and (in lower concentration) quinone are formed with the maximum attained total yield and turnover number 17% and 680, respectively. Other tested rhodium carbonyl complexes, containing cyclopentadienyl ligands, **59** and **60**, are less efficient catalysts (TON values were 130 and 150, respectively). It is noteworthy that cyclopentadienyl derivatives of rhodium which do not contain the carbonyl ligands, **61**, **62** and **63**, turned out to be absolutely inactive (TON = 0) in the benzene hydroxylation.



# 7 Non-transition metals: one ligand helps other ligand to generate hydroxyl radicals

Derivatives of various *transition* metals are known as excellent catalysts for both epoxidation of olefins<sup>48</sup> and oxygenation of alkanes and aromatics.<sup>1</sup> The opposite situation can be found for the compounds of *non-transition* metals. Only a few number of epoxidation and benzylic oxidation reactions catalyzed by non-transition metals are known, for example, catalysis by compounds of As,<sup>49a</sup> Sn,<sup>49b</sup> Ca,<sup>49c</sup> and Bi.<sup>49d-f</sup> Zaburdaeva, Dodonov and Stepovik described the oxidation of C–H bonds with peroxides of Al and Bi.<sup>49g</sup> Dodonov and coworkers proposed the participation of radicals in the oxidation of alkenes by the (*t*-BuO<sub>3</sub>)Al/*t*-BuOOH system.<sup>49h</sup>

Table 1 Cyclohexane oxidation with H<sub>2</sub>O<sub>2</sub> in acetonitrile catalyzed by various metal complexes

Entry	Catalyst	Concentration/M	Co-catalyst	t/h	TON	$\mathrm{TON}_{\mathrm{per ion}}/\mathrm{h}^{-1}$	Initial TOF/h <sup>-1</sup>	Initial TOF <sub>per ion</sub> /h <sup>-1</sup>	Yield <sup>a</sup> (%)	Ref.
1	54	$1 \times 10^{-7}$	Pvridine	24	200 200	100 100	14 000	7000	2	47 <i>k</i>
2	57	$2 \times 10^{-7}$	Pyridine	24	90 000	90 000	9200	9200	2	47l
3	$51^b$	$5 \times 10^{-6}$	Pyridine	13	60 000	20 000	24 000	8000	56	29 <i>e</i>
4	$Cp_{2}^{*}Os^{c}(53)$	$1 \times 10^{-6}$	Pyridine	24	51000	51 000	6000	6000	6	47j
5	$(n-\mathrm{Bu}_4\mathrm{N})[\mathrm{VO}_3]^d$	$1 \times 10^{-5}$	PCA	6	5000	5000	700	700	12	40m, 41b
6	$(n-\mathrm{Bu}_4\mathrm{N})[\mathrm{VO}_3]^d$	$1 \times 10^{-6}$	PCA	17	20000	20 000	2100	2100	5	40m, 41b
7	24	$1 \times 10^{-6}$	PCA	17	38 000	19 000	3300	1650	10	41 <i>b</i>
8	$17^e$	$5 \times 10^{-5}$	HCl	2	200	50	600	150		38 <i>c</i>
9	$Cu(MeCN)_4[BF_4]^f$	$5 \times 10^{-5}$	None	5	2200	2200			14	37 <i>a</i>
10	$[Mn_2L_2O_3][PF_6]^g$	$3 \times 10^{-5}$	MeCOOH	2	3300	1650	2700	1350	46	33 <i>b</i> –е
11	$[Co_4Fe_2OSae_8]^{b,h}$	$5 \times 10^{-5}$	$HNO_3$	6	2280	380			46	38 <i>i</i>
12	$\left[\operatorname{Co}_{4}\operatorname{Fe}_{2}\operatorname{OSae}_{8}\right]^{h}$	$11 \times 10^{-5}$	HNO <sub>3</sub>	5	720	120	11 200	1870	21	38 <i>i</i>
13	Co <sub>4</sub> Fe <sub>2</sub> OSae <sub>8</sub> <sup>h</sup>	$4.4 \times 10^{-5}$	HNO <sub>3</sub>	5	3570	600			26	38 <i>i</i>
14	$Cp_2Fe^i$	$1  imes 10^{-4}$	PCA	1.5	1200	1200	1800	1800	32	44d

<sup>*a*</sup> Yield was based on cyclohexane in cases when its amount was lower than the oxidant amount. <sup>*b*</sup> Cyclooctane was used instead of cyclohexane. <sup>*c*</sup> Decamethylosmocene (compound 53), Cp\* is pentamethylcyclopentadienyl. <sup>*d*</sup> The efficient oxidizing reagent (*n*-Bu<sub>4</sub>N)[VO<sub>3</sub>]/PCA/H<sub>2</sub>O<sub>2</sub> (PCA is pyrazine-2-carboxylic acid) was initially described in ref. 40*a*-*c*. <sup>*e*</sup> Compound 17 is tetracopper(II) triethanolaminate complex [OCCu<sub>4</sub>-{N(CH<sub>2</sub>CH<sub>2</sub>O<sub>3</sub>]<sub>4</sub>(BOH)<sub>4</sub>][BF<sub>4</sub>]<sub>2</sub>. <sup>*f*</sup> Complex Cu(MeCN)<sub>4</sub>BF<sub>4</sub>; *t*-BuOOH was used instead of H<sub>2</sub>O<sub>2</sub>. <sup>*g*</sup> L = 1,4,7-trimethyl-1,4,7-triazacyclononane. <sup>*h*</sup> [Co<sub>4</sub>Fe<sub>2</sub>OSae<sub>8</sub>] is complex [Co<sub>4</sub>Fe<sub>2</sub>OSae<sub>8</sub>]·4DMF·H<sub>2</sub>O, where H<sub>2</sub>Sae = salicylidene-2-ethanolamine. <sup>*i*</sup> Ferrocene, Cp is cyclopentadienyl ligand.

Mandelli, Sheldon, Schuchardt and co-workers developed olefin epoxidation with hydrogen peroxide catalyzed by aluminum oxide<sup>50*a*-*f*</sup> and certain soluble aluminium salts.<sup>50*g*,*h*</sup> Jacobs, Pescarmona and co-workers<sup>50*i*-*l*</sup> as well as other authors<sup>50*m*</sup> described the epoxidation with H<sub>2</sub>O<sub>2</sub> catalyzed by gallium compounds. Recently, Goldsmith and co-workers <sup>50*n*</sup> reported on the selective epoxidation of olefins with peroxyacetic acid catalyzed by the soluble complex [Ga(phen)<sub>2</sub>Cl<sub>2</sub>]Cl (phen = 1,10-phenanthroline).

A few years ago we began our studies on oxidation of completely saturated hydrocarbons with peroxides catalyzed by nontransition metal compounds. It has been found that solid aluminum oxide<sup>51a</sup> and soluble aluminum nitrate<sup>51b</sup> efficiently promote the alkane hydroperoxidation with hydrogen peroxide. It has been proposed that interacting with an aluminum derivative hydrogen peroxide decomposes to afford hydroxyl radicals which attack the alkane molecule. At that time, a question arose: how aluminum can stimulate the hydroxyl radical generation? This was a puzzle. The first idea was not original and not pleasant: admixtures of iron ions in aluminum compounds stimulate the H<sub>2</sub>O<sub>2</sub> decomposition via a Fenton-like mechanism. Indeed, it was reasonable to propose such a route for the catalysis by montmorillonites which contain some amount of iron.<sup>51a</sup> However, there was no wish to believe such a route with the participation of "pure" aluminum oxide or nitrate. Determination of iron content in alumina by inductively coupled plasma atomic emission spectroscopy (ICP) method demonstrated<sup>51c</sup> that the amount of iron in alumina employed in the limonene epoxidation equals to 56  $\pm$  5 mg kg<sup>-1</sup> (ppm) corresponding to 0.0056% (w/w). Is this amount sufficient for the noticeable catalytic generation of hydroxyl radicals from hydrogen peroxide? I tried to invent some other possible routes. The first "reasonable" idea was the following: the hydroxyl radical is generated via the homolysis of the O-O bond in the fragment O-OH which

is bound to the  $Al^{3+}$  ion. The driving force of this process might be weakening the O–O bond when one of two oxygens is bound to aluminum (*L* is ligated H<sub>2</sub>O molecule):

$$[L_5 \text{Al-O-OH}]^{2+} \rightarrow [L_5 \text{Al-O}]^{2+} + \text{HO}^{-}$$

A colleague Maxim Kuznetsov calculated<sup>51d</sup> by DFT method the change of Gibbs free energy for the O–O bond rupture in the species  $[L_5Al-O-OH]^{2+}$  in solution. It turned out to be enormously high: 39.9 kcal mol<sup>-1</sup>. This value is even a bit higher than the energy in free hydrogen peroxide molecule (39.4 kcal mol<sup>-1</sup>). It became clear that we should discount such a mechanism. I then proposed a second route: the reaction occurs *via* the reduction of aluminum to the oxidation state (+II). Checking this idea by DFT calculation showed this idea was also wrong: the change of Gibbs free energy for splitting the Al–OOH bond was  $\Delta G = 85.8$  kcal mol<sup>-1</sup> for the reaction

$$[L_5 \text{Al}^{\text{III}}\text{-OOH}]^{2+} \rightarrow [L_5 \text{Al}^{\text{II}}]^{2+} + \text{HOO}^{-1}$$

Fortunately, at that moment another colleague Yuriy Kozlov remembered the main idea of the mechanism proposed by him many years ago for the iron-catalyzed decomposition of hydrogen peroxide.<sup>51e</sup> That scheme was a modification of the Haber–Weiss mechanism (see, for example, ref. 15*b*, 51*f*)



**Scheme 1** A mechanism of the  $H_2O_2$  decomposition on iron ions proposed by Kozlov<sup>51e</sup> and modified in ref. 51*d*. The figure is based on the material from ref. 51*e*, *d*.



Scheme 2 A catalytic cycle proposed for the Al-catalyzed decomposition of hydrogen peroxide. The scheme is based on the material from ref. 51d.



Fig. 11 A schematic presentation of the mechanisms for  $H_2O_2$  activation with the participation of the Fe<sup>II</sup>–Fe<sup>III</sup> manifold (top) and the easily oxidizable ligand  $HOO^-$  at  $AI^{III}$  (bottom).

proposed for a Fenton-like system. The Haber–Weiss route includes two key stages:

$$\begin{split} & [L_6 {\rm Fe}^{\rm III}]^{2+} + {\rm H_2O_2} \to [L_5 {\rm Fe}^{\rm II}({\rm OH})]^{2+} + {\rm HOO}^{\,\cdot} \\ & [L_6 {\rm Fe}^{\rm II}]^{2+} + {\rm H_2O_2} \to [L_5 {\rm Fe}^{\rm III}({\rm OH})]^{2+} + {\rm HO}^{\,\cdot} + {\rm H_2O}^{\,\cdot} \end{split}$$

In the Kozlov mechanism, in a chain initiation stage *two* hydrogen peroxide fragments interact with one iron ion to afford the hydroxyl radical:

$$[Fe^{III}]^{2+} + 2H_2O_2 \rightarrow [Fe^{II}]^{2+} + HO \ \cdot + H_2O + O_2 + H^+$$

The reaction with the transition state is presented in Scheme 1.

Kuznetsov applied this idea to the aluminum complex  $[L_6 \text{Al}]^{3+}$  and his DFT calculations<sup>51d</sup> led to the breathtaking result! The calculations predicted that hydrogen peroxide

molecule coordinated to aluminum ion in complex 64 (Scheme 2) is highly activated toward the homolytic O-O bond cleavage compared to free molecule: the  $\Delta G$  value for O-O bond splitting in the coordinated molecule H2O2 within complex 64 is only 6.1 kcal mol<sup>-1</sup> vs. 39.4 kcal mol<sup>-1</sup> in free  $H_2O_2$ . The change of Gibbs free energy for the homolytic Al-OOH bond rupture in complex 65 formed from 64 is only  $3.0 \text{ kcal mol}^{-1}$ . The calculations show that a highly reactive (in the H-atom abstraction from the alkane) hydroxyl radical is formed before than the less reactive HOO' is generated in this stepwise process. The ability of the hydroperoxy ligand to be relatively readily oxidized by one electron provides the delocalization of the spin density in the formed complex  $[AL_4(OOH)-$ (OH)]<sup>2+</sup>. This dramatically decreases the O-O bond energy in the coordinated hydrogen peroxide molecule within species **64.** The same authors<sup>51d</sup> assumed further that introduction of certain other easily oxidizable ligand to the catalyst molecule instead of the HOO<sup>-</sup> ligand can lead to the dramatic activation of the H<sub>2</sub>O<sub>2</sub> molecule as has been demonstrated for species 64. It is worthy to repeat here that the HOO<sup>-</sup> or other easily oxidizable ligand in a catalyst analogous to the species 64 plays the role similar to the role of transition metal in catalysts based on transition metals. The one-electron oxidation of either the HOO<sup>-</sup> species or of transition metal ion stabilizes the product of the O-O bond cleavage. The comparison of the activation on a transition metal ion (iron) and in the presence of easily oxidizable ligand (HOO<sup>-</sup>) is shown in a simplified form in Fig. 11.

Recently, DFT calculations by Kuznetsov and co-workers<sup>51g</sup> of the catalytic H<sub>2</sub>O<sub>2</sub> decomposition by other non-transition metal derivatives with homolytic O–O bond cleavage in the key species  $[M(H_2O)_{(n-2)}(H_2O_2)(OOH)]^{2+}$  predicted that the catalytic activity of simple aqua-complexes  $[M(H_2O)_n]^{3+}$  increases along the row of the metals M: Al  $\approx$  La < Y  $\approx$  In < Sc < Ga. A joint presence of the HOO<sup>-</sup> and H<sub>2</sub>O<sub>2</sub> ligands in complexes  $[M(H_2O)_4-(H_2O_2)(OOH)]^{2+}$  (M = Ga, In, Sc),  $[Y(H_2O)_6(H_2O_2)(OOH)]^{2+}$  and  $[La(H_2O)_7(H_2O_2)(OOH)]^{2+}$  dramatically activates the

hydrogen peroxide. The change of Gibbs free energy for HO–OH bond splitting in these species is in the range of 4.4–15.3 kcal mol<sup>-1</sup> which is 24.1–35.0 kcal mol<sup>-1</sup> lower than that in free H<sub>2</sub>O<sub>2</sub>. The HOO<sup>-</sup> ligand is not activated in these species. The overall activation barriers (kcal mol<sup>-1</sup>) of the generation of hydroxyl radicals for all metals do not differ too much from each other: Ga (19.5) < Sc (22.2) < In (23.5)  $\approx$  Y (23.7) < La (25.2)  $\approx$  Al (25.6).

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