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Review

Oxidative functionalization of alkanes under dioxygen in the presence of homogeneous noble metal catalysts



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ABSTRACT

Basic approaches to design of catalytic systems for homogeneous oxidative functionalization of alkanes in the presence of noble metals are overviewed. Special attention was given to catalytic systems for oxidation of C1–C4 alkanes with dioxygen as a green oxidant and to methods for dioxygen activation with reducing agents. The mechanisms of the relevant reactions are considered.

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1. Introduction

Nowadays, natural and associated petroleum gases are being used not only as fuel but also as important raw materials

for synthesis of key products and semi-products of modern chemical/petrochemical industry. A constraint for industrial-scale production of oxygenates via direct oxidation of alkanes with dioxygen is the lack of appropriate technological processes. The gas-phase oxygenation of methane over heterogeneous catalysts has shown low selectivity [1]. Homogeneous catalysis with metal complexes is effective and highly selective at lower temperatures but the available catalysts and catalytic systems exhibit low activity and some other drawbacks [2a]. For most recent reviews see [2b,c].

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Below we will consider some recent advances in the field that can be regarded as instilling some optimism.

As early as 1968, the brilliant chemist J. Halpern drew the attention of chemical community to the phenomenon of so-called activation of C-H bond in alkanes [3]. Earlier, Chatt and Davidson reported [4] on the activation of C-H bond in the methyl group of phosphine ligand in the complex of Ru with 1,2-bis(dimethylphosphino)ethane and on the possibility of oxidative addition of naphthalene to this complex. Subsequent extensive researches have led to discovery of numerous metal complexes capable of activating the C-H bond in alkanes. However, much more difficult turned out the problem of functionalization of the C-H bond, that is, the replacement of H atom by OH, COOH, Hal, OSO₃H, etc. groups. The problem of activation and functionalization of alkanes was a subject of numerous research papers, reviews, and monographs that can be found in [2].

In this overview, we will consider the state-of-art in the functionalization of alkanes involving dioxygen as an oxidant in the presence of noble metal compounds as catalysts.

2. Biomimetic approach

The biomimetic approach as used by us aimed not at imitation of natural oxygenases but at activation of dioxygen. In biocatalysts, this function is performed by a reducing agent (NADH) whose electrons are transferred to an active site over a complex conjugated system, after which the active site converts dioxygen into a reactive O-oxidant. Since direct interaction of the latter with the reducing agent is spatially separated, the selectivity of the process in biological systems is close to 100%. In chemical systems this value can hardly be attained in the nearest future but a value of 25–40% (typical of H₂O₂) would be quite acceptable. In chemical systems, it seems reasonable to use H₂ or CO as a reducing agent.

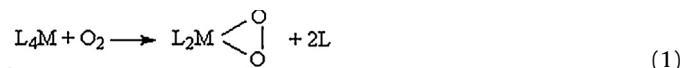
3. Activation of dioxygen

Under normal conditions, molecular oxygen is exceedingly inert, which is highly important for living organisms on the Earth. The nature also found the ways for activation of dioxygen, and the mankind has a chance to discover these mechanisms and utilize this knowledge in its technological processes.

To date, a number of hydroperoxo, oxo, and peroxy complexes of Rh, Pd, Pt, and Au are being prepared from dioxygen. Therefore, the above complexes can be used as good models for activation of dioxygen and even as intermediates in the oxidation of alkanes.

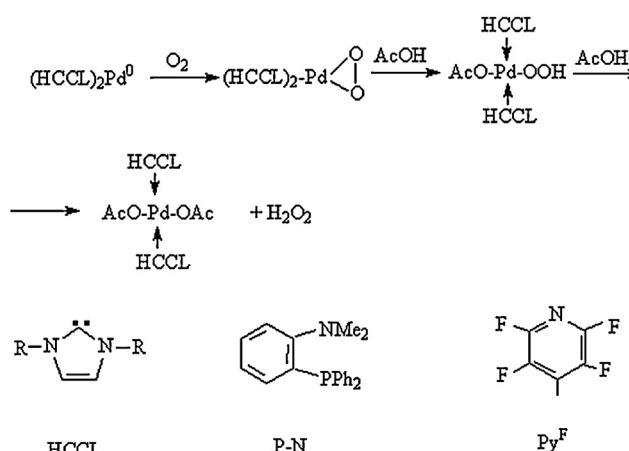
3.1. Peroxo complexes

Peroxo complexes of Pd and Pt are readily formed upon interaction of low-valent phosphine complexes with dioxygen (reaction (1)) and are capable of catalyzing the oxidation of triphenylphosphine to triphenylphosphine oxide in mild conditions (reaction (2)) [5]:



To date, the following complexes have been reported in the literature: (PPh₃)₂Ir(CO)(O₂)Cl [6], (PPh₃)₂Ru(O₂)(NCS)(NO) [7], and [Cl Py₄Rh–O–ORhPy₄Cl]⁺ [8]). Interaction of O₂ with the Pd(0) complex containing carbene ligands L (HCCL) was found to yield, in acetic acid (AcOH), hydrogen peroxide [9].

The synthesis of the following Rh complexes are reported: (HCCL)(PPh₃)₂Rh(O₂)Cl, (P-N)(PPh₃)₂Rh(O₂)Cl, and (PtEt₃)₂(Bu^tCN)Py^F-Rh(O₂) [10]. Oxygen expels ethylene from

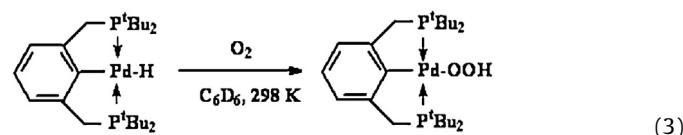


Scheme 1. Stoichiometric formation of H₂O₂ from O₂ and Pd(0). Adapted with permission from [9]. Copyright (2004) American Chemical Society.

the coordination sphere of Rh [11] to give a peroxy complex. In similar reaction of the Ir complex, ethylene remains intact due to stronger bonding with the complex. Recently, some new Rh peroxy complexes have been synthesized [12]. In the above peroxy complexes, the O–O bond is longer than that in dioxygen, which is indicative of its activation.

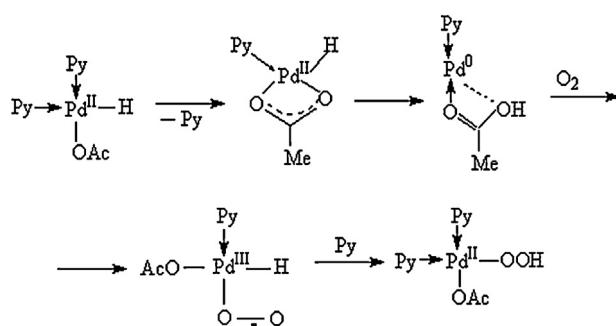
3.2. Hydroperoxy complexes

As mentioned in Section 2.1, in acetic acid the peroxy complex of Pd transformed into the hydroperoxy complex (Scheme 1). As it is known [13], Rh, Pd, Ir, and Pt form similar complexes upon interaction of respective phosphine hydride complexes with O₂. Direct insertion of dioxygen into the Pd–H bond (reaction (3)) was explored in [14] and the kinetic isotope effect, k_H/k_D, was found to have a value of 5.8. The reaction proceeds by molecular mechanism via coordination of dioxygen and its migratory insertion into the Pd–H bond the pincer complex of Pd.



Activation of dioxygen in catalytic oxidation of alcohols in nonpolar media was also explored theoretically [15a]. Reactions of (-spartein)Pd(II)(H)(Cl) and bipyPd(H)(Cl) with O₂ involve hydrogen abstraction by triplet dioxygen yielding stable L₂Pd(I)(³OOH)(Cl). This is followed by spin transition into a stable L₂Pd(II)(OOH)(Cl) accompanied by evolution of H₂O₂. These reactions require the presence of withdrawing ligands and a cis-H bond acceptor.

Theoretical study of Py₂Pd(H)OAc taken as an example [15b] considered the following possible reaction routes: (a) homolytic reaction involving abstraction of H[•] by O₂; (b) reductive elimination of AcOH to form a Pd(0) complex, its interaction with O₂, and conversion of peroxy-complex into hydroperoxide one under the action of AcOH; (c) migratory insertion of O₂ into the Pd–H bond; and (d) oxidative addition of O₂ to Pd(II) yielding a peroxyhydride Pd(IV) complex and its transformation into Pd(II) hydroperoxide. In authors' opinion, of key importance here is the type of ligand. In case of labile ligands (Py), the reaction of detached Py can yield coordination-unsaturated compounds, so that the reaction shown in Scheme 2 seems more likely [15b].



Scheme 2. Interaction of palladium hydride with dioxygen [15b].

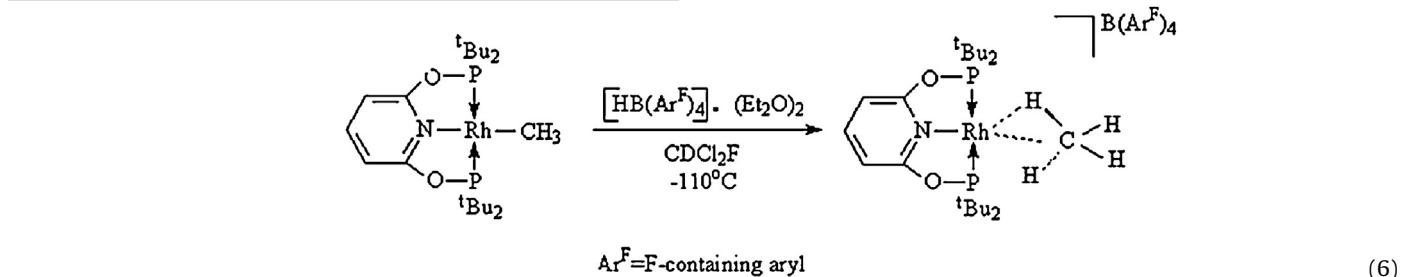
According to [15b], this scheme has been termed as “an unprecedented, kinetically favorable mechanism for dioxygen reduction by Pd(0)”.

Some examples of organic substrate (Sub) oxidation by hydroperoxo complexes of palladium have been given in [16]:



According to [17], the peroxy complexes of Rh are capable of transforming into the hydroperoxo ones.

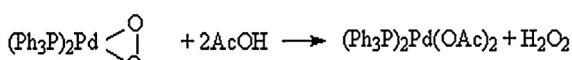
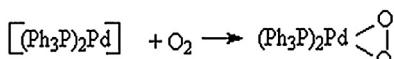
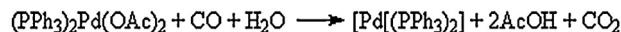
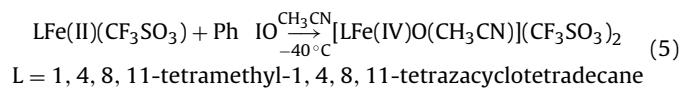
Note that the hydroperoxides in question are in some sense the analogs of hydrogen peroxide. Indeed, the reactions in Scheme 1



can be used for stoichiometric generation of H_2O_2 . A catalytic cycle can be closed if Pd(II) is reduced to Pd(0). And this was done by Likholobov and coworkers [18] (Scheme 3).

3.3. Oxo complexes

Oxo complexes are the intermediates formed under the action of oxygenases. Recently, the non-gem complex of Fe(IV) was synthesized [19] through reaction (5):

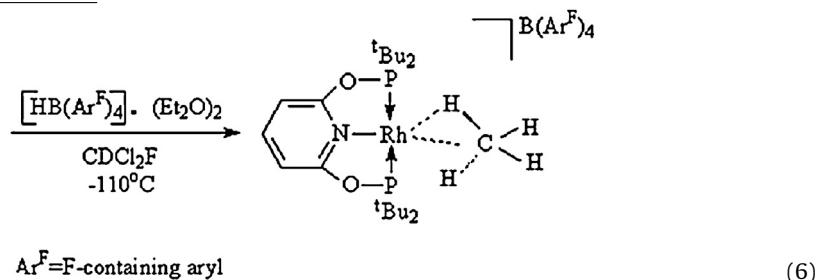


Scheme 3. Catalytic generation of hydrogen peroxide [18].

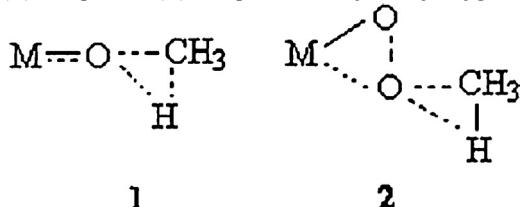
To date, the oxo complexes of Pt, Pd, and Au have not been reported so far, although the oxo compounds of Ru and Os are known for a long time. In order to stabilize oxo complexes of metals with 5-valent *d* electrons, one has to use strong π -acceptors. This explains high stability of $[\text{mesityl}_3\text{Ir}=\text{O}]$ in which the interaction of *d* electrons with the oxo group is minimized due to tetrahedral configuration of the complex and acceptor properties of aromatic mesityl ligands [20]. Synthesis and XRD characterization of the oxo complexes of Pt(IV) [21a], Pd(IV) [21b], and Au(III) [21c] have been reported in the years of 2004–2007. Oxidative behavior of these complexes still remains unknown. Nevertheless, it has been claimed that the pincer oxo complexes of Pt(IV) are capable of oxidizing KH, H_2 , PPh_3 , and even CO [21d]. Recently Hill et al. [21e] critically revised the available data evidencing the formation of terminal oxo-complexes of Pd, Pt, and Au. The authors recognized the fallibility of earlier assumptions about the existence of such oxo-complexes and analyzed possible error sources.

4. Activation of C–H bond

Interaction of alkanes with metal compounds has been found (by physical methods) to yield so-called σ -complexes. The IR spectroscopy of σ -complexes has been summarized in review [22]. The synthesis of relatively stable σ -complex of Rh with methane was reported in (reaction (6)) [23].



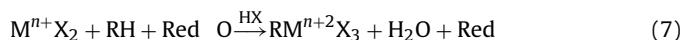
Recently, the hydrogenation of similar methyl complex of Ir with the same pincer ligand was performed at -90°C [24]. Such σ -complexes can act as precursors for metal–alkyl intermediates that are much more stable in activation of alkanes. For formation of alkyl intermediates, several mechanisms have been suggested [2]: (i) electrophilic substitution, (ii) oxidative addition, (iii) metathesis reaction, and (iv) addition of alkanes to the M=X bonds. Of considerable interest are the biomimetic mechanisms of alkanes' activation on oxo (1) and peroxy (2) complexes catalyzed by oxygenases.

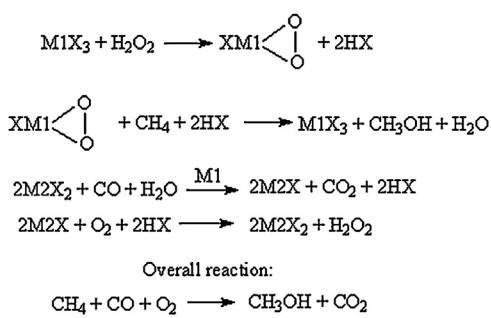


Unfortunately, no evidence for formation of such adducts has been obtained so far.

5. Design of catalytic systems for oxidative functionalization of alkanes: basic principles

(1) *First basic principle* is the activation of alkane in the inner coordination sphere of metal in its low oxidation state. This tough stage can be facilitated by the action of oxidant (reaction (7)) (here Red O stands for two-electron oxidant):



**Scheme 4.** Oxidation of methane via peroxy complexes.

This is followed by reductive elimination of product RX (reaction (8)):



(when one of X groups is OH, alcohol ROH can be formed)

Another process is hydrolysis (reaction (9)):



Reduced form of oxidant reacts with dioxygen (reaction (10)): (10) Red + $\frac{1}{2}\text{O}_2 \rightarrow \text{Red O}$

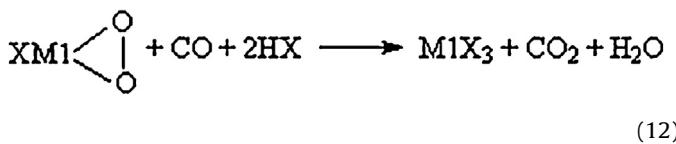
Overall reaction: (11) RH + $\frac{1}{2}\text{O}_2 \rightarrow \text{ROH}$

Such (or similar) reactions are adopted in the catalytic systems suggested by Shilov et al. (partially) [25], Periana et al. [26] (upon inclusion of regeneration stage $\text{SO}_2 + 1/2\text{O}_2 \rightarrow \text{SO}_3$), and Bao et al. [27a,b].

(2) *Second principle* is a proper choice of catalytic systems in which one component (catalyst) is responsible for activation of alkane while another (co-catalyst), for activation of dioxygen. The choice of co-catalyst is dictated by the following considerations. In its reduced form, a co-catalyst in reaction with O_2 must generate either H_2O_2 or its analogs. The oxidized co-catalyst must be readily regenerated with an external reducing agent (CO, H_2). But this approach requires catalysts for activation of CO or H_2 . This role can be played by a metal-catalyst in addition to its main function, activation of alkane. The role of co-catalyst can be played by iodine-containing compounds, copper salts, and iron salts [2]. The kinetic studies on oxidation of Fe(III) with O_2 revealed the formation of H_2O_2 as an intermediate [28]; similarly, the oxidation of Cu(I) was accompanied by accumulation of marked amounts of H_2O_2 [29].

Given that M^nX_3 stands for metal-catalyst while M^nX_2 , for co-catalyst, let us assume that the reducing agent is CO (it is better than H_2 because it does not yield water as by-product). In this case, the reaction mechanism (**Scheme 4**) can be represented in the form:

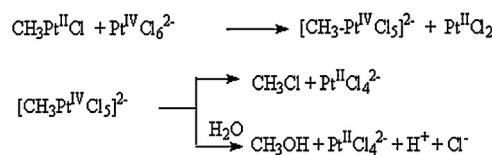
In parallel, the useless oxidation of CO takes place:



The oxidation of CO may also proceed by conventional mechanism (reaction (13)) [30]:



The above principle is being used in catalytic systems suggested by Sen et al. [31], Likhobolov et al. [32], and Chepaikin et al. [2], as well as the other systems involving a reducing agent. It follows that the oxidation of alkanes is better to perform in protonic media. It should also be kept in mind that the primary oxidation product, alcohol, is oxidized faster than starting alkane. In view of this, some

**Scheme 5.** Oxidation of methane in terms of Shilov chemistry [25].

precaution measures should be taken, such as addition of carboxylic acid (reaction (14)):



Thus formed esters are much more resistant to oxidation.

It should be kept in mind that the catalytic systems designed by following the above principles in reality can operate by others, more complicate mechanisms.

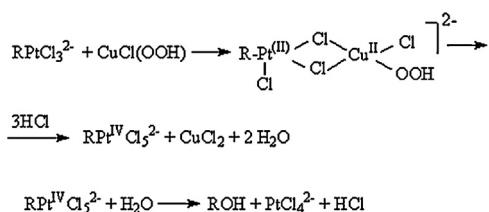
6. Oxidative functionalization of alkanes

Back in 1967 it has been disclosed that Pt(II) is capable of catalyzing H-D exchange between aromatic compounds and AcOD-D₂O medium [33]. Later Shilov and co-workers have found the activation of methane in the same medium [34a]. It has also been established that – in the $\text{H}_2\text{PtCl}_4-\text{H}_2\text{PtCl}_6-\text{H}_2\text{O}-\text{AcOH}$ system – alkanes undergo conversion to alkyl chlorides [34b] while acetic acid, to chloracetic acid [34c]. After pioneering works by Shilov and co-workers, this system was explored by several research groups. Possible mechanisms of catalytic action in the above system (termed now Shilov chemistry) were analyzed in [35].

Note that, in the Shilov chemistry (**Scheme 5**), Pt(II) activates alkane while Pt(IV) acts as an oxidant. In the methyl complex, Pt(II) is oxidized to Pt(IV) due to electron transfer via chloride bridging groups. Reductive elimination from the methyl complex of Pt(IV) yields CH_3Cl , while the reaction with water, methanol.

According to Shilov [25], the activation of methane gets started as oxidative addition to Pt(II) and accomplishes by synchronous (a) formation of Me-Pt(II) and (b) release of H^+ and Cl^- . Purely oxidative addition is unfavorable thermodynamically while electrophilic substitution, kinetically [34d]. The oxidation of Pt(II) to Pt(IV) requires a strong oxidant. There is however the example when the above system was operative in the presence of dioxygen as an ultimate oxidant. Thus, Sen and co-workers have found that, upon addition of CuCl_2 into the Shilov system (instead of H_2PtCl_6), methane, ethane, and propane sulfo acids, propanoic acid, and ethane phosphonic acid can be oxidized in acidified (H_2SO_4) aqueous solution at 120–160 °C under 2–9 MPa of O_2 [36a]. A mechanism of catalytic action for this system is unknown. But this is one of few examples for the oxidation of alkanes at the C–H bond with dioxygen in the absence of reductants, which seems to be of fundamental importance. In this context, it seems reasonable to present here my own vision of the problem. Below are the main features of the system.

- (1) Hydroxylation of EtSO_3H (hereinafter RH) takes place in the absence of O_2 and gives a stoichiometric yield of ROH and Pt(0) precipitate.
- (2) For $\text{Na}_2\text{PtCl}_6/\text{CuCl}_2$ system, a highest yield of ROH (TON 52 in 4 h) is attained in the presence of O_2 .
- (3) Excessive Cl^- inhibits the process.
- (4) The H–D exchange takes place between sulfurized alkane and D₂O; in case of $\text{C}_4\text{H}_9\text{SO}_3\text{H}$ (24 h), about 90% H atoms in the methyl groups are replaced by D and about 70%, in the neighboring methylene group.

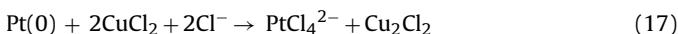


Scheme 6. Oxidation of alkanes with participation of copper (II) hydroperoxide. Adapted with permission from [2]. Copyright (2011) Turpion-Moscow Ltd.

All this is indicative of the formation of the R–Pt bond. From thermochemical considerations, CuCl_2 can oxidize neither alkane nor Pt(II) [to Pt(IV)] but is capable of oxidizing Pt(0) to Pt(II). CuCl_2 is chemically inert with respect to oxygen. According to existing experimental data, we have:



The Cu(I) required for activation of O_2 may be generated in the reaction (17):

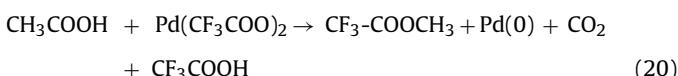


Subsequent reaction of Cu_2Cl_2 with O_2 may be expected to yield copper hydroperoxide or hydrogen peroxide:



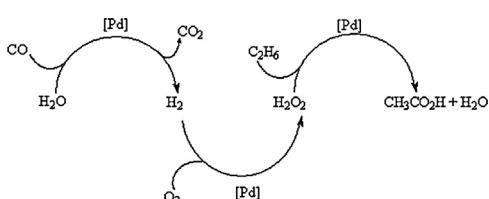
In acidic medium (Scheme 6), copper hydroperoxide acts as a strong oxidant that is capable of oxidizing Pt(II) to Pt(IV), by analogy with the action of Rh complexes [2].

In 1987, Sen et al. reported on the stoichiometric oxidation of methane and adamantane in trifluoroacetic acid (Ac_fOH) with palladium acetate to methyl and 1-adamantyl trifluoroacetate, respectively [36b]. Later two research groups [37] established that $\text{Pd}(\text{OAc}_f)_2$ cannot oxidize methane. It seems more likely that the MeOAc_f observed in [36b] was a result of acetic acid decomposition [37a–c]:

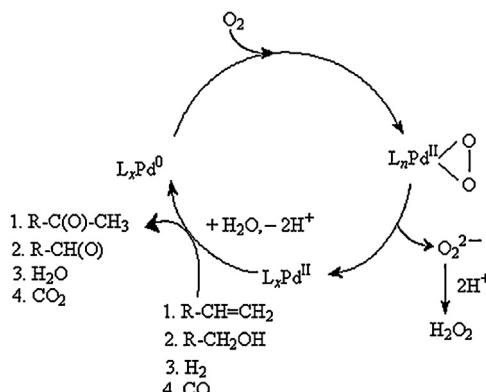


But it turned out that in Ac_fOH the oxidation of methane in the presence of Pd(II) was caused by H_2O_2 [36c], perfluoroacetic acid being assumed to act as effective oxidant. Suggested itself a conclusion that O_2 should be converted in H_2O_2 , e.g., through reduction of O_2 with hydrogen. It was suggested (Scheme 7) to generate hydrogen in the WGSR process and use the following reaction scheme [36d].

With Pd/C as a catalyst, ethane in $\text{DCl}/\text{D}_2\text{O}$ is oxidized to ethanol, acetic acid, and formic acid. Later (Scheme 8), the oxidation of



Scheme 7. Oxidation of alkanes in situ generated hydrogen peroxide. Reprinted with permission from [36d]. Copyright (1992) American Chemical Society.



Scheme 8. Generation of hydrogen peroxide [36e].

cyclohexane with O_2-H_2 mixture in the presence of $\text{Pd}/\text{Al}_2\text{O}_3$ and vanadium or iron compounds was carried out by the scheme [36e].

In this scheme, Pd is used to generate H_2O_2 . Besides hydrogen, the role of reducing agent can be played by olefins, alcohols, and CO. Newly formed H_2O_2 oxidized cyclohexane on Fe or V catalysts. Sen and co-workers have established that the addition of co-catalysts – copper or iron salts – in a catalytic system containing Pd/C or K_2PdCl_4 affords to oxidize methane, ethane, and butane with O_2 and CO in $\text{Ac}_f\text{OH}-\text{H}_2\text{O}$ more effectively than in case of sole Pd/C [36f]. The H_2O_2 (which is formed from O_2 and H_2O in the presence of CO) somehow activated on Pd is assumed to act as oxidant. Later the Pd/ CuCl_2 system was found to effectively catalyze the hydroxylation of remote primary C–H bonds in functionalized organics [36g].

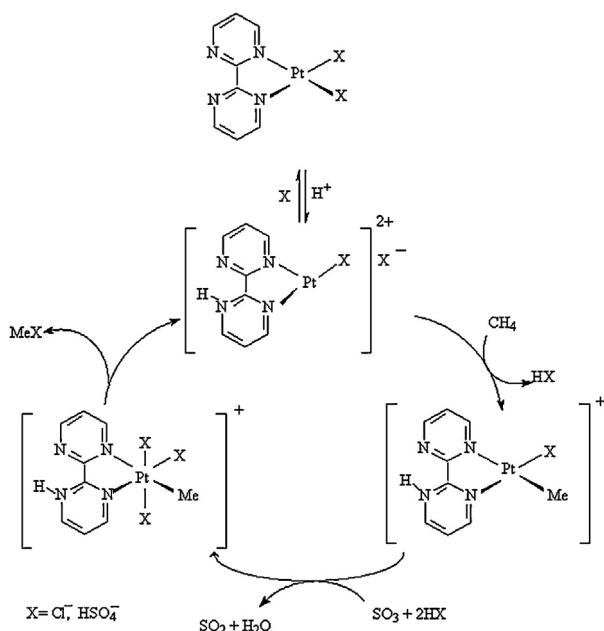
The oxidation of methane by O_2 and CO on the Pd/C– CuCl_2 catalytic system in Ac_fOH was reinvestigated in [38]. These workers also believe that H_2 is generated in the WGSR process, which is followed by formation of H_2O_2 from H_2 and O_2 . The type of active Pd particles was found to depend on the type of co-catalyst, solvent composition, and presence/absence of Cl^- . It is assumed that Pd is partially oxidized with H_2O_2 and that most active are Pd(II) species. But it seems doubtful that the action of CO is preceded by formation of H_2 . This is not confirmed by experimental evidence. Dihydrogen can hardly compete with carbon monoxide for a coordination site on Pd. Moreover, H_2O_2 can be generated in reaction of CO with O_2 and H_2O [18].

Typical co-catalysts for platinum metals are the compounds of copper, iron, and vanadium. Recently, tetrachloroquinone (TQ) was used in combination with Pd/C to oxidize methane to Ac_fOMe by O_2 and CO in aqueous Ac_fOH at 140 °C [27a]. In the absence of TQ, the reaction yielded formic acid.

An interesting catalyst for oxidation of methane with sulfuric acid – complex of Pt(II) with 2,2'-bipyrimidine (PtCl_2 -bipym) – was suggested by Periana et al. [26a].

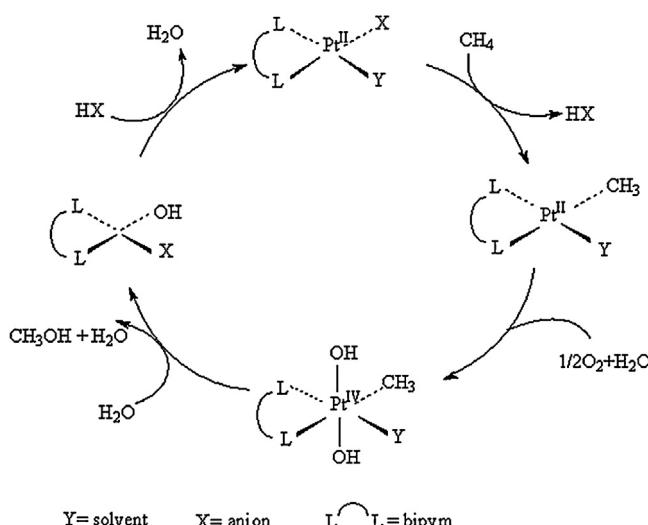
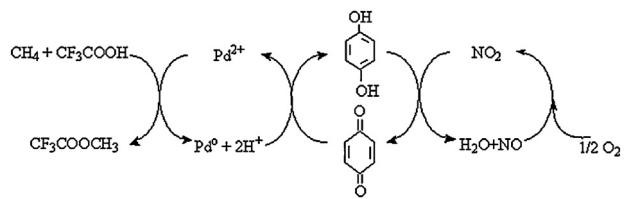
The above mechanism (Scheme 9) was confirmed by ^1H NMR spectra. At 70 °C, the methyl complex catalyzes multiple H–D exchange between methane and D_2SO_4 . This system is effective at rather high temperatures (180–220 °C), highly sensitive to the water accumulating during reaction, and exhibits high conversion of methane. After experimental investigation of SO_2 oxidation to SO_3 with O_2 and resolution of the water problem, this catalyst would become a serious candidate for its commercialization. Possible inclusion of the $\text{SO}_2 \rightarrow \text{SO}_3$ stage was discussed in [26b–d].

In order to improve the water resistance of Pt catalyst, it was suggested to use ionic liquids [39a]. The system ' H_2PtCl_6 /1-methylimidazolinium chloride' retains its catalytic activity even in 96% H_2SO_4 , when PtCl_2 -bipym becomes inactive. Another route to modification of PtCl_2 -bipym is the use of a network polymer containing aromatic triazine fragments as a macro ligand [39b]. Such a

**Scheme 9.** Oxidation of methane in the Periana system [26a].

heterogenized catalyst showed the activity close to that of molecular PtCl₂-bipy. Recently, that same research group suggested to help Pt catalyst in H₂SO₄ by using, as a chelating agent, the N-doped coal ($s = 400 \text{ m}^2 \text{ g}^{-1}$) derived from lobster chitin [39c]. In this case, the activity of PtCl₂-bipy grew by a factor of two and showed the same service life. Still another example of PtCl₂-bipy application was given in [40]. The bipyridine ligand was methylated in the complex and used as a counter-ion in the phosphovanadomolybdate [PV₂Mo₁₆O₄₀]²⁻. Thus prepared salt was deposited onto SiO₂ and used as catalyst for methane oxidation (30 bar) with O₂ (2 bar) in acidified water at 50 °C. Oxidation products were found to contain CH₃OH, HCOH, and CH₃CHO. Experiments with H₂¹⁸O, ¹⁸O₂, and ¹³CH₃OH isotopes afforded to suggest the following mechanism of catalytic action.

Key intermediates here are the methyl complexes of Pt(II) and Pt(IV). It is assumed that the oxidation of Pt(II) to Pt(IV) with O₂ involves polyoxometallate, but no further details have been presented (see Scheme 10).

**Scheme 10.** Oxidation of methane in water. Adapted with permission from [40]. Copyright (2004) American Chemical Society.**Scheme 11.** Oxidation of methane with involvement of quinones. Reprinted with permission from [27b]. Copyright (2006) American Chemical Society.

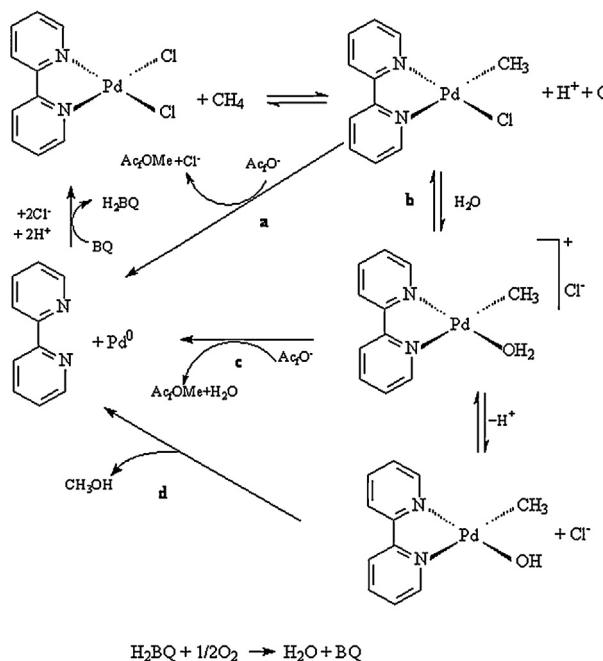
Chinese researchers have reported (Scheme 11) on oxidation of methane with O₂ in the presence of the Pd(OAc)₂-benzoquinone-NaNO₂ system in Ac_fOH [27b].

As already mentioned above, methane is not oxidized with Pd(OAc)₂ [37a–c]. In this context, the above scheme casts some doubt. Moreover, since NO₂ is a two-electron oxidant, the actual role of quinone remains unclear. Although quinone is capable of oxidizing Pd(0) to Pd(II), but this reaction can also proceed under the action of NO₂. It is possible that quinone prevents the precipitation of Pd metal and that the role of oxidant is played by some compound containing Pd + NO₂ such as a nitrite complex that is known to act as methane oxidant [37d]. In addition, Pd and NO₂ can also be expected to form an oxo complex.

Meanwhile, another Chinese group [27c,27d] have recently found that the system 'Pd(OAc)₂-benzoquinone (BQ)-H₅Mo₁₀V₂O₄₀' in Ac_fOH/(Ac_fO)₂O catalyzes the oxidation of methane to methyl trifluoroacetate at 80–90 °C ($P_{\text{CH}_4} = 2.5 \text{ MPa}$, $P_{\text{O}_2} = 0.5 \text{ MPa}$) at a moderate efficiency (TON 2–3 in 8 h) [27c]. (Ac_fO)₂O is added to bind water. The origin of byproduct, CO₂, is not discussed. CO₂ could be derived from methane but in this case we would have expected for formation of formic acid. Another possible route is decarboxylation of Ac_fOH. It is interesting to note that the addition of 1 ml perfluoro octane per 1 ml Ac_fOH enhances the yield of methyl trifluoroacetate by a factor of 100. This can be associated with (a) better solubility of O₂ in the presence perfluoro octane and (b) improved mass exchange between the gas and liquid phases. Later it was suggested [27d] to replace Pd(OAc)₂ by BipyPdCl₂, and such a catalytic system turned out less sensitive to water and even exhibited some maximum at Ac_fOH:H₂O = 5. At 100 °C, $P_{\text{CH}_4} = 2.5 \text{ MPa}$, and $P_{\text{O}_2} = 0.5 \text{ MPa}$, TOF was found to have a value of 1 h⁻¹. The influence of perfluoro octane on the yield of Ac_fOMe was less pronounced than that reported in [27c]. For this system, the mechanism of catalytic action (with my minor corrections!) can be represented as shown in Scheme 12.

The activation of methane proceeds just as in the Shilov chemistry. At low water concentration, the methyl complex of Pd(II) is subjected to the nucleophilic attack of Ac_fO⁻ to give ester (route a); at higher water concentrations, Cl⁻ is replaced by H₂O (route b). The methyl group in the newly formed cationic complex is attacked (just as in route a) by Ac_fO⁻ to give ester (route c). The aqua complex undergoes deprotonation while the newly formed methylhydroxy complex, and subsequent reductive elimination yields methanol (route d). Pd(0) is oxidized to starting Pd(II) by BQ; the latter is regenerated upon interaction of hydroquinone with O₂.

It was reported [27c,d] that the yield of Ac_fOMe grew with increasing concentration of H₅PMo₁₀V₂O₄₀ but its role had not been discussed. According to [27d], BQ is capable of oxidizing Pd(0) to Pd(II). It turns out that in the overall scheme of the process methane is oxidized with BQ, which is impossible from thermochemical considerations. For the same reason, the oxidized form of PMo₁₀V₂ polyoxometallate also cannot oxidize methane. In reaction with Pd(OAc)₂, oxidized is not methane but the acetic acid formed in reaction of Pd(OAc)₂ with Ac_fOH (see above and refs. [37a–c]). Methane can be oxidized only with dioxygen but not at



Scheme 12. Oxidation of methane on bipyPdCl₂ [27d].

such relatively low temperatures. In 2010, we have reported that the bipy-PdCl₂ complex in combination with Cu(OAc)₂ under the action of O₂ and CO (reducing agent) in AcOH/H₂O can effectively catalyze the oxidation of C₁–C₄ alkanes [41a]. At 80 °C, $P_{\text{CH}_4} = 6.0 \text{ MPa}$, $P_{\text{O}_2} = 0.56 \text{ MPa}$, $P_{\text{CO}} = 1.6 \text{ MPa}$, and AcOH:H₂O = 4, we obtained TOF = 7.1 h⁻¹. This catalytic system turned out more effective than that reported in [27c,d]. For some unclear reasons, the authors of [27c,27d] did not cite our publications. It is worthy to note that, to our knowledge, bipy-PdCl₂ is incapable of catalyzing H–D exchange between CH₄ and solvent at 80 °C, $P_{\text{CH}_4} = 6.0 \text{ MPa}$, and AcOD:D₂O = 4 [41b]. After 5 h of processing at [bipy-PdCl₂] = 5 × 10⁻³ M in 300 cm³ CH₄, we did not find any traces of deuteration. These results cast some doubt on route a and the entire mechanism on aggregate.

In this context, I am going to make the following comments. The use of tetrachlorobenzoquinone in [27a] is not accidental; it was used to avoid the oxidation of BQ. If BQ can be oxidized during reaction, it will be able to act as a reducing agent. In this case, the mechanism of catalytic action will be similar to that of *Second principle* in Section 5.

Likhobolov et al. sometimes used H₂–O₂ mixtures for oxidation of cyclohexane [32] as a measure to overcome low selectivity of the process in case of H₂O₂. They used Pd/SiO₂ or Pt/SiO₂ in combination with poly oxo metallates as catalytic systems. The effectiveness of oxo metallates increased in the order: H₆[P₂Mo₁₂O₆₂] < H₄[PMo₁₁VO₄₀] < H₄[PMo₁₀V₂O₄₀]. Active centers are formed upon adsorption of hetero polyacids to Pd/SiO₂ and Pt/SiO₂. A solid two-component catalyst was prepared from the complex salt [Pt(NH₃)₄]·[H₂PMo₁₂O₄₀]₂·7H₂O by calcining followed by subsequent reduction. Oxidation of alkanes is thought to proceed by non-chained radical mechanism. Dioxygen is activated on Pt(0) and, upon interaction with proton, yields the hydroperoxide Pt–OOH. Under the action of protons and Mo⁵⁺, it forms the hydroxyl radical coordinated with Pt as an active oxidation center, although the formation of such a radical has not been supported by experimental evidences.

Shilov and co-workers investigated some Au-containing catalysts [42]. They used auophilic bacteria *Micrococcus luteus* to activate and oxidize methane to methanol in water [42a]. The

suggested model of this bacteria is comprised of the active site of HAuCl₄, bioflavonoid rutin (quercetin-3-O- rutinoside), K₃Fe(CN)₆, and NADH as a reductant [42b]. The system is operative at r.t. in the presence of 0.33 μm HAuCl₄, the process generated 33 μm methanol. The following is the mechanism of action. First is the oxidative addition of methane to Au(I). Dioxygen is activated on Au and under the action of NADH is converted into active oxidant to react with the methyl hydride complex of Au to give methanol and Au(I)OH. The latter is oxidized to Au(III) with O₂, which is favored by the presence of K₃Fe(CN)₆.

There exist a number of flavonoids whose structure is similar to that of rutin. Among these, only quercetin can play the role of rutin as a ligand in a complex with Au; and such a complex together with K₃Fe(CN)₆ and NADH is a biomimetic model of NADH-dependent oxidation of methane with dioxygen [42c].

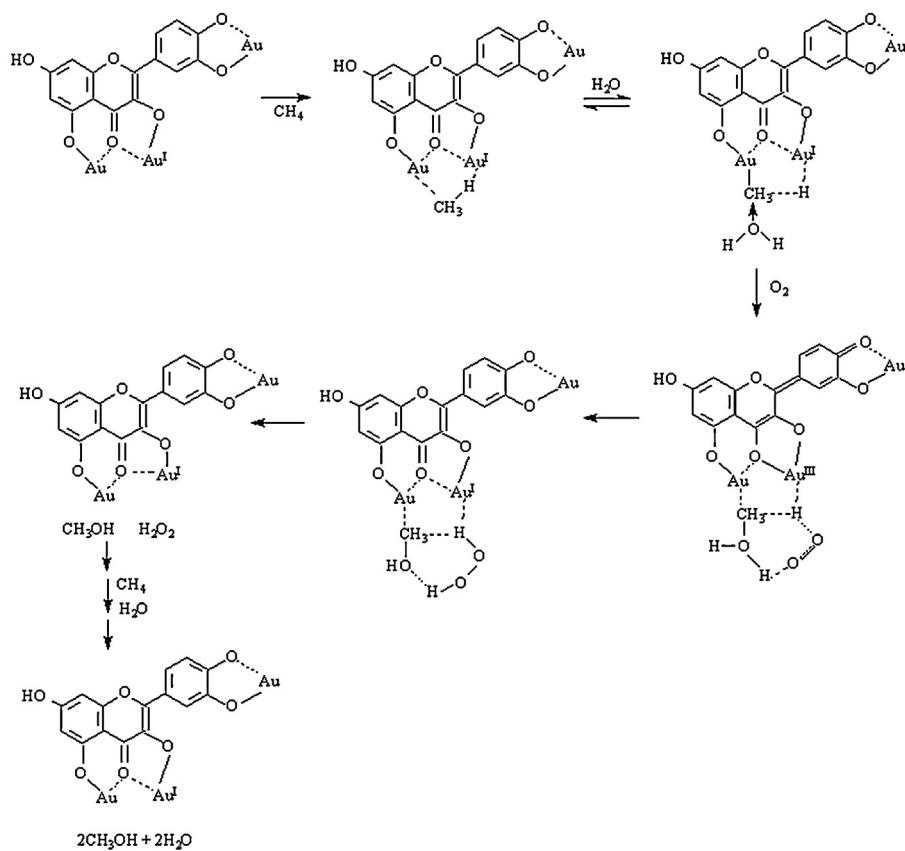
Later it has been demonstrated that, in the catalytic system with rutin, ethane oxidizes to ethanol while propane, to isopropanol at a higher efficiency compared to oxidation of methane to methanol [42d]. Note that ethane and propane are oxidized and, in the absence of rutin, the Au-protein oxidizing methane contains three Au ions per one rutin fragment. The authors believe that the Au–CH₃ bond is resistant to hydrolysis. Another possibility – the detachment of H atom from the Au–CH₃ bond, formation of the Au=CH₂ bond, and subsequent hydrolysis – has not been confirmed by experiment: the oxidation of propane in H₂O or D₂O yielded only isopropanol. In view of this observation, the authors proposed that methane can be activated on two Au ions, which is followed by coordination of water with the carbon from the methyl group and insertion of dioxygen into a space between H atoms of water and methane. All this leads to formation of methanol and H₂O₂ that is capable of oxidizing still another methane molecule. In Scheme 13, the added NADH has not been indicated. For the sake of simplicity, Scheme 13 shows quercetin rather than rutin. The Au-rutin (just as Au-quercetin) complex acts as a component of the catalytic system for oxidation of methane.

Quantum-chemical study [43a] on methane activation with aqua-chloride complexes of Au (III) have revealed that [Au(H₂O)₂Cl₂][–] reacts with methane at a low energy barrier. The coordination of the hydroxyl group of alcohol at the active site of the catalyst was found to prevent the oxidation of alcohol due to an increase in the energy barrier. As a result, the rate of alcohol oxidation appears to be much lower than that of alkane [43b]. In [43c], the same authors have suggested a mechanism of action for Au-containing catalysts: methane is activated by the aqua-complex of Au(I) to yield (Scheme 14) the methyl complex and subsequent proton binding with water. Dioxygen is activated on Au(I) to give the hydroperoxide complex, which is followed by oxidation of Au(I) to Au(III). The catalytic cycle is accomplished by reductive elimination of methanol.

The oxidation of methane in water in the presence of Au-Pd/TiO₂ catalyst was reported in [44]. Added H₂O₂ and the H₂O₂ synthesized in-situ from H₂ and O₂ or from NADH and O₂ were used as oxidants. Under mild conditions (50 °C, $P_{\text{CH}_4} = 3.0 \text{ MPa}$, 0.86% H₂, 1.72% O₂, 75.86% CH₄, 21.55% N₂, 28 mg 5% Au-Pd/TiO₂ catalyst; 1:1 ratio of Au to Pd), TOF had a value of 0.32 h⁻¹. In this process proceeding by radical mechanism, methane is oxidized to methanol and methyl hydroperoxide, with formation of CO₂ as a byproduct. The Au-Pd/TiO₂ catalyst exhibited the effect of synergism: the mixture of Au/TiO₂ and Pd/TiO₂ showed a lower activity.

6.1. Catalytic systems based on Rh/co-catalyst complexes

In 1994, Sen et al. have reported that the system RhCl₃/KI/NaCl (or DCl) in D₂O (95 °C, $P_{\text{CH}_4} = 6.8 \text{ MPa}$, $P_{\text{CO}} = 1.36 \text{ MPa}$, and $P_{\text{O}_2} = 0.68 \text{ MPa}$) catalyzes the oxidative carbonylation of methane to acetic acid (27.6 mol/mol Rh in 420 h) and small admixture of

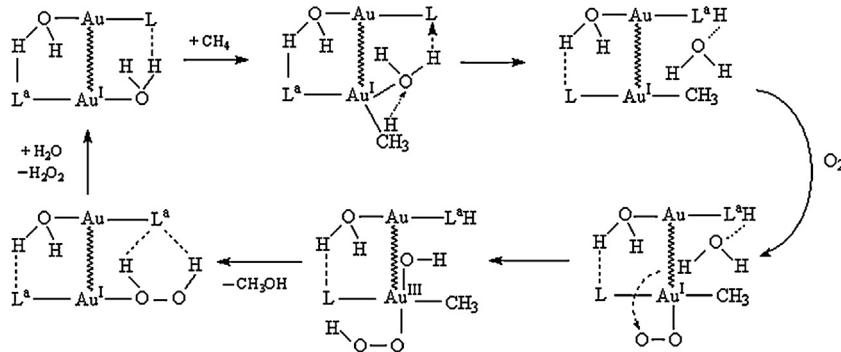


Scheme 13. Oxidation of methane on gold quercetin complex [42d].

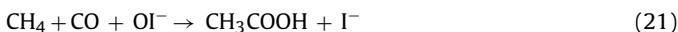
methanol and formic acid [45a]. We expected that the process rate could be enhanced on going to aqua-organic mixtures such as water–carboxylic acid (see e.g. [46]). Indeed, the partial replacement of water by heptafluorobutyric acid (C_3F_7COOH) [45b], AcOH [47a,b] or Ac_fOH [47c,d] increased the efficiency of this catalytic system.

The oxidation and oxidative carbonylation of C₁–C₄ alkanes in solution of heptafluorobutyric acid ($C_3F_7COOH:D_2O = 6:1$) was explored in [45b]. The use of ¹³CO and non-labeled methane was found to yield ¹²CH₃¹³COOH. Alkanes C₂–C₄ exhibited higher reactivity and reacted at the C–H bonds as well as through cleavage of the C–C bonds. The overwhelming majority of CO₂ originated from CO rather than from CH₄. In control experiments (¹³CH₄ + ¹²CH₃OH) methane exhibited higher activity than methanol, and acetic acid originated only from methane. Sen et al. [45b] however neglect that methanol in $C_3F_7COOH-D_2O$ (6:1)

is present largely in the form of ester. Nevertheless, the reaction mechanism strongly differs from the carbonylation according to Monsanto involving oxidative addition of CH₃I to Rh(I) [48]. The stage of methane activation is omitted and reaction products are assumed to form in reaction of nucleophilic agents with the complexes containing Rh–CH₃ or Rh–CH₃C(O)CH₃. The role of the iodide co-catalyst is not discussed altogether. Active oxidant is assumed to appear in reaction of O₂ with H₂. The latter is normally generated in the WGSR process, which in case of Rh complexes is unlikely. As a rule, Rh compounds catalyze the WGSR in alkaline media [49]. In the Monsanto process, this reaction is possible but at exceedingly high concentrations of HI [48]. Moreover, we have demonstrated previously that—at $P_{CO} = 0.64\text{--}1.84$ MPa, 95 °C, and $C_{H_2O} = 0.64\text{--}0.91$ mol fractions in Ac_fOH—the system Rh–iodide–chloride (hereinafter Rh–I–Cl) is incapable of catalyzing the WGSR process [47d].

Scheme 14. Oxidation of methane on gold quercetin complex [43c]. $[Au_2(Qc)(Qc^a)(H_2O)_2]^-$ = quercetin anionic binuclear aqua-complex of Au(I) L = Qc, L^a = Qc^a

Slightly later after [45b], we have reported that the Rh–I–Cl system is effective in CD_3COOD – D_2O – DCl [47a,b]. Just as in water, the main reaction product was acetic acid with an admixture of methanol, methyl acetate and formic acid. The overall efficiency of the process was higher than in water by a factor of 5–6. Tentatively, the intermediate oxidant was the DIO derived from reaction between DI and O_2 . The synthesis of acetic acid with involvement of OI^- is thermochemically favorable ($\Delta G = -21 \text{ J mol}^{-1}$) (reaction (21)) [47]:



We have also demonstrated that methanol is converted to methylacetate while methyl iodide, to methyl chloride, but no carbonylation of the above compounds has been noticed. Just as previously [45b], we believe that the reaction mechanism is different from that of the Monsanto process that requires high HI concentrations [48].

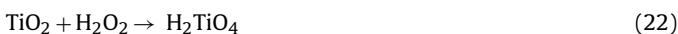
Preparative synthesis of oxygen-containing compounds via oxidation of alkanes [50] and catalytic oxidation of alkanes are better to perform in Ac_fOH . Its use afforded to markedly improve the efficiency of the Rh–I–Cl catalytic system.

The yield of reaction products (CH_3OD , Ac_fOCH_3 , HCOOD , CH_3COOD) in the presence of the above catalytic system in Ac_fOH – H_2O mixture as a function of $[\text{H}_2\text{O}]$, $[\text{I}^-]$, and P_{CO} exhibited a maximum [47c,d].

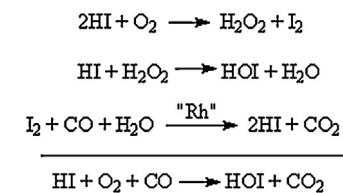
In view of numerous complications caused by the presence of iodine, it seemed currently important to design non-iodide catalytic systems. Under some certain conditions, hydrogen peroxide can be generated through oxidation of $\text{Fe}(\text{II})$ to $\text{Fe}(\text{III})$ or $\text{Cu}(\text{I})$ to $\text{Cu}(\text{II})$ [28,29]. It turned out that RhCl_3 – $\text{Cu}_2\text{O}(\text{CuO})$ – NaCl systems (hereinafter Rh–Cu–Cl) [51a–c] and RhCl_3 – $\text{FeO}(\text{Fe}_2\text{O}_3)$ – NaCl [51e] in Ac_fOH – H_2O mixture readily catalyzed the oxidation and oxidative carbonylation of methane. The use of Fe and Cu oxides as co-catalysts was dictated by convenience and by necessity of experiments at low $[\text{Cl}^-]$. In adopted conditions, copper and iron oxides rapidly transform to trifluoroacetates and partially to chlorides. The systems Rh–Cu–Cl and Rh–I–Cl generate similar products and exhibit close dependence of the yield of methane oxidation products on $[\text{Cl}^-]$ and P_{CO} . Both systems are incapable of catalyzing H–D exchange with solvent but oxidize Ti. As is known, dissolution of Ti metal (covered with an oxide film) is used as a test for the presence of H_2O_2 (cf. reaction (22)). Close dependences of the curves CH_4 and Ti oxidation as a function of $[\text{H}_2\text{O}]$ give grounds to assume the oxidation of Ti and CH_4 involves on and that same oxidation agent, viz. H_2O_2 or its equivalents.

The differences are as follows. The Rh–Cu–Cl system is 1.5-fold more active in methane conversion, less sensitive to water, and less corrosion-aggressive to Ti. Different is also the kinetic isotope effect (KIE) of solvent.

In Section 5, we discussed possible formation of H_2O_2 or its equivalents as active oxidants. Hydrogen peroxide can be detected with $\text{Ti}(0)$. Indeed, the oxidation and oxidative carbonylation of methane was found to be accompanied by oxidation of $\text{Ti}(0)$ in the presence of the Rh–I–Cl or Rh–Cu–Cl system. At this, the oxidation curve passes through maxima at the same $[\text{H}_2\text{O}]$ as the yield of organic products. Apparently, methane and Ti are oxidized by that same oxidant, viz. H_2O_2 or its equivalent. As is known [52], Ti oxidation is preceded by decomposition of oxide film (reaction (22)):



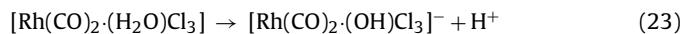
Reaction Scheme 15 for generation of active oxidant in the Rh–I–Cl system is given below (here “Rh” stands for catalytically active Rh complex). A narrow activity range of this system with respect to $[\text{H}_2\text{O}]$ can be explained by intersection of stability



Scheme 15. Generation of HOI. Reprinted with permission from [2]. Copyright (2011) Turpion-Moscow Ltd.

conditions for HOI and conditions required for activation/oxidation of methane.

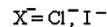
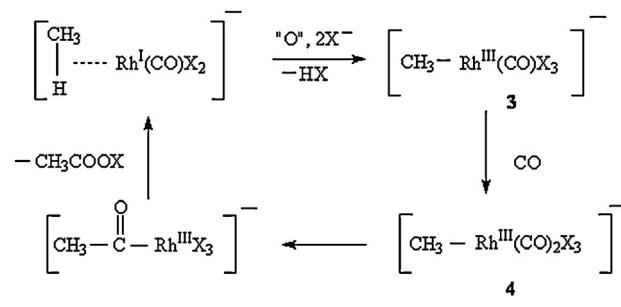
The Rh–I–Cl and Rh–Cu–Cl systems exhibit the KIE ($k_{\text{H}}/k_{\text{D}}$) of solvent in oxidation of CO to CO_2 , 2.0 and 1.6, respectively [47d,51d], which can be associated with the equilibrium deprotonation of aqua-carbonyl complex of Rh(III) prior to its reductive decarbonylation (reaction (23)) [30]:



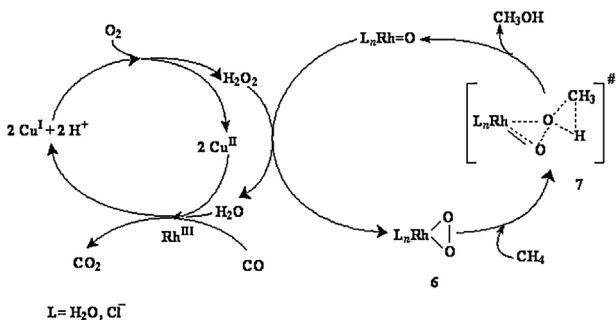
The complex $\text{Rh}(\text{CO})_2(\text{H}_2\text{O})\text{Cl}_3$ is a weak acid whose dissociation constant in D_2O is 2–3-fold smaller than in H_2O [53]. It is well known that when KIE is above unity, the protonic dissociation of the intermediate takes place prior to the first irreversible stage. In homogeneous catalysis this is typical of: (a) oxidation of ethylene to acetaldehyde in the presence of PdCl_2 ($k_{\text{H}}/k_{\text{D}} \approx 4$) [54a], (b) WGSR in the presence of phosphine complexes of Pd in Ac_fOH ($k_{\text{H}}/k_{\text{D}} \approx 3$) [53b], and (c) oxidative carbonylation of acetylene in alcohol solution of Pd complexes ($k_{\text{H}}/k_{\text{D}} \approx 1.7$ –1.8) [54c].

Oxidation of methane in both the systems proceeds by molecular mechanism. It is insensitive to the presence of added radical traps. These systems do not catalyze H–D exchange between methane and solvent. The $k_{\text{H}}/k_{\text{D}}$ values for methane are about 4.3 for the Rh–I–Cl system and around 3.9 for the Rh–Cu–Cl system [51d]. These data support the molecular mechanism and suggest that the rate-controlling stage is cleavage of the C–H bond. For reaction products, $k_{\text{H}}/k_{\text{D}}$ by solvent is close to unity in the presence Rh–Cu–Cl [51b]. The measured KIE of solvent (in the Rh–I–Cl system) was 2.0 for formation of CH_3OH , Ac_fOCH_3 , and AcOH and about 1.7 for HCOOH [47d]. KIE must be more pronounced at the stage of active oxidant formation. In the Rh–I–Cl system, the formation of HOI and its reaction with Rh must be associated either (1) with dissociation of HI as a weak acid in aqueous Ac_fOH or (2) with dissociation of HOI as a very weak acid.

Two mechanisms for the activation of methane have been suggested. First (Scheme 16) is the dissociation-mediated route leading to Rh(III) complex **3**. This scheme well explains the formation of acetic acid [2].

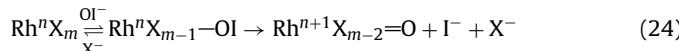


Scheme 16. Oxidative carbonylation of methane to acetic acid on the Rh–I–Cl system. Adapted with permission from [2]. Copyright (2011) Turpion-Moscow Ltd.

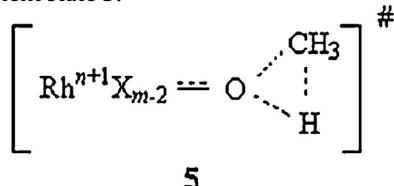


Scheme 17. Oxidation of methane on the Rh–Cu–Cl system. Adapted with permission from [2]. Copyright (2011) Turpion-Moscow Ltd.

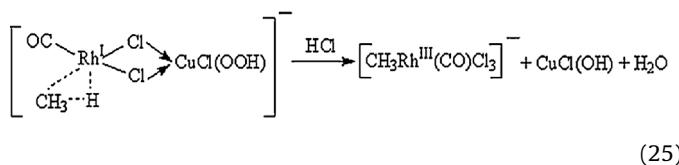
In the Monsanto process, the stages of oxidative addition of methyl iodide to Rh(I) and incorporation are reversible, so that upon heating complex **4** yields methyl iodide rather than methane [48]. This explains the absence of H–D exchange between CH_4 with solvent. Another mechanism involves the formation of the oxo complex of Rh is formed upon interaction of Rh with OI^- (reaction (24)):



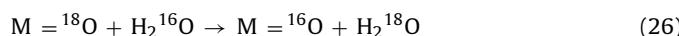
Methanol is formed upon insertion of oxo oxygen into the C–H bond of transient state **5**:



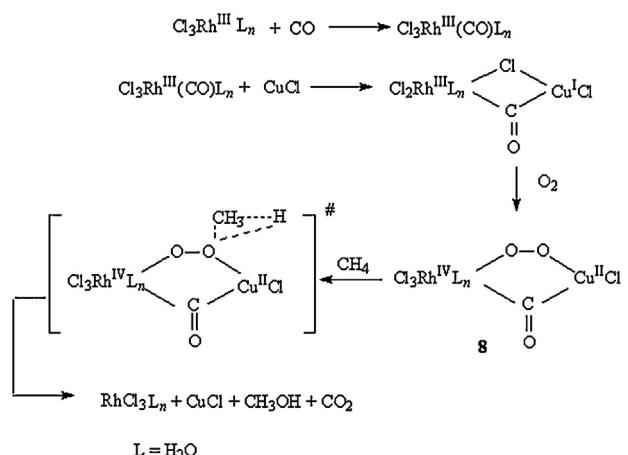
In Rh–Cu(Fe)–Cl systems, the formation of the oxo complex of Rh and oxidation of methane to methanol can proceed under the action of any two-electron oxidant generated *in situ* (H_2O_2 , Ac_fOOH , $\text{M}-\text{OOH}$, etc.). For formation of acetic acid, the suggested mechanism involves a hetero binuclear intermediate [51b]. Initially methane is assumed to a weak associate with Rh(I) (like a σ -complex). This is followed by transfer of two electrons from Rh(I) via chloride bridge and Cu atom to the hydroperoxide group, the electrophilicity of Rh grows, and this results in formation of the Rh(III)–methyl bond (reaction (25)).



Later, the oxidation of methane in the presence of Rh–Cu–Cl system was investigated using $^{18}\text{O}_2$ and light-weight liquid and, conversely, $^{16}\text{O}_2$ and H_2^{18}O – $\text{Ac}_f^{18}\text{OH}$ solution [51d]. The results are indicative of incorporation of O atom from O_2 into oxygenates. The formation of peroxy and hydroperoxy compounds of Rh seems more likely than the formation of oxo complex. In case of the oxo complex, the isotope composition of product would correspond to that of solvent in view of the following exchange by oxygen with a medium (reaction (26)):



The primary product was methanol which further underwent esterification to Ac_fOMe . The reaction Scheme 17 involving peroxy compound of Rh **6** is given below. Hydrogen peroxide or its



Scheme 18. Oxidation of methane via heteronuclear Rh–Cu complexes. Adapted with permission from [2]. Copyright (2011) Turpion-Moscow Ltd.

equivalents are generated in the left cycle. The activation of methane takes place at one of oxygen atoms via transient state **7**.

In view of the fact that KIE of solvent is close to unity in reference to organic products, there is no dissociation of any weak acid. Upon replacement of CO by H_2 , no oxidation was found to occur. This seems unexpected because the reduction potentials of CO and H_2 are close. Note that in the Rh–I–Cl system dihydrogen acts as a reducing agent, although less effective than CO.

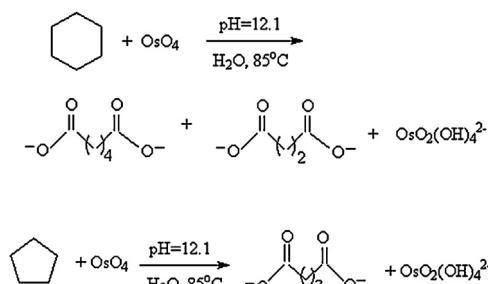
It is well known [8] that Rh compounds are capable of forming complexes with a bridging peroxy group, as well as copper compounds [55]. In order to rationalize the exclusive role of CO in the oxidation of methane with $\text{CO}-\text{O}_2$ mixture, the following reaction Scheme 18 involving Rh(IV) was suggested in [2]. The existence of such Rh(IV) complexes was discussed in [56].

It follows that a catalytically active intermediate here may be the heteronuclear μ -carbonyl– μ -peroxy complex **8**. This intermediate may oxidize both CH_4 and CO. At this, CO is oxidized mostly by conventional route [30]. The scheme is consistent with the results of kinetic isotope studies [51a,b,d]. It also explains the incapability H_2 to act as an active component of gaseous mixture. The equilibrium constant for rhodium hydride in acidic media is exceedingly low [56]. Moreover the hydride bridges in protonic media can form only if there exists another, stronger bridge. It should also be kept in mind that a coordinated CO molecule acts as a stabilizing ligand [57]. Heteronuclear complexes of Pd with Co, Ni, and Cu containing acetate bridging groups were reported in [58], while their structure was characterized in [59].

Oxidative carbonylation of methane to acetic acid was also performed with a heterogeneous catalyst – $\text{Rh}_4\text{Se}_{18}\text{Cl}_{10}$ immobilized on a carbon support – at 400–450 °C and atmospheric pressure [60].

6.2. Reactions of alkanes at C–C bonds

The reasons why the C–C bonds are harder to activate and cleave compared to the C–H bonds have been formulated by Halpern [61]. One is the stereochemical hindrance caused by ligand coating of metal. The second is associated with the fact that cleavage of the C–H bond yields the M(H)R fragment while that of the C–C bond, the MR₂ fragment. Cleavage of the C–H bond is preferable because the strength of the C–H bond is markedly lower than that of the C–C bond. Cleavage of the C–C bond in the absence of stereochemical hindrance was observed in reactions of alkanes with ‘undressed’ metal cations [62]. Stoichiometric oxidation of cyclohexane and cyclopentane with OsO₄ was reported in [63] (Scheme 19).



Scheme 19. Oxidation of alkanes with OsO_4 . Adapted with permission from [63]. Copyright (2005) American Chemical Society.

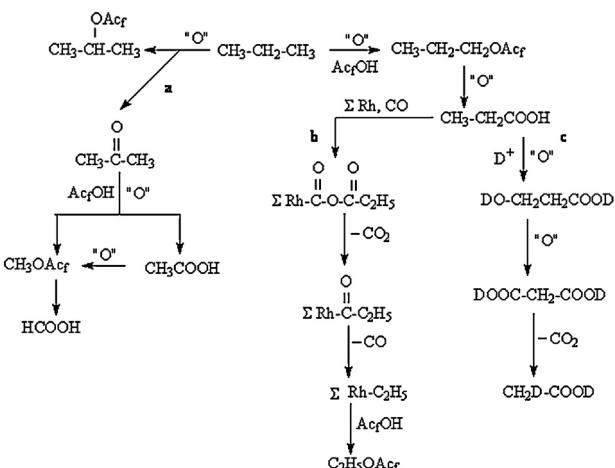
The oxidation of *cis*-decaline with OsO_4 proceeds by concert molecular mechanism [3+2], on retention of the *cis*-9-decalinol configuration [63]. This is indicative of a molecular mechanism.

The C–C bonds can be subjected to oxidative functionalization in the presence of Rh–I–Cl system in aqueous heptafluorobutyric acid [45b]. The reaction with ethane yields methanol, ethanol, their esters, and acetic acid. Propanoic acid is formed in trace amounts due to stronger tendency of the ethyl complex of Rh (compared to the methyl one) to undergoing nucleophilic attack. Experiments with ^{13}CO have shown that 80% acetic acid are formed from ethane while 20%, via cleavage of the C–C bond in ethane, subsequent formation of $\text{CH}_3\text{-Rh}$ species, and their carbonylation. Labeled ethane, $^{13}\text{C}_2\text{H}_6$, yielded only labeled methanol and methyl heptafluorobutyrate. Similar result was obtained in experiments with simultaneously added $^{13}\text{C}_2\text{H}_6$ and $^{12}\text{C}_2\text{H}_5\text{OH}$: methanol is not formed from ethanol. Propane yields largely *i*-propyl, propyl heptafluoroacetate (5:1), and acetone, with some admixture of methanol, ethanol, and acetic acid.

A bright example of functionalization for the C–C bond in butane was given in [45b]. Practically all reaction products arrived due to cleavage of C–C bonds. Several reaction mechanisms have been suggested. But the formation of intermediate radical cations upon ionization of alkanes and homolysis of the C–C bond were rejected. The activation and cleavage of C–C bonds is assumed to happen within the coordination sphere of Rh but no evidence has been provided. Upon replacement of catalyst and CO/O_2 by $\text{K}_2\text{S}_2\text{O}_8$ (Scheme 20) ethane yielded ethylene glycol and its esters (not generated in catalyzed reaction). All this gives grounds to assume that the catalytic reaction proceeds by molecular mechanism.

The reaction of $\text{C}_2\text{–C}_4$ alkanes via cleavage of the C–C bond was also observed [41a,64] for the Rh–Cu–Cl system in Ac_fOH – H_2O under the action of O_2/CO mixture. The composition of products differed from that reported in [45b].

The results obtained in [41a] support the reaction mechanism presented in Scheme 21. The reaction yields primary and secondary alcohols and their esters – typical oxygenates formed upon cleavage of the C–H bonds with metal complexes – as well as ketones and acids. Aldehydes appear in trace amounts apparently because of rapid oxidation. Cleavage of the C–C bonds leads to formation of Ac_fOCH_3 and HCOOH . Moreover, the oxidation of propane and butane results in formation of CH_3COOH and $\text{Ac}_f\text{OC}_2\text{H}_5$ while



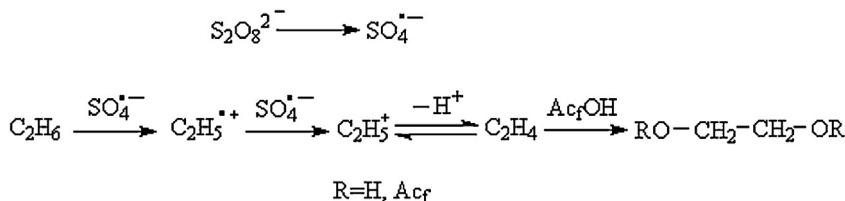
Scheme 21. Oxidation of propane on the Rh–Cu–Cl system. Here ΣRh stands for a catalytically active complex. Adapted with permission from [41a]. Copyright (2010) Springer Science + Business Media B.V.

that of isobutane, of acetone and $\text{Ac}_f\text{OC}_3\text{H}_7^i$. Note that methyl trifluoroacetate and isopropyl trifluoroacetate are formed in equal amounts in case of symbate behavior of kinetic curves.

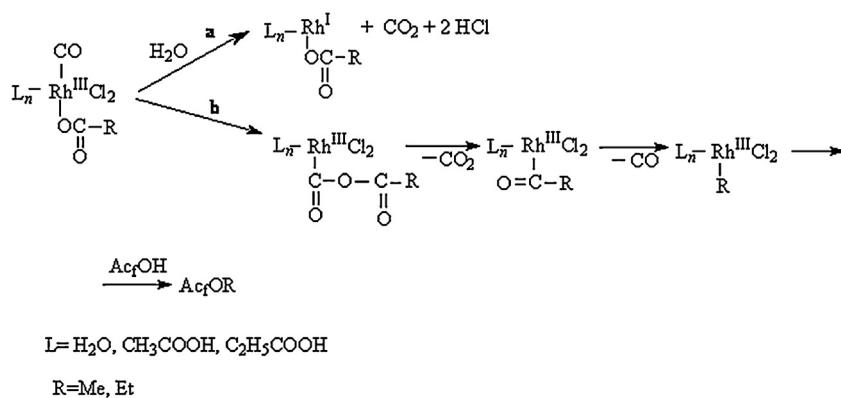
A wide range of oxidation products is indicative of low selectivity of the process. In processing natural and petroleum gases, it would be desirable that $\text{C}_2\text{–C}_4$ hydrocarbons yielded a narrow set of products, such as lower alcohols and acetic acid. The ‘heavy’ products (esters of butyric alcohols and propanoic acid) are minor, while predominant is the fraction of ‘light’ oxygenates $\text{C}_1\text{–C}_3$. In the presence of the Rh–Cu–Cl system, the activation of C–C bonds involves electron withdrawal by electrophilic fragment of catalytically active intermediate to form a reactive radical-cation pair [64]. This is supported by nearly equal amounts of Ac_fOCH_3 and $\text{Ac}_f\text{OC}_2\text{H}_5$ derived from propane, as well as of Ac_fOCH_3 and $\text{Ac}_f\text{OC}_3\text{H}_7^i$ derived from isobutane. But the majority of experimental data are consistent with the following Scheme 21 (“O” stands for active oxidant).

Scheme 21 suggests that we managed to perform almost all depicted stoichiometric reaction. Route (a) leads to isopropanol (in the form of ester) and acetone; and the oxidation of acetone yields methanol (in the form of ester), acetic acid, and formic acid. *n*-Propanol (which in equilibrium with ester) oxidizes to propanoic acid which in turn oxidized via routes (b) and (c). In case (b), the oxidation takes place within the coordination sphere of Rh. First CO intrudes into the Rh–OOCEt bond, after which the consecutive processes of decarboxylation and decarbonylation lead to formation of $\Sigma\text{Rh-Et}$. End product is ethanol (in the form of esters). Route (c) leads to β -oxypropanoic and then to malonic acid. In deuterated solvent ($\text{CF}_3\text{COOD-D}_2\text{O}$), proton exchange in malonic acid takes place. Decarboxylation of $\text{DOOC-CH}_2\text{-COOD}$ results in formation of DCH_2COOD .

Recently, we have established that the composition of oxidation products can be affected by addition of ionic liquids. This was found [41b] to improve the selectivity with respect to

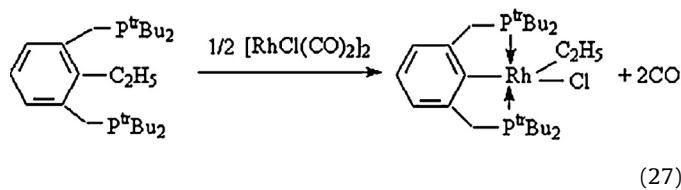


Scheme 20. Oxidation of ethane with $\text{K}_2\text{S}_2\text{O}_8$. Adapted with permission from [45b]. Copyright (1996) American Chemical Society.

**Scheme 22.** Oxidation of carboxylic acids on the Rh–Cu–Cl system. Adapted with permission from [66c]. Copyright (2011) Springer Science + Business Media B.V.

acetone and slightly decrease the overall yield. Acetone was found to form with no involvement of isopropanol; although intentionally added isopropanol oxidized to acetone in the absence of propane. Joint oxidation of propane and isopropanol-¹⁸O with ¹⁶O₂ yielded only acetone-¹⁶O. The absence of ¹⁸O in reaction products affords to assume that propane exhibits higher reactivity in competition with isopropanol.

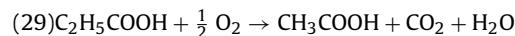
The capability of metal complexes in activation of C–C was also observed [65] upon interaction of so-called ‘pincer’ systems with aryl alkanes (reaction (27)):



Oxidation of acetic and propanoic acids in water along with appropriate mechanistic details will be discussed in the next section.

7. Oxidative destruction of carboxylic acids

In the presence of the Rh–Cu–Cl system in aqueous acetic (propanoic) acid, the destruction of carboxylic acids can be represented as shown below (reactions (28)–(30)) [66]:



The formation of methyl acetate and ethyl propionate can be rationalized in terms of well-known [67] reaction of CO insertion into metal–carboxylate bond followed by the decarboxylation yielding the acyl derivative (**Scheme 22**).

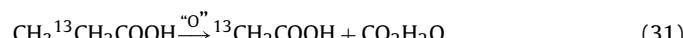
The nucleophilic attack of H₂O on the carbon of coordinated carbonyl group leads to formation of CO₂ (route a). This stage is a chain in the catalytic oxidation of CO. The acyl complex formed upon decarboxylation undergoes decarbonylation to the alkyl derivative whose reaction with acid yields the resultant ester (route b).

The yield of ethylpropionate as a function of [H₂O] and [H₂SO₄] (in case of propanoic acid) behaved differently from those of acetic acid and methylpropionate. In addition, C₂D₅OD did not oxidize to acetic acid but underwent esterification, thus indicating different reaction mechanisms.

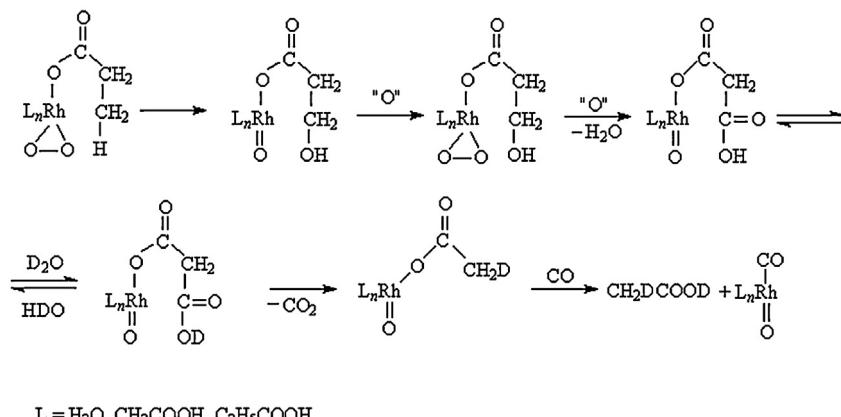
For formation of acetic acid, the following reaction scheme has been suggested (**Scheme 23**).

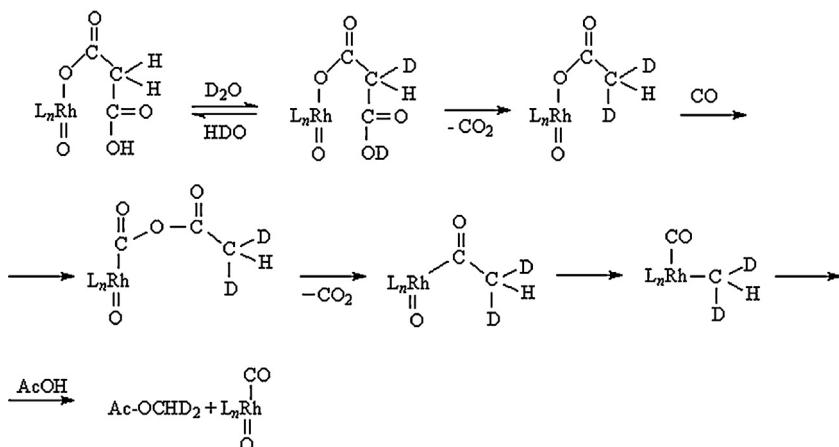
The formation of C₂H₅COOCH_nD_{3-n} suggests the possibility of oxidation of already deuterated acetic acid as shown in **Scheme 24**.

The formation of intermediate malonic acid is in line with earlier results by Sen et al. [36g]. It has been established that the carbon in the methylene group of propanoic acid may become primary in the newly formed acetic acid (reaction (31)):



Such a reaction is possible only in terms of the consequences depicted in **Schemes 22 and 23**.

**Scheme 23.** Oxidation of propanoic acid in deuterated solvent. Adapted with permission from [66c]. Copyright (2011) Springer Science + Business Media B.V.



Scheme 24. Formation of methyl acetate during oxidation of propanoic acid. Adapted with permission from [66c]. Copyright (2011) Springer Science + Business Media B.V.

Note that the above decomposition reactions of carboxylic acids can be regarded as a convenient model for the production of biofuels via decarboxylation of fatty acids.

8. Concluding remarks

In conclusion, I would like to outline recent data on oxidative functionalization of alkanes from the viewpoint of their practical implementation. According to Periana [26c], an ideal catalyst must have the catalytic activity $\text{TOF} = 1 \text{ s}^{-1}$. Such a requirement seems to be strongly overestimated. In real catalytic systems for synthesis of acetic acid via carbonylation of methanol (effective Monsanto process), the reaction rate of about 6 M/h at $[\text{Rh}] = 3 \times 10^{-3} \text{ M}$, $P_{\text{CO}} 3.0 \text{ MPa}$, and 170°C . In this case, $\text{TOF} = 0.55 \text{ s}^{-1}$. In view of chemical inertness of methane, the tolerable activity can be adopted on a level of 0.1 s^{-1} . The activity of (bipy) PtCl_2 is 10^{-3} s^{-1} (the Catalytica process), but here attractive are the high conversion of methane and no need for external reducing agent. A large drawback is the use of sulfuric acid. Moreover, separation of methanol requires hydrolysis that produces large amounts of dilute sulfuric acid. All this casts strong doubts as for economic efficiency of the Catalytica process.

For similar reasons, the processes involving sodium persulfate [68] can hardly become economically promising. Much more attractive seem to be the processes involving hydrogen peroxide developed by research groups headed by Shul'pin et al. [69a,b], Pombeiro et al. [69b,c]. No doubt, hydrogen peroxide is inexpensive, environment-friendly and its application requires no noble metals. Meanwhile, it should be kept in mind that one of production methods for hydrogen peroxide [13] needs the use of Pd/C for reduction of ethyl anthraquinone. Moreover, due to spontaneous decomposition of H_2O_2 , the efficiency of its action can hardly exceed 25%. In this context, it seems reasonable to generate hydrogen peroxide *in situ*. Effective catalytic systems for direct oxidation of alkanes require the use of external reductant to activate molecular oxygen. In contrast to biological systems, the efficiency of reducing agent in chemical systems never exceeds 5–10%. Moreover, affordable reducing agents (such as H_2 and CO) demand the use of noble metals. Therefore it turns out that neither the preparation of hydrogen peroxide nor the processes with involvement of dioxygen can be managed without the assistance of noble metals.

At 95°C , the catalytic activity of the Rh–Cu–Cl system attains a practically meaningful value of 0.09 s^{-1} [51]. But this system is operative in toxic trifluoroacetic acid. In this process, 9–10 molecules of CO are spent to convert one methane molecule. Moreover, the reactor material should be highly corrosion-resistant (dissolution of even Ti in Ac_2OH was reported).

Therefore, all existing homogeneous catalysts (in their present state) for direct oxidation and oxidative carbonylation of alkanes can hardly find their industrial implementation.

One of possible routes to further advance in this direction is processing in liquid films deposited onto a support. For instance, acetoxylation of ethylene was carried out with the film of acetic acid covering the Pd/SiO_2 surface [70]. Solutions of metal complexes in high-boiling solvents can be immobilized on solid porous substrates just as it is done in gas chromatography. Design of hybrid catalysts would afford to combine the advantages of homogeneous and heterogeneous catalysis two in one. At relatively low temperatures (100 – 200°C) ensuring high selectivity of the process, there would be no need for solvents and for measures of their removal.

Inevitable difficulties in a search for oxidation-resistant immobile liquid phase with good heat/mass transfer characteristics seem to be surmountable. At least, studies on metal complex solutions in ionic liquids grafted on solid substrates [71] or in porous substrates such as silica gel [72] for use in pseudo-gas phase hydroformylation of olefins are in progress. The perspectives for the use of such catalysts in catalytic processes were outlined in [73].

Acknowledgments

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References

- [1] (a) O.V. Krylov, *Heterogeneous Catalysis*, Akademkniga, Moscow, 2004; (b) J. Chorkendorff, J.W. Neimantsverdriet, *Concepts of Modern Catalysis and Kinetics*, Wiley-VCH, Weinheim, 2007.
- [2] (a) E.G. Chepaikin, Russ. Chem. Rev. (Engl. transl.) 80 (2011) 363–396; (b) C.D. Pina, E. Falletta, M. Rossi, Chem. Soc. Rev. 41 (2012) 350–369; (c) E. Roduner, W. Kainz, B. Sarkar, V.B. Urlacher, J. Pleiss, R. Gläser, W.-D. Einicke, W.A. Sprenger, U. Beifuß, E. Klemm, C. Liebner, H. Hieronymus, S.-F. Hsu, B. Plietker, S. Laschat, ChemCatChem 5 (2013) 82–112.
- [3] J. Halpern, Discuss. Faraday Soc. 46 (1968) 7–19.
- [4] J. Chatt, J.M. Davidson, J. Chem. Soc. (1965) 843–855.
- [5] G. Wilke, H. Schott, P. Heimbach, Angew. Chem. Int. Ed. 6 (1967) 92–93.
- [6] L. Vaska, Science 140 (1963) 809–810.
- [7] B.W. Graham, K.R. Laing, C.J. O'Connor, W.R. Roper, J. Chem. Soc. Dalton Trans. (1972) 1237–1243.
- [8] A.W. Addison, R.D. Gillard, J. Chem. Soc. A (1970) 2523–2526.
- [9] M.M. Konnick, I.A. Guzei, S.S. Stahl, J. Am. Chem. Soc. 126 (2004) 10212–10213.
- [10] X.-Y. Yu, B.O. Patrick, B.R. James, Organometallics 25 (2006) 4870–4877.
- [11] B. Bruin, T.P.J. Peters, J.B.M. Wilting, S. Thewissen, J.M.M. Smits, A.W. Gal, Eur. J. Inorg. Chem. (2002) 2671–2680.
- [12] J. Cipot-Wechsler, D. Covelli, J.M. Praetorius, N. Hearns, O.V. Zenkina, E.C. Keske, R. Wang, P. Kenneppohl, C.M. Crudden, Organometallics 31 (2012) 7306–7315.

- [13] G. Strukul, Catalytic Oxidation with Hydrogen Peroxide as Oxidant, Kluwer, Dordrecht, 1992.
- [14] M.C. Denney, N.A. Smythe, K.L. Cetto, R.A. Kemp, K.I. Goldberg, J. Am. Chem. Soc. 128 (2006) 2508–2509.
- [15] (a) J.M. Keith, R.J. Nielsen, J. Osgaard, W.A. Goddard III, J. Am. Chem. Soc. 127 (2005) 13172–13179;
 (b) B.V. Popp, S.S. Stahl, Chem. Eur. J. 15 (2009) 2915–2922.
- [16] (a) T. Nishimura, N. Kakiuchi, T. Onoue, K. Ohe, S. Uemura, J. Chem. Soc. Perkin Trans. 1 (2000) 1915;
 (b) M.M. Konnick, B.A. Gandhi, I.A. Guzei, S.S. Stahl, Angew. Chem. Int. Ed. 45 (2006) 2904–2907.
- [17] M. Ahijado, T. Braun, D. Noveski, N. Kocher, B. Neumann, D. Stalke, H.-G. Stammel, Angew. Chem. Int. Ed. 44 (2005) 6947–6951.
- [18] V.N. Zudin, V.A. Liholobov, Yu.I. Ermakov, Kinetika i Kataliz 20 (1979) 1599–1600.
- [19] J.-U. Rohde, J.-H. In, M.H. Lim, W.W. Brennessel, M.R. Bukowski, A. Stubna, E. Müncz, W. Nam, L. Que Jr., Science 299 (2003) 1037–1039.
- [20] (a) G. Hay-Motherwell, B. Wilkinson, M.B. Hussain-Babes, Hurtshouse, Polyhedron 12 (1993) 2009–2012;
 (b) C. Limberg, Angew. Chem. Int. Ed. 48 (2009) 2270–2273.
- [21] (a) T.M. Anderson, W.A. Neiwert, M.L. Kirk, P.M.B. Piccoli, A.J. Schultz, T.F. Koetzle, D.G. Musaev, K. Morokuma, R. Cao, C.L. Hill, Science 306 (2004) 2074–2077;
 (b) T.M. Anderson, R. Cao, E. Slonkina, B. Hedman, K.O. Hodgson, K.I. Hardcastle, W.A. Neiwert, S. Wu, M.L. Kirk, S. Knottenbelt, E.C. Depperman, B. Keita, L. Nadjo, D.G. Musaev, K. Morokuma, C.L. Hill, J. Am. Chem. Soc. 127 (2005) 11948–11949;
 (c) R. Cao, T.M. Anderson, P.M.B. Piccoli, A.M. Schultz, T.F. Koetzle, Y.V. Geletii, E. Slonkina, B. Hedman, K.O. Hodgson, K.I. Hardcastle, X. Fang, M.L. Kirk, S. Knottenbelt, P. Kögerler, D.G. Musaev, K. Morokuma, M. Takahashi, C.L. Hill, J. Am. Chem. Soc. 129 (2007) 11118–11133;
 (d) E. Poverenov, I. Efremenko, A.I. Frenkel, Y. Ben-David, L.J.W. Shimon, G. Leitus, L. Konstantinovski, J.M.L. Martin, D. Milstein, Nature 455 (2008) 1093–1096;
 (e) K.P. O'Halloran, C. Zhao, N.S. Ando, A.J. Schultz, T.F. Koetzle, P.M.B. Piccoli, B. Hedman, K.O. Hodgson, E. Bobyr, M.L. Kirk, S. Knottenbelt, E.C. Depperman, B. Stein, T.M. Anderson, R. Cao, Y.V. Geletii, K.I. Hardcastle, D.G. Musaev, W.A. Neiwert, X. Fang, K. Morokuma, S. Wu, P. Kögerler, C.L. Hill, Inorg. Chem. 51 (13) (2012) 7025–7031.
- [22] A.J. Cowan, M.W. George, Coord. Chem. Rev. 252 (2008) 2504–2511.
- [23] W.H. Bernskoetter, C.K. Schauer, K.I. Goldberg, M. Brookhart, Science 326 (2009) 553–556.
- [24] J. Campos, S. Kundu, D.R. Pahls, M. Brookhart, E. Carmona, T.R. Cundari, J. Am. Chem. Soc. 135 (2013) 1217–1220.
- [25] A.E. Shilov, G.B. Shul'pin, Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes, Kluwer Academic Publishers, New York–Boston–Dordrecht–Moscow, 2000.
- [26] (a) R.A. Periana, D.J. Taube, S. Gamble, H. Taube, T. Saton, H. Fujii, Science 280 (1998) 560–564;
 (b) R.A. Periana, G. Bhalla, W.J. Tenn III, K.J.H. Young, X.Y. Liu, O. Mironov, C.J. Jones, V.R. Ziatdinov, J. Mol. Catal. A Chem. 220 (2004) 7–25;
 (c) B.L. Conley, W.J. Tenn III, K.J.H. Young, S.K. Ganesh, S.K. Meier, V.R. Ziatdinov, O. Mironov, J. Osgaard, J. Gonzales, W.A. Goddard III, R.A. Periana, J. Mol. Catal. A Chem. 251 (2006) 8–23;
 (d) B.G. Hashiguchi, S.M. Bischof, M.M. Konnick, R.A. Periana, Acc. Chem. Res. 45 (2012) 885–898.
- [27] (a) Y. Fan, Z. An, X. Pan, X. Liu, X. Bao, J. Chem. Soc. Chem. Commun. (2009) 7488–7490;
 (b) Z. An, X. Pan, X. Liu, X. Han, X. Bao, J. Am. Chem. Soc. 128 (2006) 16028–16029;
 (c) J. Yuan, L. Wang, Y. Wang, Ind. Eng. Chem. Res. 50 (2011) 6513–6516;
 (d) J. Yuan, Y. Wang, C. Hao, Catal. Lett. 143 (2013) 610–615.
- [28] R.D. Gray, J. Am. Chem. Soc. 91 (1969) 56–62.
- [29] A. Zuberbuhler, Helv. Chim. Acta 50 (1967) 466–474.
- [30] D.V. Sokol'skii, Ya.A. Dorfman, in: Kataliz ligandami v vodnykh rastvorakh (Catalysis by Ligands in Aqueous Solutions), Nauka, Alma-Ata, 1972, p. 336.
- [31] A. Sen, Acc. Chem. Res. 31 (1998) 550–557.
- [32] (a) N.I. Kuznetsova, L.G. Detusheva, L.I. Kuznetsova, M.A. Fedotov, V.A. Liholobov, J. Mol. Catal. A Chem. 114 (1996) 131–139;
 (b) N.I. Kuznetsova, L.I. Kuznetsova, L.G. Detusheva, V.A. Liholobov, M.A. Fedotov, S.V. Koshcheev, E.B. Burgina, Stud. Surf. Sci. Catal. 110 (1997) 1203–1211;
 (c) N.V. Kirillova, N.I. Kuznetsova, L.I. Kuznetsova, V.A. Liholobov, Russ. Chem. Bull., Int. Ed. (2002) 975–981;
 (d) N.V. Kirillova, N.I. Kuznetsova, L.I. Kuznetsova, V.I. Zaikovskii, S.V. Koshcheev, V.A. Liholobov, Catal. Lett. 84 (2002) 163–168.
- [33] J.L. Garnet, R.J. Hodges, J. Am. Chem. Soc. 89 (1967) 4546–4547.
- [34] (a) N.F. Gol'dshleger, M.B. Tyabin, A.E. Shilov, A.A. Shtainman, Zh. Fiz. Khim. 43 (1969) 2174–2175;
 (b) N.F. Gol'dshleger, V.V. Es'kova, A.E. Shilov, A.A. Shtainman, Zh. Fiz. Khim. 46 (1972) 1353–1354;
 (c) V.V. Es'kova, A.E. Shilov, A.A. Shtainman, Kinetika i Kataliz 13 (1972), 534–534;
 (d) L.A. Kusch, V.V. Lavrushko, Yu.S. Misharin, A.P. Moravsky, A.E. Shilov, Nouv. J. Chim. 7 (1983) 729–733.
- [35] (a) R.H. Crabtree, J. Chem. Soc. Dalton Trans. (2001) 2437–2450;
 (b) M. Lersh, M. Tilset, Chem. Rev. 105 (2005) 2471–2526.
- [36] (a) M. Lin, C. Shen, E.A. Garcia-Zayas, A. Sen, J. Am. Chem. Soc. 123 (2001) 1000–1001;
 (b) E. Gretz, T.F. Oliver, A. Sen, J. Amer. Chem. Soc. 109 (1987) 8109–8111;
 (c) L.C. Kao, A.C. Hutson, A. Sen, J. Am. Chem. Soc. 113 (1991) 700–701;
 (d) M. Lin, A. Sen, J. Am. Chem. Soc. 114 (1992) 7307–7308;
 (e) J.E. Remias, A. Sen, J. Mol. Catal. A Chem. 189 (2002) 33–38;
 (f) M. Lin, T. Hogan, A. Sen, J. Am. Chem. Soc. 119 (1997) 6048–6053;
 (g) C. Shen, E.A. Garcia-Zayas, A. Sen, J. Am. Chem. Soc. 122 (2000) 4029–4031.
- [37] (a) I.P. Stolyarov, M.N. Vargaftik, I.I. Moiseev, Kinetika i Kataliz 30 (1989) 1513–1514;
 (b) M.N. Vargaftik, I.P. Stolyarov, I.I. Moiseev, J. Chem. Soc. Chem. Commun. (1990) 1049–1050;
 (c) N.F. Gol'dshleger, E.N. Kresova, A.P. Moravskii, Kinetika i Kataliz 24 (1991), 1023–1023;
 (d) I.P. Stolyarov, I.I. Moiseev, Presented at Int. Conf. on Organometallic and Coordination Chemistry, Nizhnii Novgorod, 2008, 051.
- [38] E.D. Park, S.H. Choi, J.S. Lee, J. Catal. 194 (2000) 33–34.
- [39] (a) J. Cheng, Z. Li, M. Haught, Y. Tang, J. Chem. Soc. Chem. Commun. (2006) 4617–4619;
 (b) R. Palkovits, M. Antonietti, P. Kuhn, A. Thomas, F. Schüth, Angew. Chem. Int. Ed. 48 (2009) 6909–6912;
 (c) M. Soorholtz, R.J. White, T. Zimmermann, M.M. Titirici, M. Antonietti, R. Palkovits, F. Schüth, J. Chem. Soc., Chem. Commun. 49 (2013) 240–242.
- [40] I. Bar-Nahum, A.M. Khenkin, R. Neumann, J. Am. Chem. Soc. 126 (2004) 10236–10237.
- [41] (a) E.G. Chepaikin, A.P. Bezruchenko, G.N. Menchikova, N.I. Moiseeva, A.E. Gekhman, Petrol. Chem. (Engl. transl.) 50 (2010) 332–337;
 (b) E.G. Chepaikin, A.P. Bezruchenko, G.N. Menchikova, N.I. Moiseeva, A.E. Gekhman, I.I. Moiseeva, Petrol. Chem. (Engl. transl.) (2014), in press.
- [42] (a) L.A. Levchenko, A.P. Sadkov, N.V. Lariontseva, E.M. Koldasheva, A.K. Shilova, A.E. Shilov, Dokl. Biochem. Biophys. (Engl. Transl.) 377 (2001) 123–124;
 (b) L.A. Levchenko, A.P. Sadkov, N.V. Lariontseva, V.S. Kulikova, A.K. Shilova, A.E. Shilov, Dokl. Biochem. Biophys. (Engl. Transl.) 394 (2004) 33–34;
 (c) L.A. Levchenko, V.G. Kartsev, A.P. Sadkov, A.F. Shestakov, A.K. Shilova, A.E. Shilov, Dokl. Chem. (Engl. Transl.) 412 (2007) 35–37;
 (d) L.A. Levchenko, N.G. Lobanova, V.M. Martynenko, A.P. Sadkov, A.F. Shestakov, A.K. Shilova, A.E. Shilov, Dokl. Chem. (Engl. Transl.) 430 (2010) 50–53.
- [43] (a) D.A. Pichugina, A.F. Shestakov, N.E. Kuz'menko, Russ. Chem. Bull., Int. Ed. 55 (2006) 195–206;
 (b) N.G. Nikitenko, A.F. Shestakov, Dokl. Chem. (Engl. Transl.) 450 (2013) 127–130;
 (c) N.G. Nikitenko, A.F. Shestakov, Kinet. Catal. (Engl. Transl.) 54 (2013) 168–178.
- [44] M.H.A. Rahim, M.M. Forde, R.L. Jenkins, C. Hammond, Q. He, N. Dimitratos, J.A. Lopez-Sánchez, A.F. Carley, S.H. Taylor, D.J. Wilcock, D.M. Murphy, C.J. Kiely, G.J. Hutchings, Angew. Chem. Int. Ed. 52 (2013) 1280–1284.
- [45] (a) M. Lin, A. Sen, Nature 368 (1994) 613–615;
 (b) M. Lin, T. Hogan, A. Sen, J. Am. Chem. Soc. 118 (1996) 4574–4580.
- [46] (a) E.C. Baker, D.E. Hendriksen, R. Eisenberg, J. Amer. Chem. Soc. 102 (1980) 1020–1027;
 (b) E.G. Chepaikin, A.P. Bezruchenko, A.A. Leshcheva, G.N. Boiko, Russ. Chem. Bull. (Engl. Transl.) 43 (1994) 360–363.
- [47] (a) E.G. Chepaikin, G.N. Boiko, A.P. Bezruchenko, A.A. Leshcheva, E.A. Grigoryan, Dokl. Phys. Chem. (Engl. Transl.) 353 (1997) 120–122;
 (b) E.G. Chepaikin, G.N. Boiko, A.P. Bezruchenko, A.A. Leshcheva, E.H. Grigoryan, J. Mol. Catal. A Chem. 129 (1998) 15–18;
 (c) A.P. Bezruchenko, G.N. Boiko, E.A. Grigoryan, A.A. Leshcheva, E.G. Chepaikin, A.E. Shilov, Dokl. Phys. Chem. (Engl. Transl.) 363 (1998) 396–399;
 (d) E.G. Chepaikin, A.P. Bezruchenko, A.A. Leshcheva, G.N. Boiko, I.V. Kuzmenkov, E.H. Grigoryan, A.E. Shilov, J. Mol. Catal. A Chem. 169 (2001) 89–98.
- [48] (a) T.W. Dekleva, D. Forster, Adv. Catal. 34 (1986) 81–130;
 (b) P.M. Maitlis, A. Haynes, G.J. Sunley, M.J. Howard, J. Chem. Soc. Dalton Trans. (1996) 2187–2196.
- [49] E.G. Chepaikin, M.L. Khidekel, Koordinatz. Khim. 8 (1982) 1011–1021.
- [50] A.H. Haines, Methods for the Oxidation of Organic Compounds, Academic Press, London–Orlando–San Diego–New York–Toronto–Montreal–Sydney–Tokyo, 1985.
- [51] (a) E.G. Chepaikin, A.P. Bezruchenko, A.A. Leshcheva, E.A. Grigoryan, Dokl. Phys. Chem. (Engl. Transl.) 373 (2000) 105–107;
 (b) E.G. Chepaikin, A.P. Bezruchenko, A.A. Leshcheva, Kinet. Catal. (Engl. Transl.) 43 (2002) 507–513;
 (c) E.G. Chepaikin, A.P. Bezruchenko, G.N. Boiko, A.A. Leshcheva, Petrol. Chem. (Engl. Transl.) 43 (2003) 395–398;
 (d) E.G. Chepaikin, A.P. Bezruchenko, G.N. Boiko, A.E. Gekhman, I.I. Moiseev, Kinet. Catal. (Engl. Transl.) 47 (2006) 12–19.
- [52] G.P. Luchinskii, Khimiya titana (Chemistry of Titanium), Khimiya, Moscow, 1971.
- [53] R. Bell, The Proton in Chemistry, Chapman and Hall, London, 1973.
- [54] (a) I.I. Moiseev, M.N. Vargaftik, Ya.K. Syrkin, Dokl. Akad. Nauk SSSR 153 (1963) 140–143;
 (b) V.N. Zudin, V.D. Chinakov, V.M. Nekipelov, V.A. Rogov, V.A. Liholobov, Yu.I. Ermakov, J. Mol. Catal. 52 (1989) 27–48;
 (c) L.G. Bruk, I.V. Oshanina, A.P. Kozlova, O.N. Temkin, K.Yu. Odintsov, Russ. Chem. Bull. (Engl. Transl.) 47 (1998) 1071–1073.
- [55] (a) T. Matsumoto, K. Ohkubo, K. Honda, A. Yazawa, H. Furutachi, S. Fujinami, S. Fukuzumi, M. Suzuki, J. Am. Chem. Soc. 131 (2009) 9258–9267;

- (b) O. Sander, A. Henß, C. Näther, C. Würtele, M.C. Holthausen, S. Schindler, F. Tuczek, *Chem. Eur. J.* 14 (2008) 9714–9729.
- [56] A. Bakac, *Dalton Trans.* (2006) 1589–1596.
- [57] G. Henrici-Olive, S. Olive, *Coordination and Catalysis*, Verlag Chemie, Weinheim–New York, 1980.
- [58] R.W. Brandon, D.V. Claridge, *Chem. Commun.* (1968) 677–678.
- [59] N.Yu. Kozitsyna, S.E. Nefedov, N.V. Cherkashina, V.N. Ikorskii, M.N. Vargaftik, I.I. Moiseev, *Russ. Chem. Bull., Int. Ed.* 54 (2005) 2215–2218.
- [60] (a) G.R. Kosmambetova, P.E. Strizhak, V.I. Gritsenko, S.V. Volkov, L.B. Kharkova, O.G. Yanko, O.M. Korduban, *J. Nat. Gas Chem.* 17 (2008) 1–7;
(b) S.V. Volkov, G.R. Kosmambetova, L.B. Kharkova, O.V. Shvets, O.G. Yanko, V.I. Gritsenko, P.E. Strizhak, *J. Nat. Gas Chem.* 18 (2009) 399–406.
- [61] (a) J. Halpern, *Inorg. Chim. Acta* 100 (1985) 41–48;
(b) J. Halpern, *Acc. Chem. Res.* 15 (1982) 238–244.
- [62] (a) H.G. Cho, X. Wang, L. Andrews, *J. Am. Chem. Soc.* 127 (2005) 465–473;
(b) H.G. Cho, L. Andrews, *Organometallics* 26 (2007) 633–643.
- [63] B.C. Bales, P. Brawn, A. Dehestani, J.M. Mayer, *J. Am. Chem. Soc.* 127 (2005) 2832–2833.
- [64] E.G. Chepaikin, A.P. Bezruchenko, G.N. Menchikova, N.I. Moiseeva, A.E. Gekhman, *Kinet. Catal. (Engl. Transl.)* 51 (2010) 666–671.
- [65] B. Rybchinski, D. Milstein, *The Chemistry of Pincer Compounds*, Elsevier B.V., Amsterdam, 2007, pp. 87–105.
- [66] (a) E.G. Chepaikin, A.P. Bezruchenko, G.N. Menchikova, N.I. Moiseeva, A.E. Gekhman, I.I. Moiseev, *Dokl. Phys. Chem. (Engl. Transl.)* 437 (2011) 41–44;
(b) E.G. Chepaikin, A.P. Bezruchenko, G.N. Menchikova, N.I. Moiseeva, A.E. Gekhman, I.I. Moiseev, *Russ. Chem. Bull., Int. Ed.* 60 (2011) 49–54;
(c) E.G. Chepaikin, A.P. Bezruchenko, G.N. Menchikova, N.I. Moiseeva, A.E. Gekhman, I.I. Moiseev, *Petrol. Chem. (Engl. Transl.)* 51 (2011) 133–142.
- [67] I.I. Moiseev, M.N. Vargaftik, O.I. Gentosh, N.M. Zhavoronkov, I.V. Kalechitz, Yu.A. Pazderskii, T.A. Stromnova, L.S. Shcherbakova, *Dokl. Akad. Nauk SSSR* 237 (1977) 645–647.
- [68] C. Jia, T. Kitamura, Y. Fujiwara, *Acc. Chem. Res.* 34 (2001) 633–639.
- [69] (a) G.B. Shulpin, *Mini Rev. Org. Chem.* 6 (2009) 95–104;
(b) M.V. Kirillova, Y.N. Kozlov, L.S. Shul'pina, O.Y. Lyakin, A.M. Kirillov, E.P. Talsi, A.J.L. Pombeiro, G.B. Shul'pin, *J. Catal.* 268 (2009) 26–38;
(c) K.R. Gruenwald, A.M. Kirillov, M. Naukka, J. Sanchiz, A.J.L. Pombeiro, *Dalton Trans.* (2009) 2109–2120.
- [70] I.I. Moiseev, *Kinet. Catal. (Engl. Transl.)* 42 (2001) 1–22.
- [71] C.P. Mehnert, *Chem. Eur. J.* 11 (2005) 50–56.
- [72] M. Haumann, K. Dentler, J. Joni, A. Riisager, P. Wasserscheid, *Adv. Synth. Catal.* 349 (2007) 425–431.
- [73] H. Olivier-Bourbigou, L. Magna, D. Morvan, *Appl. Catal. A Gen.* 373 (2010) 1–56.