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Review

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

E.G. Chepaikin*

Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka, Moscow 142432 Russia

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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.

Contents

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].

* Corresponding author. Tel.: +7 496 524 6489.
E-mail addresses: echep@ism.ac.ru, grig@ism.ac.ru

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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, OSO_3H, 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 H_2O_2) would be quiet acceptable. In chemical systems, it seems reasonable to use H_2 or CO as a reducing agent.

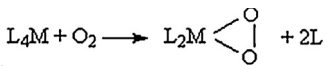
3. Activation of dioxygen

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 peroxo 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]:

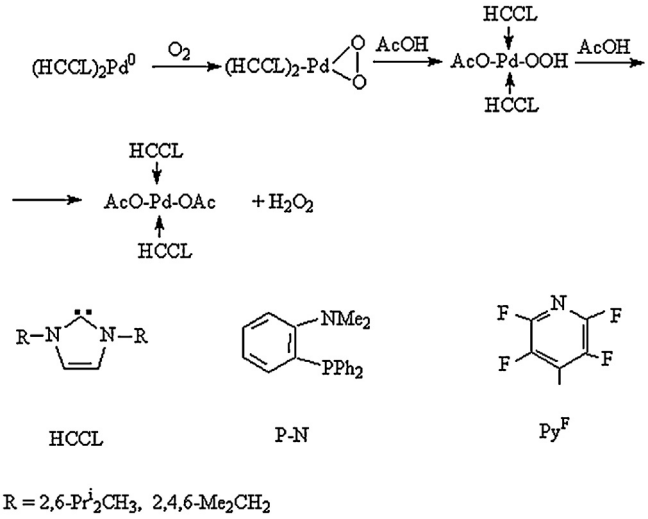


(1)

$$Ph_3P + \frac{1}{2}O_2 \rightarrow Ph_3PO \quad (2)$$

To date, the following complexes have been reported in the literature: $(PPh_3)_2Ir(CO)(O_2)Cl$ [6], $(PPh_3)_2Ru(O_2)(NCS)(NO)$ [7], and $[ClPy_4Rh–O–ORhPy_4Cl]^+$ [8]). Interaction of O_2 with the Pd(0) complex containing carbene ligands L (HCCL) was found to yield, in acetic acid (AcOH), hydrogen peroxide [9].

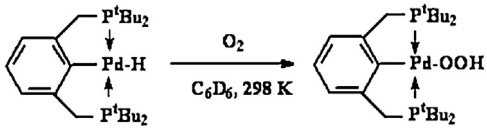
The synthesis of the following Rh complexes are reported: $(HCCL)(PPh_3)_2Rh(O_2)Cl$, $(P\text{-}N)(PPh_3)_2Rh(O_2)Cl$, and $(PtEt_3)_2(Bu^tCN)Py^F\text{-}Rh(O_2)$ [10]. Oxygen expels ethylene from the coordination sphere of Rh [11] to give a peroxo complex. In similar reaction of the Ir complex, ethylene remains intact due to stronger bonding with the complex. Recently, some new Rh peroxo complexes have been synthesized [12]. In the above peroxo complexes, the O–O bond is longer than that in dioxygen, which is indicative of its activation.



Scheme 1. Stoichiometric formation of H_2O_2 from O_2 and Pd(0). Adapted with permission from [9]. Copyright (2004) American Chemical Society.

3.2. Hydroperoxo complexes

As mentioned in Section 2.1, in acetic acid the peroxo complex of Pd transformed into the hydroperoxo complex (Scheme 1). As it is known [13], Rh, Pd, Ir, and Pt form similar complexes upon interaction of respective phosphine hydride complexes with O_2. 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.



(3)

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 O_2 involve hydrogen abstraction by triplet dioxygen yielding stable $L_2Pd(I)(^{\bullet}OOH)(Cl)$. This is followed by spin transition into a stable $L_2Pd(II)(OOH)(Cl)$ accompanied by evolution of H_2O_2. These reactions require the presence of withdrawing ligands and a *cis*-H bond acceptor.

Theoretical study of $Py_2Pd(H)OAc$ taken as an example [15b] considered the following possible reaction routes: (a) homolytic reaction involving abstraction of $H^{\bullet}$ by O_2; (b) reductive elimination of AcOH to form a Pd(0) complex, its interaction with O_2, and conversion of peroxo-complex into hydroperoxide one under the action of AcOH; (c) migratory insertion of O_2 into the Pd–H bond; and (d) oxidative addition of O_2 to Pd(II) yielding a peroxohydride 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].