Homogeneous oxidation of alkanes: Role of rhodium–alkyl complexes

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ABSTRACT

Catalytic systems $RhCl_3$–KI–NaCl and $RhCl_3$–$Cu(OAc_f)_2$–NaCl in aqueous perfluorinated carboxylic acids (CF_3COOH, C_3F_7COOH) are effective in coupled oxidation of alkanes and carbon monoxide with dioxygen. In their presence, predominant is the outer-sphere oxidation of alkanes into respective esters (alcohols) with involvement of peroxo rhodium species as an oxidant (mechanism A). The process occurs partially by the inner-sphere mechanism B involving Rh–alkyl intermediates. Mechanism B is supported by (a) formation of alkyl chlorides, (b) synthesis of acetic acid in conversion of methane, and (c) positional selectivity in oxidation of propane.

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1. Introduction

Oxidation of lower alkanes on homogeneous metal-complex catalysts seems promising for use in reprocessing natural and associated petroleum gas [1]. The problem has been a subject of several monographs [2–5] and numerous reviews [6–10]. It is widely adopted that the activation of C—H bonds proceeds largely by the following two mechanisms (Scheme 1).

The outer-sphere mechanism (**A**) postulates that the activation of alkanes takes place with participation of oxygen atoms in oxo or peroxo metal complexes [2]. Mechanism **A** is also applicable to the action of oxygenases and related compounds. For such a mechanism, the kinetic isotopic effect, k_H/k_D, is above 3.5 (and about 5.0 for methane monooxygenase). The inner-sphere mechanism (**B**) involving the formation of metal–alkyl bond is effective in other catalytic systems such as those developed by Shilov [3] and Periana [8]. For the Shilov system, mechanism **B** is supported the isotopic exchange between methane (CH_4) and deuterated media and also by the value of $k_H/k_D \approx 3$ at 100 °C. Chloride-containing systems (e.g. $PtCl_4^{2-}$–$PtCl_6^{2-}$) catalyze the formation of not only alcohols but also alkyl chlorides. Metal–alkyl complexes were obtained by independent synthesis from e.g. H_2PtCl_6 and alkyl iodides. Prof. Shul'pin was the first who managed to synthesize aryl–Pt(IV) com-

pounds directly from arenes [11]. Some catalytic systems can operate via combined action of mechanisms **A** and **B**. As an example, we can mention the catalytic systems based on Rh and Pd complexes and I-, Cu-, and Fe-containing compounds acting as co-catalysts [9,10e,12–15]. Such systems catalyze coupled oxidation of alkanes and CO with dioxygen.

Rh–I–Cl, Rh–Cu–Cl, and Rh–Fe–Cl catalytic systems, just as the other ones [16–20], are most effective in aqueous solution of trifluoroacetic acid (Ac_fOH) and heptafluorobutyric acid (Pr_fCOOH).
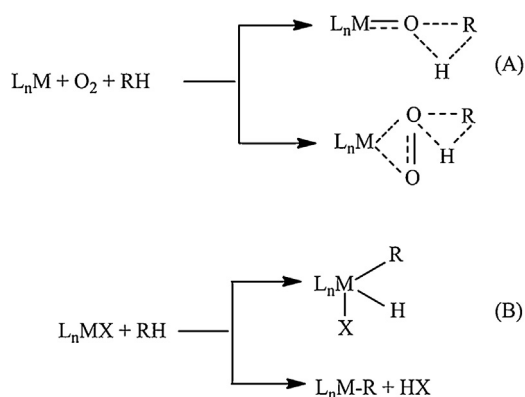
As shown in Scheme 2, the reactions of methane in Ac_fOH/H_2O media may yield methanol (ester), acetic acid (upon oxidative carbonylation of methane), and formic acid (deep oxidation of methane).

There are grounds to assume that the oxidation of methane to methanol (methyl trifluoroacetate) in the presence of rhodium–iodide–chloride (Rh–I–Cl) and rhodium–copper–chloride (Rh–Cu–Cl) catalytic systems in aqueous trifluoroacetic acid proceeds largely by mechanism **A** [12–14] while the concomitant oxidative carbonylation of methane to acetic acid, by mechanism A is hard to explain.
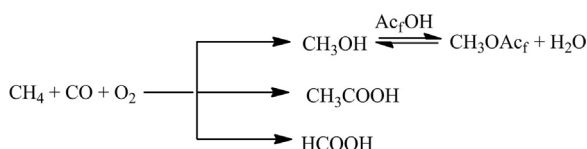
In this communication, we will overview the relevant experimental evidences for formation of Rh–alkyl intermediates under the action of the above Rh-containing catalytic systems.

Scheme 1. Outer-sphere (A) and inner-sphere (B) mechanisms of C—H bond activation in alkanes.

Scheme 2. Reactions of methane in Ac_fOH/H_2O medium in the presence of Rh–I–Cl, Rh–Cu–Cl, and Rh–Fe–Cl catalytic systems.

2. Experimental

The following chemicals were used in our experiments: $RhCl_3 \cdot (H_2O)_x$ (34.5 wt% Rh), NaCl and CuO (reagent grade), H_2O (bidistillate), Ac_fOH (Aldrich, extra pure), Pr_fCOOH (Aldrich, extra pure) and pyridine (reagent grade, distilled). Dioxane (reagent grade) was boiled over Na for 2 h and then distilled. Alkyl trifluoroacetates and heptafluorobutyrates (used in chromatographic calibrations) were prepared by esterification and distilled. Reaction products were identified by gas chromatography and gas chromatography/mass spectrometry. Copper trifluoroacetate $Cu(OAc_f)_2$ was obtained by dissolution of CuO in boiling Ac_fOH. Filtered-out $Cu(OAc_f)_2$ crystals were dried in vacuum and stored in an exsiccator. Gaseous reagents—CO (99.9% pure), CH_4 (99.8%), C_3H_8 (99.8%), O_2 (99.9%), and H_2 (brand A)—were used without further purification. Our experimental and analytical procedures are described in detail elsewhere [12–15].

3. Results and discussion

According to mechanism A, the activation and oxidation of methane takes place without formation of intermediate complexes with an Rh–methyl bond. However, the formation of acetic acid (Scheme 2) requires the carbonylation of Rh–methyl intermediate.

In [18–20] it is assumed that mechanism **B** is in effect and dioxygen only plays a role of reoxidant for Pd(0) and Pd(II), despite the fact that Pd(II) compounds are incapable of oxidizing alkanes by thermodynamic considerations. According to literature data and our previous results [9,10e,12–14], the role of oxidant can be readily played by hydrogen peroxide or its equivalents such as hypoiodic acid and hydroperoxides of Cu (II) and Fe(III) formed under the action of reducing agents (H_2, CO) on dioxygen. In the presence of Rh and Pd complexes, the formation of active oxidants takes place with involvement of co-catalysts (compounds of I, Cu, and Fe).

The important role of Rh–alkyl intermediates in realization of mechanism **B** is supported by the following observations: (*i*) formation of alkyl chlorides; (*ii*) induction period at elevated concentration of Cl^-; (*iii*) formation of acetic acid upon oxidative

carbonylation of methane, and (*iv*) positional selectivity in oxidation of propane.

In case of Rh and Pd catalysts, the process takes place with involvement of co-catalysts (I-, Cu-, and Fe-containing compounds). Catalytic oxidation of alkanes to alkyl chlorides (RCl) by mechanism **B** (Reaction (1)) may proceeds only via metal–alkyl intermediate followed by reductive elimination of RCl from the inner coordination sphere [2–4].

$$L_nM(Cl)R \rightarrow L_nM + RCl \tag{1}$$

The oxidation of alkanes was found to yield alkyl chlorides in the presence of Rh–I–Cl and Rh–Cu–Cl catalytic systems, whereas the oxidation of *n*-butane in the presence of Rh–Cu–Br catalytic system gave butyl bromides. The yield of target products in oxidation of methane in Ac_fOH/H_2O attained a maximum at $[Cl^-] = 0.02$ g-ion L^{-1} and then gradually decreased with increasing $[Cl^-]$ [13]. For catalytic system Rh–Cu–Cl in aqueous heptafluoro butyric acid a maximal yield of propane oxidation products is observed at $[Cl^-] \approx 0.06$ g-ion L^{-1}. The oxidation of propane was almost completely suppressed at $[Cl^-] = 0.105$ g-ion L^{-1} (Fig. 1).

At some certain Cl^- concentrations, the kinetic curves exhibit an induction period in the oxidative functionalization of both methane (Fig. 2) and propane (Fig. 3). At $[Cl^-] = 0.03$ g-ion L^{-1}, the oxidation of propane proceeds without an induction period (Fig. 4). The presence of an induction period can be associated with reprocessing of excessive amount of Cl^- ions into respective alkyl chlorides via Reaction (1). The induction period is most pronounced at $[Cl^-] = 0.2$ g-ion L^{-1} (curves 3, 4 in Fig. 2).

Our previous results [12] give grounds to assume that, in Rh–I–Cl catalytic system, the role of active oxidant is played by the HOI intermediate formed in Reaction (2).

$$O_2 + 2HI \rightarrow 2HOI \tag{2}$$

$$½O_2 + HI \rightarrow I_2 + H_2O \tag{3}$$

$$4.2I_2 + CO + H_2O \rightarrow 2HI + CO_2 \tag{4}$$
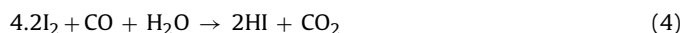
In the above scheme, Reaction (3) is a side one, while Reaction (4) of HI regeneration is catalyzed by Rh complexes. A most likely catalytic cycle for formation of acetic acid in this system is illustrated in Scheme 3.

In the Rh–Cu–Cl system, one of active two-electron oxidants is copper hydroperoxide [13] formed through Reaction (5).
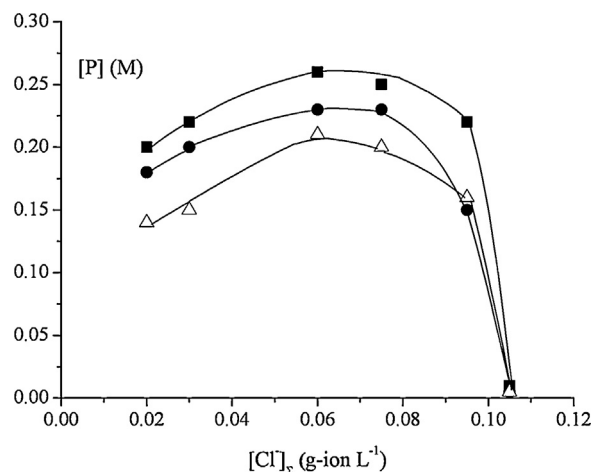
$$Cu_2Cl_2 + ½O_2 + H_2O \rightarrow 2Cu(OOH)Cl \tag{5}$$

Fig. 1. Yield of oxidation products [P] —(△) *n*-Pr-OC(O)Pr$_f$, (●) *i*-PrOC(O)Pr$_f$, and (■) acetone—vs. concentration $[Cl^-]_\Sigma$ of chlorine ions: $[RhCl_3] = 5 \times 10^{-3}$ M, $[Cu(OAc_f)_2] = 0.1$ M, $C_3F_7COOH/H_2O = 4/1$ (v/v), $T = 80\,°C$, 12 mmol propane, 8 atm O_2, 16 atm CO, 40 atm He.