



Review

Rhodium complexes in homogeneous catalytic systems for oxidative functionalization of alkanes: Experiment and quantum-chemical calculations



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This paper is dedicated to memory of Professor Aleksander Shilov, our teacher, colleague and friend. The authors were lucky to work for many years in the Department of Homogeneous Catalysis headed by Prof. Shilov and to publish a number of research papers with his co-authorship.

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ABSTRACT

Due to their stability, rhodium halides are attractive for use in redox reactions without additional ligands. In this review, we analyzed the available data on the catalytic systems containing rhodium halides and redox co-catalysts and their implementation to oxidation of methane and other lower alkanes. Based on experimental data and DFT results, we suggest possible mechanisms for oxidative functionalization of methane and propane. Activation of methane may get started with formation of a σ -complex with Rh. Activation of dioxygen takes place at the activated species of redox co-catalysts—iodine, copper or iron compounds—and leads to formation of two-electron oxidants. The redox co-catalysts may also interact with Rh. The activation of dioxygen is favored by the presence of added reducing agent (CO) which returns oxidized redox co-catalysts to their reduced form. The necessity of preliminary dioxygen reduction brings about analogy with biocatalysts for oxidation of alkanes. The oxidative carbonylation of methane to acetic acid most likely proceeds via an intermediate with the $\text{CH}_3\text{-Rh}$ bond. The formation of alcohols and acetone is consistent with formation of intermediate complexes containing the Rh-OI and Rh-O-O-Cu fragments. The esterification of alcohols with ingressed perfluorocarboxylic acids prevents from deep oxidation.

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Introduction

As is known, pioneering work [1] by Prof. Shilov and co-workers gave strong impetus to numerous extensive studies on the activation and functionalization of alkanes with metal complexes later summarized in a number of reviews and monographs [2–8]. The catalytic reactions of aqua-chloride Pt complexes were termed Shilov chemistry [4]. Over the past years, Shilov and co-workers have discovered (based on biomimetic approach) and explored the Au-containing catalytic systems for oxidation of methane and propane in very mild conditions [9]. But this aspect is beyond our scope and will not be analyzed in this paper.

The catalysts capable of activating C–H bonds in alkanes are numerous but those capable of their functionalization are not so common. Important task objectives of the functionalization are the oxidation of alkanes to alcohols, aldehydes, ketones as well as oxidative carbonylation to carboxylic acid. At the dawn of such studies (1996), Prof. Shilov drew our attention to the paper by Sen and Lin [10a]. The authors used a simple catalytic system, RhCl₃–NaI–DCl in D₂O, in order to perform oxidative carbonylation of methane to acetic acid (Table 1). Despite a low yield of acetic acid, the following reaction features have drawn our attention:

- use of dioxygen as an oxidant
- very mild temperature conditions
- higher stability of Rh complexes as compared to Pd and Pt complexes
- for oxidation, protonic media turned more plausible than neutral or aprotic ones
- catalytic mechanism and the role of iodides remained obscure

The above circumstances opened up wide horizons for our own studies in the field in terms of the biomimetic approach formulated by Shilov [2d].

Reactions of methane catalyzed by the rhodium–iodide–chloride system in different media

Acetic acid–water

Having analyzed communication [10a], we came to a conclusion that the efficiency of Rh–I–Cl catalytic system can be improved in a mix solvent containing water and organic solvent such as acetic

acid. Note that in their earlier studies on the activation and oxidation of methane with Pt complexes, Shilov and co-workers also used acetic acid as a solvent [11]. In our paper [12a] we soon reported that the efficiency of RhCl₃–KI–DCl catalyst in CD₃COOD/D₂O was higher than that in water (Table 1). In the presence of Rh–I–Cl system, the reaction proceeds by the Scheme 1.

In the system under consideration, the following two reactions take place:

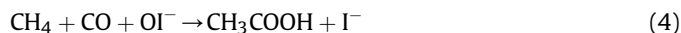


In this catalytic system, it is more convenient to use KI rather than HI since in strongly acidic media the former converts into HI.

Thermodynamically, molecular iodine cannot oxidize methane. In view of this, we assumed that iodine was involved in the generation of some reactive two-electron oxidant, such as HOI, from dioxygen [12b]:



Then oxidative carbonylation of methane (4) becomes thermodynamically favored ($\Delta G^\circ_{298} = -5 \text{ kcal/mol}$):



When performing these experiments, we still had no any notion about the possibility of oxidative destruction of acetic and propionic acids (cf. Section Destruction of acetic and propionic acids during oxidative functionalization of methane). Since the reaction products were analyzed by ¹H NMR in CD₃COOD, we could not detect the above destruction products.

Heptafluorobutyric acid–water

In continuation of [10a], the authors continued their research in a mix solvent, heptafluorobutyric acid–water [10b]. The activity of the Rh–I–Cl catalytic system in such a solvent was found to markedly grow as compared to that in CD₃COOD–D₂O.

The ratio of methylheptafluoro butyrate to acetic acid was associated with solvent-dependent difference between k_{Nu} and k_{CO} in Scheme 2:

Table 1
Catalytic properties of the rhodium–iodide–chloride system in different solvents.

Catalytic system	Solvent	[RhCl ₃], M × 10 ³	P, MPa ^a			T, °C	τ, h	Products, M ^b			r × 10 ^{4c} , M h ⁻¹	TOF ^c , h ⁻¹	Refs.
			CH ₄	CO	O ₂			CH ₃ OD(H) + R(O)COCH ₃	Acetic acid	Formic acid			
RhCl ₃ –KI–DCl	D ₂ O	10	6.80	1.36	0.68	95	420	Traces	0.276	Traces	7.4	0.074	[10a]
RhCl ₃ –KI–DCl	D ₂ O/CD ₃ COOD	15	6.00	1.60	0.40	95	24	0.036(R = CD ₃)	0.15	0.028	67.0	0.45	[12a,b]
RhCl ₃ –KI–NaCl	D ₂ O/C ₃ F ₇ COOH	5	8.50	2.55	0.68	80	80	0.90 (R = C ₃ F ₇)	0.16	–	192 ^d	3.84 ^d	[10b]
RhCl ₃ –KI–NaCl	D ₂ O/Ac ₂ O	5	6.00	1.84	0.58	95	4	0.012 ^e (R = CF ₃)	0.035	0.075	2370	47.4	[13a,b]
RhCl ₃ –KI–NaCl	H ₂ O/Ac ₂ O	5	6.00	1.84	0.58	95	3	0.014 ^e (R = CF ₃)	0.055	0.07	4650	92.0	[13a,b]
RhCl ₃ –CuO–NaCl ^f	D ₂ O/Ac ₂ O	2.5	6.00	1.84	0.56	95	1.5	0.20 ^c (R = CF ₃)	0.05	0.025	2900	116	[24a,b]
RhCl ₃ –CuO–NaCl ^f	H ₂ O/Ac ₂ O	2.5	6.00	1.84	0.56	95	1.5	0.18 ^c (R = CF ₃)	0.05	0.030	3600	144	[24a,b]

^a Initial pressure.

^b For deuterated solvents, ¹H NMR data.

^c Initial reaction rate and TOF.

^d Reaction could be controlled by diffusion of gases so that the actual values might be markedly higher.

^e Reaction decelerated due to the lack of oxygen and CO.

^f CuO rapidly dissolved; in Ref. [10] V_{liquid} = 3.5 cm³, V_{gas} = 120 cm³; in Refs. [12,13,24]. V_{liquid} = 2.5 cm³, V_{gas} = 31 cm³.

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