

Copper complexes for catalytic, aerobic oxidation of hydrocarbons*

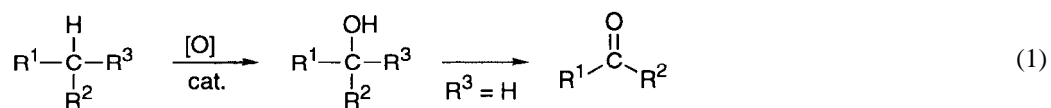
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Abstract: Catalytic oxidation of hydrocarbons can be performed efficiently upon treatment with *tert*-butylhydroperoxide or peracetic acid in the presence of a low-valent ruthenium catalyst. Furthermore, aerobic oxidation of hydrocarbons can be performed in the presence of acetaldehyde using ruthenium, iron, and copper catalysts. Copper derived from copper chloride/crown ether or copper chloride/crown ether/alkaline metal salts have proved to be efficient catalysts. Further study revealed that specific copper complexes formed from copper salts and acetonitrile are convenient and highly useful catalysts for the aerobic oxidation of unactivated hydrocarbons.

Selective oxidation of alkanes is an important topic in view of the economical and ecological use of natural raw materials. However, catalytic oxidation of unactivated hydrocarbons remains as a challenging topic (eq. 1). Direct oxidation of hydrocarbons is one of the important functions of cytochrome P-450. During the course of simulation of the enzymatic functions of cytochrome P-450 with transition-metal complexes, we found that catalytic oxidation of various substrates can be performed highly efficiently [1]. Ruthenium porphyrins bearing meso-pentafluorophenyl group (Ru[TPFPP][CO]) are highly efficient catalysts for aerobic oxidation of alkanes in the presence of acetaldehyde [2]. In contrast, without using porphyrin catalysts, oxidation of alkanes can be performed highly efficiently upon treatment with *tert*-butylhydroperoxide [3] or peracetic acid [4] in the presence of low-valent ruthenium catalysts. Importantly, aerobic oxidation of alkanes can be performed in the presence of acetaldehyde using ruthenium [5], iron [5], and even copper [6] catalysts. The precise mechanistic study revealed that oxo-metal intermediates are involved in these reactions.

The copper complexes derived from copper chloride and crown ethers were found to be extremely efficient catalysts [7,8]. Furthermore, specific copper complexes formed from copper salts and acetonitrile are convenient and highly useful catalysts for the aerobic oxidation of unactivated hydrocarbons [9].



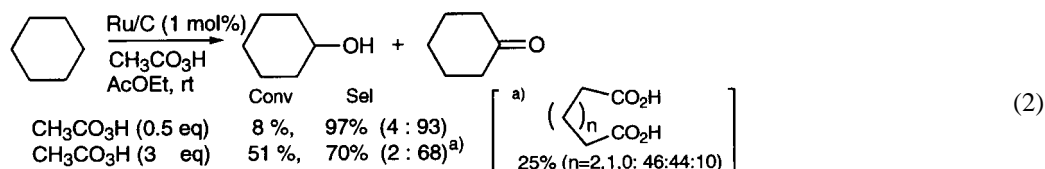
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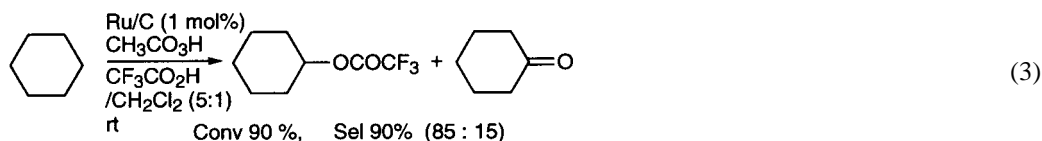
RUTHENIUM-CATALYZED OXIDATIONS OF ALKANES WITH *TERT*-BUTYL HYDROPEROXIDE AND PERACETIC ACID

The oxidation of hydrocarbons with peroxides in the presence of ruthenium catalysts is highly useful. The catalytic system $\text{RuCl}_2(\text{PPh}_3)_3/t\text{-BuOOH}$ is convenient for selective oxidation of alkylated arenes to give aryl ketones [3]. Typically, catalytic oxidation of fluorene with *t*-BuOOH in the presence of $\text{RuCl}_2(\text{PPh}_3)_3$ catalyst in benzene at room temperature gave 9-fluorenone in 87% yield. The kinetic study revealed that the ρ value obtained from the $\text{RuCl}_2(\text{PPh}_3)_3$ -catalyzed oxidation of substituted toluenes with *t*-BuOOH is -1.4 , which is similar to that (-1.6) obtained from the oxidation with cytochrome P-450 but quite different from those with *t*-BuO \cdot (-0.4) and *t*-BuOO \cdot (-0.6). Intramolecular and intermolecular deuterium isotope effects ($k_{\text{H}}/k_{\text{D}}$) were determined to be 9.0 and 9.2 for the oxidation of 1,1-dideuterio-1,3-diphenylpropane and cyclohexane/cyclohexane- d_{12} , respectively. These facts support an intermediacy of oxo-ruthenium rather than alkoxy radical [10,11].

The system $\text{Ru}/\text{C}-\text{CH}_3\text{CO}_3\text{H}$ is suitable for the synthesis of ketones and alcohols from alkanes [4]. Oxidations of cyclohexane with peracetic acid in the presence of ruthenium on charcoal (1 mol %) gives cyclohexanone along with small amount of cyclohexanol (eq. 2). Typically, the oxidation of cyclohexane with 0.5 equiv of $\text{CH}_3\text{CO}_3\text{H}$ proceeds to give cyclohexanol and cyclohexanone (4:93) with 97% selectivity (conversion 8%). In contrast, the reaction with 3 equiv of $\text{CH}_3\text{CO}_3\text{H}$ afforded cyclohexanol and cyclohexanone (2:68) with 70% selectivity along with dicarboxylic acids (adipic acid:glutaric acid:succinic acid = 46:44:10), which were formed from the oxidation of 1,2- and 1,3-cyclohexanediones under the reaction conditions, with 25% selectivity (conversion 51%) [10]. Generally, acylperoxo-metal complexes undergo heterolytic cleavage of the O–O bonds to give oxo-metal species readily.

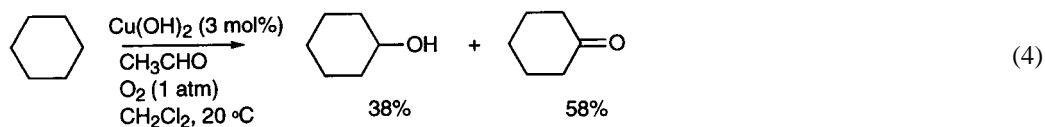


Next, we aimed at both high conversion and high selectivity for the oxidation of alkanes. One can expect that active oxo-metal species bearing electron-withdrawing ligands would show higher reactivity. Actually, we found that trifluoroacetic acid is suitable for such a purpose. The $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ -catalyzed oxidation of cyclohexane with $\text{CH}_3\text{CO}_3\text{H}$ in a mixture of trifluoroacetic acid and dichloromethane (5:1) gave cyclohexyl trifluoroacetate and cyclohexanone in 90% selectivity (85:15) with 90% conversion (eq. 3). It is particularly important that the over-oxidation was suppressed in spite of extremely high conversion. Although trifluoroacetoxylation of hydrocarbons has been reported to occur upon treatment with hydrogen peroxide in trifluoroacetic acid without metal catalyst [12], the reaction is very slow ($k = 10^{-5} \text{ M}^{-1}\text{s}^{-1}$). The second-order rate constant of our ruthenium-catalyzed oxidation of cyclohexane with $\text{CH}_3\text{CO}_3\text{H}$ in trifluoroacetic acid ($-\text{d}[\text{cyclohexane}]/\text{dt} = k[\text{RuCl}_3 \cdot n\text{H}_2\text{O}][\text{CH}_3\text{CO}_3\text{H}]$) is very fast ($k = 5.4 \text{ M}^{-1}\text{s}^{-1}$) [10]. The present reaction provides a general and efficient method for conversion of alkanes to the corresponding trifluoroacetates.

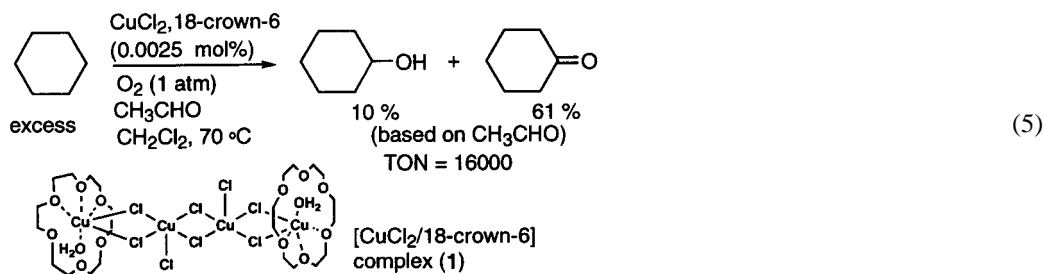


AEROBIC OXIDATIONS OF HYDROCARBONS USING RUTHENIUM, IRON, OR COPPER CATALYSTS

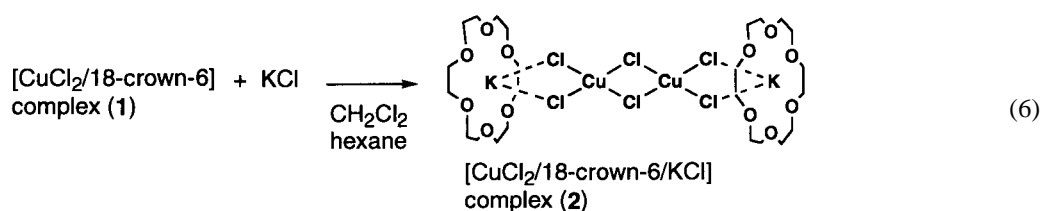
Industrially peracetic acid has been prepared upon treatment of acetaldehyde with molecular oxygen in the presence of cobalt catalyst. On the basis of the reaction, we found that ruthenium-catalyzed oxidation of alkanes with molecular oxygen can be performed in the presence of acetaldehyde [5]. Furthermore, we found that even iron and copper catalysts are effective for the oxidation of unactivated hydrocarbons at room temperature under molecular oxygen (1 atm) [5,6]. Actually, $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, iron powder, and $\text{Cu}(\text{OH})_2$ have proved to be effective catalysts. Typically, oxidation of cyclohexane in the presence of acetaldehyde and $\text{Cu}(\text{OH})_2$ catalyst can be performed under O_2 (1 atm) at 20 °C for 24 h (conversion 4.5%) (eq. 4).



The catalytic activity of copper salts is in the order of $\text{Cu}(\text{OH})_2 \sim \text{Cu}(\text{OAc})_2 \gg \text{Cu}(\text{OCOCF}_3)_2 > \text{CuCl}_2$, indicating that a copper salt bearing an electron donating ligand is suitable for the present oxidation. On the basis of these results, we found that a combination of a copper salt and a crown ether is an effective catalyst for the aerobic oxidation of alkanes [7]. Thus, the catalytic system CuCl_2 and 18-crown-6 has proved to be highly efficient. Typically, the oxidation of cyclohexane with molecular oxygen (1 atm) and acetaldehyde in the presence of CuCl_2 (0.0025 mol %) and 18-crown-6 (0.0025 mol %) gave cyclohexanol and cyclohexanone with extremely high turnover number (16 000) and reasonable yields based on acetaldehyde (71%) (eq. 5). The $\text{CuCl}_2/18\text{-crown-6}$ complex (**1**), whose structure was determined by X-ray analysis, showed a similar catalytic activity toward the aerobic oxidation of cyclohexane.

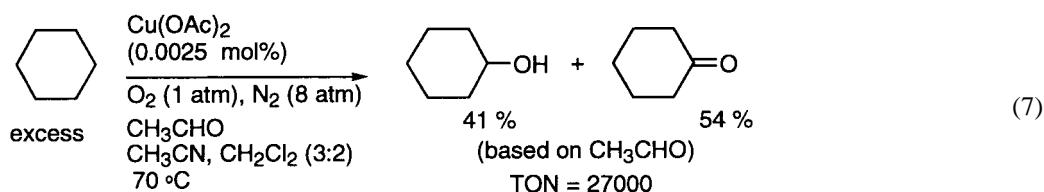


In order to clarify which copper, that is, outer coppers or inner coppers of the complex **1**, participates as the active site, we examined substitution of the outer copper with an alkaline metal [8]. We succeeded in isolation of the $\text{CuCl}_2/18\text{-crown-6}/\text{KCl}$ complex upon treatment of the complex **1** with KCl in a mixture of dichloromethane and *n*-hexane (eq. 6). Recrystallization from dichloromethane and ethyl acetate gave $\text{CuCl}_2/18\text{-crown-6}/\text{KCl}$ complex (**2**), of which structure was determined by X-ray crystallographic study. The complex **2** consists of a dinuclear $[\text{Cu}_2\text{Cl}_6]^{2-}$ anion and two $[\text{K}(18\text{-crown-6})]^+$ cations, and each copper is ligated in a square-planar environment with four $\mu_2\text{-Cl}$ anions. The complex **2** is much more efficient than complex **1** for the aerobic oxidation of cyclohexane [8]. The combination of KCl with 18-crown-6, which corresponds to the complex **2**, is highly efficient for the oxidation. Similar matching pairs such as $\text{CuCl}_2/15\text{-crown-5}/\text{NaCl}$ are also effective catalysts.



COPPER-ACETONITRILE SYSTEM FOR SIMPLE AND HIGHLY EFFICIENT AEROBIC OXIDATION OF HYDROCARBONS

In order to develop a simple and efficient system for the oxidation of hydrocarbons without using crown ethers, we looked for suitable ligands and found that specific copper complexes derived from copper salts and acetonitrile are convenient and highly useful catalysts for the aerobic oxidation of unactivated hydrocarbons [9]. For example, oxidation of cyclohexane with molecular oxygen (1 atm of O_2 diluted with 8 atm of N_2) in the presence of acetaldehyde and $\text{Cu}(\text{OAc})_2$ catalyst (0.0025 mol %) in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ (3:2) at 70 °C in an autoclave proceeds efficiently (95% based on CH_3CHO) with extremely high turnover number (27 000) (eq. 7).



In the present oxidation, Cu(I) complex bearing acetonitrile ligands seems to be the key complex to generate oxo-copper (III) species. The reaction of copper(II) acetate and acetaldehyde in acetonitrile gives acetyl radical, which reacts with O_2 to give peracetic acid by radical chain mechanism. Copper(I) species and peracetic acid thus formed would afford oxo-copper (III) species, which abstracts hydrogen atom from alkanes. Subsequent oxygen rebound would give alcohols and Cu(I) to complete the catalytic cycle. Under the reaction conditions, alcohols are converted to the corresponding ketones.

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