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Oxidation of alkanes and benzene with hydrogen peroxide catalyzed by ferrocene in the presence of acids

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This article is dedicated to the memory of Aleksandr Evgenievich Shilov (1930–2014).

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ABSTRACT

The efficient (turnover numbers attained 1200) oxidation of alkanes to the corresponding alkyl hydroperoxides by H_2O_2 in the presence of catalytic amounts of ferrocene proceeds in MeCN at 40–50 °C. Benzene is oxidized in the same system to phenol. An obligatory component of the catalytic system for both reactions is pyrazine-2-carboxylic acid (PCA) or trifluoroacetic acid (TFA). Kinetic study as well as selectivity parameters testified that the oxidation proceeds with the participation of hydroxyl radicals. In the case of PCA as a co-catalyst the initial rate W_0 of the reaction with both cyclohexane and benzene depends quadratically on $[Cp_2Fe]_0$ whereas the two reactions in the presence of TFA are of half order in ferrocene. The ferrocene-catalyzed reaction of cyclohexane with $H_2{}^{16}O_2$ in an atmosphere of labeled $^{18}O_2$ gave after 2 h a mixture of labeled and unlabeled cyclohexyl hydroperoxide (total yield 20% based on starting cyclohexane) containing up to 69% of ^{18}O (the analysis was after reduction of cyclohexyl hydroperoxide into cyclohexanol with PPh_3).

Introduction

Transition metal complexes [1], particularly, iron derivatives [2], often play roles of good catalysts in the oxidation of saturated and aromatic hydrocarbons with peroxides, especially with green oxidants such as hydrogen peroxide. In contrast, organometallic compounds, particularly iron complexes, have so far been rarely used as catalysts in oxidation processes [3].

The most well-known organometallic derivative of iron, ferrocene, was used in the synthesis of pristine and doped carbon nanotubes, the transition metal catalyzed coupling and carbonylation reactions of ferrocene derivatives, in the exploitation for the development of mechanically interlocked and non-interlocked synthetic molecular machines [4a,b], chiral ferrocenes are used in asymmetric catalysis [4c], burning rate catalysts [4d], preparation of biosensors [4e], anticancer agents [4f] etc.

In the present work we report that ferrocene (compound **1**) used in catalytic amounts and in the presence of certain acids in low concentrations very efficiently induces oxidative transformations of alkanes and benzene with hydrogen peroxide. Some parts of this study have been previously published as preliminary communications.

Results and discussion

In the present article we report that cyclohexane and other alkanes as well as benzene can be oxidized to the corresponding alkyl hydroperoxides and phenol, respectively, by hydrogen peroxide in air in the presence of catalytic amounts of ferrocene and pyrazine-2-carboxylic acid (PCA; for co-catalytic role of this compound in various reactions, see a review [4g]) or trifluoroacetic acid, as shown in eqs. (1) and (2). The reaction proceeds in acetonitrile solution under mild conditions (typically at 50 °C). Alkyl hydroperoxide is relatively stable in the solution, and can be easily reduced by PPh_3 to the corresponding alcohol.

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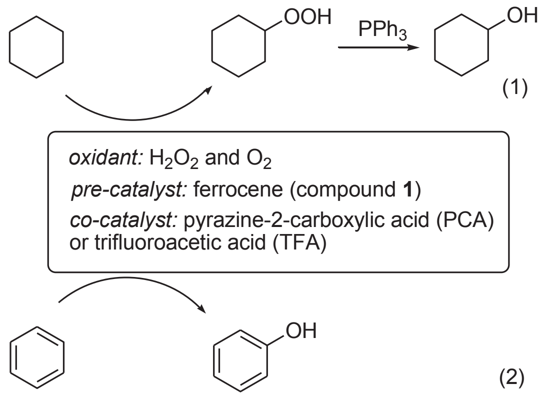

Methods for the quantification of products

We carried out a kinetic study of the cyclohexane oxidation. Products of the hydrocarbon oxidation were quantified by the GC method. If the direct injection of a reaction sample (of the alkane oxidation with O_2 or/and H_2O_2) into the chromatograph gave comparable amounts of cyclohexanol and cyclohexanone, the reduction of the sample with PPh_3 prior to the GC analysis (for this method developed by Shul'pin, see Refs. [5a–g]) led to the noticeable predominance of the alcohol. This comparison clearly indicates that cyclohexyl hydroperoxide is formed as the main primary product [5a–g]. The formation of cyclohexyl hydroperoxide and its reduction to cyclohexanol with PPh_3 is depicted in eq. (1). Our method allowed some chemists [5h–s] to obtain a very valuable information on the existence of non-existence of alkyl peroxides in the reaction mixture whereas other investigators who did not employed this method were unable [5t–z] to discuss a possible mechanism of the oxidation reaction.

Hydroperoxidation of alkanes with H_2O_2 catalyzed by the combination ferrocene/pyrazine-2-carboxylic acid (PCA)

The oxidation of alkanes to the corresponding alkyl hydroperoxides by H_2O_2 in the presence of catalytic amounts of ferrocene proceeds in MeCN at 50 °C. An obligatory component of the catalytic system is pyrazine-2-carboxylic acid (PCA). In the cyclohexane oxidation the turnover number (TON) and yield after 1.5 h attained 1200 and 32%, respectively.

In order to get insight into the nature of the oxidizing species and evaluate the mechanism of the process we determined various selectivity parameters for the reaction of the H_2O_2/ferrocene/PCA system with linear and branched alkanes. All parameters (summarized in Table 1, entry 1) were measured after reduction of the reaction mixtures with triphenylphosphine before GC analysis. A comparison with the selectivity parameters measured previously for oxygenations by some other systems (see Table 1 [6]) indicates that ferrocene-catalyzed reactions occur with the participation of hydroxyl radicals. Indeed, parameter C(1):C(2):C(3):C(4) = 1:7:7:6 and parameter 1°:2°:3° = 1:10:33 measured for the oxidation of *n*-heptane and methylcyclohexane, respectively, are typical values for the systems oxidizing via the mechanism which involves hydroxyl radicals. Parameters *trans*/*cis* which are the ratio of isomers of *tert*-alcohols with mutual *trans*- and *cis*-orientation of the methyl groups formed in the oxidation of *cis*- and *trans*-1,2-dimethylcyclohexane (DMCH) were found to equal 0.8 for both *cis*-DMCH and *trans*-DMCH. Oxidations of isomeric DMCH with hydroxyl radicals typically proceed non-stereoselectively. The oxidations of *n*-heptane and methylcyclohexane (MCH) are reflected in Tables 2 and 3, respectively.

Table 1
Selectivity parameters in the oxidation of alkanes by various systems in acetonitrile.[a]

Entry	System	*n*-Heptane	MCH	*c*-DMCH	*t*-DMCH
1	**1**–PCA–H_2O_2[b]	1:7:7:6	1:10:33	0.8	0.8
2	**1**–TFA–H_2O_2[b]	1:6:6:6	1:4:15[c]	0.9	0.9
3			1:7:18[d]		
4			1:6:17[e]		
5			1:6:18[f]		
6			1:6:20[g]		
6	$FeSO_4$–H_2O_2 (see Ref. [6a])	1:5:5:4.5		1.3	1.2
7	Cp*Os–py–H_2O_2 [6b]	1:7:7:7	1:8:23	1.0	0.9
8	VO_3^-–PCA–H_2O_2 (see Ref. [6c])	1:6:7:5	1:9:37	0.75	0.8
9	VO_3^-–H_2SO_4–H_2O_2 (see Ref. [6d])	1:7:7:6	1:7:26	0.85	0.9

[a] Abbreviations for substrates: methylcyclohexane (MCH), *cis*-1,2-dimethylcyclohexane (*c*-DMCH), *trans*-1,2-dimethylcyclohexane (*t*-DMCH). Parameters C(1):C(2):C(3):C(4) given for *n*-heptane are relative normalized (i.e., calculated taking into account the number of hydrogen atoms at each carbon) reactivities of hydrogen atoms at carbons 1, 2, 3 and 4, of the chain of the alkane. Parameters 1°:2°:3° given for the oxidation of MCH are relative normalized reactivities of hydrogen atoms at primary, secondary and tertiary carbons of this alkane. In the cases of oxidation of dimethylcyclohexanes, parameter *trans*/*cis* is given which is the ratio of *trans*- and *cis*-isomers of *tert*-alcohols. All parameters were measured after reduction of the reaction mixtures with triphenylphosphine before GC analysis and calculated based on the ratios of isomeric alcohols.

[b] This work.

[c] Reaction time 15 min.

[d] Reaction time 30 min.

[e] Reaction time 2 h.

[f] Reaction time 3 h. Total yield of products was 0.123 M (23% based on MCH).

[g] Reaction time 4 h. Total yield of products was 21%.

We have found that the rate dependence of cyclohexane oxygenation with H_2O_2 in the presence of the ferrocene/PCA system is second-order in PCA at its low ($<2 \times 10^{-3}$ M) concentrations. This dependence has a maximum (Fig. 1), thus suggesting the possible formation of adducts with PCA. The dependence of the initial oxidation rate W_0 is first-order in hydrogen peroxide (Fig. 2) and second-order in the initial ferrocene (Fig. 3). It follows from data presented in Fig. 4 (W_0 is approaching to a plateau at high concentrations of cyclohexane) that the ratio of constants k_{MeCN} and k_{CyH} for the interaction of oxidizing species with MeCN and CyH, respectively, is equal to $k_{MeCN}/k_{CyH} = 0.011$ M which is the typical for hydroxyl radicals value [6a,7a] indicates that hydroxyl radicals as oxidizing species competitively interact both with cyclohexane (CyH) and acetonitrile [6a,7a]. Addition of water to the reaction solution leads to a slight decrease of the initial oxidation rate. If a new portion of hydrogen peroxide is added when the oxidation reaction deceases, the oxidation continues although with lower rate.

Based on the data presented in Figs. 1–4 we proposed the following kinetic scheme of the alkane oxygenation. The first stage is oxidation of ferrocene $FeCp_2$ to ferricenium cation $(FeCp_2)^+$ which is in turn transformed into species Φ, where Φ is a fragment containing *one* iron ion. The formation of $(FeCp_2)^+$ is supported by the visible spectra obtained for the reaction mixture in the initial period of the reaction: a growing with time peak at $\lambda = 625$ nm corresponds to the absorption of ferricenium cation.

$$FeCp_2 + H_2O_2 \xrightarrow{H^+} (FeCp_2)^+ \tag{i.1}$$

$$(FeCp_2)^+ \rightarrow \Phi \tag{i.2}$$

Reactions (i.1) and (i.2) are the fast stages of the generation from $FeCp_2$ and H_2O_2 the main species Φ active in the catalytic process. A fragment produced in these two consecutive reactions interacts with a PCA molecule to form complex Φ(pca):