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Polyferroorganosiloxanes as catalysts of oxidation processes

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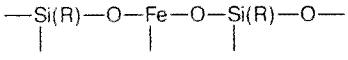
Polyferroorganosiloxanes were studied as catalysts for homogeneous oxidation of alkanes by hydrogen peroxide under mild conditions. In the oxidation of cyclohexane the catalysts are characterized by high efficiency (conversion of hydrogen peroxide is 25%) and stability (up to 80 cycles per g-at. Fe). The main product of the oxidation in the presence of 2,4,6-tri-*tert*-butylphenol is cyclohexanol (up to 35% per H_2O_2).

Key words: polyferroorganosiloxanes, catalysts, oxidation of hydrocarbons, activation of hydrogen peroxide.

The known iron-containing catalysts of homogeneous oxidation of organic compounds by hydrogen peroxide, which are mono- or polynuclear complexes of iron ions, exist in homogeneous catalytic media as individual ions of di- and triatomic clusters.[1–4] Iron-containing catalysts of a new type, in which Fe atoms exist in the covalently linked form in the siloxane chain, were studied in this work. The main structural fragment of polyferrophenylsiloxanes (PFPS) is the following:



$$\text{—}\underset{|}{\mathrm{Si(R)}}\text{—O—}\underset{|}{\mathrm{Fe}}\text{—O—}\underset{|}{\mathrm{Si(R)}}\text{—O—}$$

(R is phenyl).

The procedures of synthesis developed make it possible to control the content of Fe in PFPS. When the content of Fe increases, Fe—O—Fe metalloxane fragments appear in the polymer structure. The synthesis and structure of PFPS have been described previously.[5]

We found that PFPS are capable of catalyzing the alkane oxidation by hydrogen peroxide in the presence of $HClO_4$. The oxidation of cyclohexane results in the formation of alkylhydroperoxide and cyclohexanol, the oxidation of methane gives methanol, and styrene oxidizes to benzaldehyde and small amount of styrene oxide (Table 1).

The reaction is highly efficient: conversion of hydrogen peroxide calculated from the yield of the products of oxidation is equal to 25% (in the case of common Fe-catalysts, the efficiency of oxidation of cyclohexane by hydrogen peroxide is not greater than 8—10%). Another specific feature of PFPS is the stability of the catalyst under the reaction conditions: the number of working cycles (calculated per g-at. Fe) until the inactivation of the catalyst is equal to 70—80.

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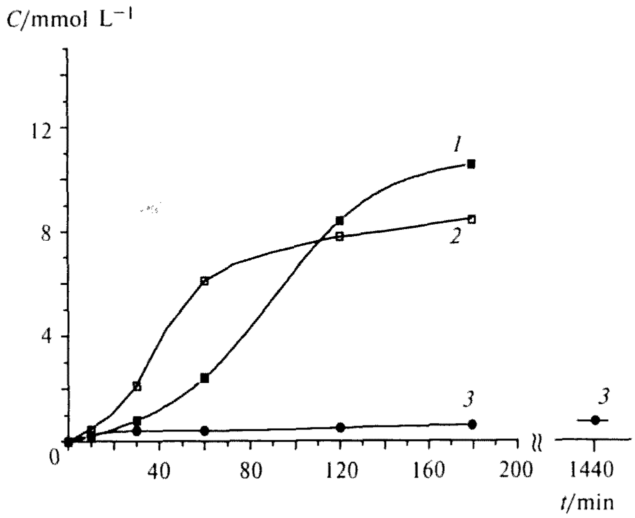

Fig. 1. Kinetics of accumulation of the products of oxidation of cyclohexane in the PFPS—H_2O_2 system under standard conditions (see Experimental): $C_6H_{11}OOH$ (*1*), $C_6H_{11}OH$ (*2*), and $C_6H_{10}O$ (*3*).

Table 1. Products of oxidation of alkanes in the PFPS—H_2O_2 catalytic system (the conditions are presented in Experimental)

Alkane	Oxidation products	Yield (in moles per mole of taken H_2O_2)	Number of working cycles of catalyst (recalculated per g-at. Fe)
Methane	Methanol	0.015	0.75
Cyclohexane	Cyclohexyl hydroperoxide[a]	0.10	5
	Cyclohexanol	0.14	7
	Cyclohexanone	0.006	0.3
Styrene[b]	Benzaldehyde	0.35	17.5
	Styrene oxide	0.015	0.75

[a] The amount of alkyl hydroperoxide was calculated by comparison of the amounts of alcohol and ketone in samples taken directly from the reaction medium and after treatment of the sample with triphenylphosphine (the reaction $Ph_3P + ROOH \longrightarrow ROH + Ph_3PO$ occurs). It was preliminarily established that the cyclohexyl hydroperoxide being chromatographed decomposes to ketone and alcohol in a ratio of 1.5 : 1. [b] A 10^{-3} *M* solution of CF_3SO_3H was used instead of $HClO_4$ in the oxidation of styrene.

The kinetics of accumulation of the products of cyclohexane oxidation is presented in Fig. 1.

The addition of the inhibitor of chain-radical oxidation 2,4,6-tri-*tert*-butylphenol (TTBP) until its concentration reached 0.1 mol L^{-1} exerts no noticeable effect on the conversion of cyclohexane at the initial concentration of cyclohexane of 0.1 mol L^{-1}. However, the composition of the products of oxidation substantially changes: as the concentration of TTBP increases, the rate of accumulation of cyclohexanol first increases and then decreases, and the rate of accumulation of alkylhydroperoxide decreases monotonically (Fig. 2). Conversion of H_2O_2 calculated from the yield of the total product (for the optimum concentration of TTBP) increases to 35—40%.

These facts indicate that the oxidation process is not a chain process, although it is likely of a radical nature. When oxygen is intensely removed during the reaction (by purging argon), the yield of the products of oxidation decreases almost to zero in both cases, which points to the existence of an $RO_2^{\cdot}$ radical, which is a common intermediate of oxidation both in the absence and presence of TTBP.[6]

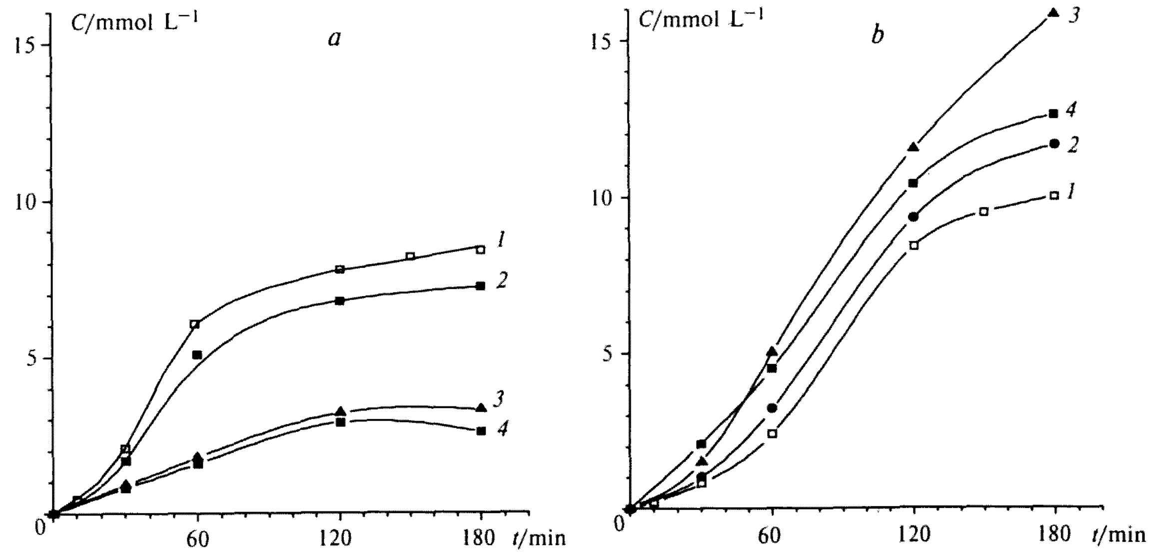

Fig. 2. Kinetics of accumulation of cyclohexyl hydroperoxide (*a*) and cyclohexanol (*b*) in the PFPS—H_2O_2 system for different concentrations of TTBP: 0 (*1*), 0.025 (*2*), 2.1 (*3*), and 0.125 (*4*) mol L^{-1}. Standard conditions (see Experimental).

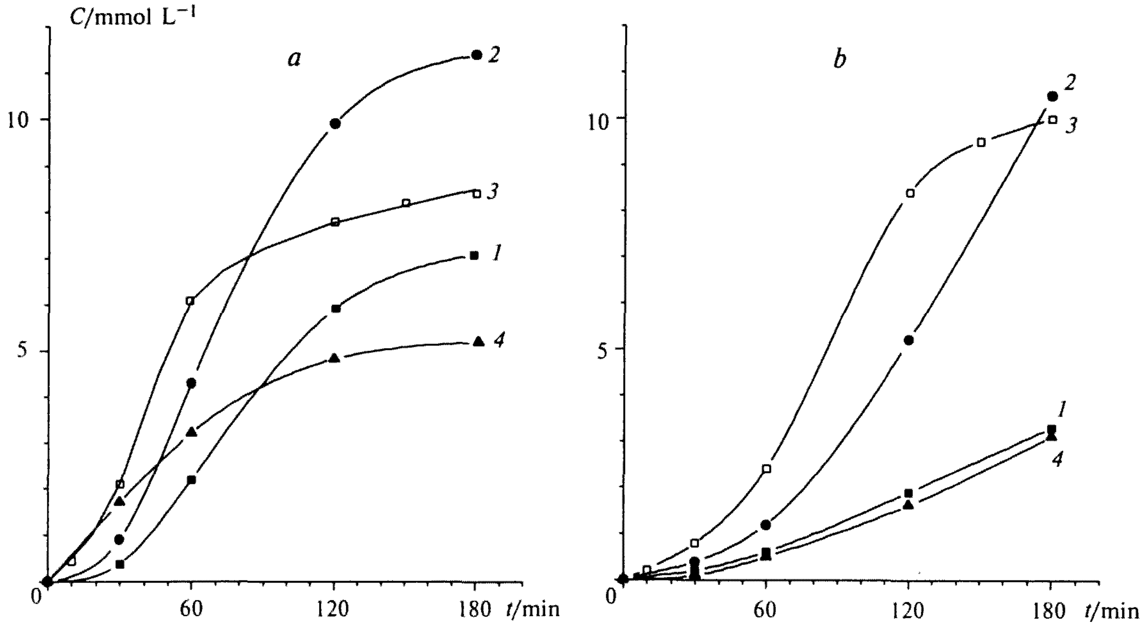

Fig. 3. Kinetics of accumulation of cyclohexyl hydroperoxide (*a*) and cyclohexanol (*b*) in the PFPS—H_2O_2 system at different concentrations of $HClO_4$: 6 (*1*), 24 (*2*), 48 (*3*), and 120 (*4*) mmol L^{-1}. The other conditions are standard.

In the absence of an acid, the rates of decomposition of hydrogen peroxide and of oxidation of cyclohexane are close to zero. When the acid is added immediately before the beginning of the reaction, the induction period appears on the kinetic curves (see Fig. 1). It can be reduced to zero by preliminary keeping of the PFPS with the acid for 1—2 h. The dependence of the rate of accumulation of the concentration of the acid passes through a maximum (Fig. 3).

When the concentration of the acid in the reaction medium becomes higher than 0.05 mol L^{-1}, the rate of oxidation of cyclohexane begins to decrease. This is explained by the fact that the rate of the reaction

$$Fe^{III} + H_2O_2 \longrightarrow Fe^{II} + HO_2^{\cdot}$$

is inversely proportional to the concentration of protons.[7]

When hydrochloric, nitric, or acetic acid is used instead of perchloric acid, the reaction almost does not occur. The addition of chloride and acetate ions to the reaction mixture containing perchloric acid inhibits the oxidation of cyclohexane. No formation of cyclohexyl chloride is observed in the presence of chloride ions.

All studies were carried out for a polymer with an Fe/Si ratio of 1.56, which contains iron metalloxide clusters.[5] In the future we suppose to study catalytic properties of PFPS with different Fe/Si ratios and, correspondingly, with different contents of clusters.

Experimental

Kinetic studies were carried out under the following standard conditions: [PFPS] = $2 \cdot 10^{-3}$ mol L^{-1} (calculated per Fe), $[H_2O_2]$ = 0.1 mol L^{-1} (30% aqueous), [alkane] = 0.5 mol L^{-1}, $[HClO_4]$ = $48 \cdot 10^{-3}$ mol L^{-1}, in an acetonitrile solution (5 mL) at 20 °C. For the indicated ratio of components, the reaction mixture is homogeneous.

An equal amount of a saturated solution of PPh_3 in acetonitrile (unreacted H_2O_2 was preliminarily neutralized by the addition of a small amount of anhydrous Na_2SO_3) was added to the reaction mixture (0.2 mL). The sample was kept for 3—5 min prior to analysis. The products were analyzed by GLC on a Hewlett Packard 58-80A chromatograph (Carbowax 20M capillary column 30 m long).

Methane was oxidized in a steel autoclave under 60 atm.

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