

Oxidations by the system ‘hydrogen peroxide—[Mn₂L₂O₃][PF₆]₂ (L=1,4,7-trimethyl-1,4,7-triazacyclononane)—carboxylic acid’.

Part 10: Co-catalytic effect of different carboxylic acids in the oxidation of cyclohexane, cyclohexanol, and acetone[☆]

Georgiy B. Shul’pin^{a,*}, Marianne G. Matthes^b, Vladimir B. Romakh^c, Marília I.F. Barbosa^b,
Jonatas L.T. Aoyagi^b, Dalmo Mandelli^b

^a *Semenov Institute of Chemical Physics, Russian Academy of Sciences, ulitsa Kosygina, dom 4, Moscow 119991, Russia*

^b *Pontifícia Universidade Católica de Campinas, Faculdade de Química, Rod. D. Pedro I, km 136, Pq. das Universidades, Campinas, SP 13086-900, Brazil*

^c *University of Heidelberg, BASF Catalysis Research Laboratory, Im Neuenheimer Feld 584, 69120 Heidelberg, Germany*

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Abstract

Hydrogen peroxide oxidation of cyclohexane in acetonitrile solution catalyzed by the dinuclear manganese(IV) complex [LMn(O)₃MnL](PF₆)₂ (L=1,4,7-trimethyl-1,4,7-triazacyclononane, TMTACN) at 25 °C in the presence of a carboxylic acid affords cyclohexyl hydroperoxide as well as cyclohexanone and cyclohexanol. A kinetic study of the reactions with participation of three acids (acetic acid, oxalic acid, and pyrazine-2,3-dicarboxylic acid, 2,3-PDCA) led to the following general scheme. In the first stage, the catalyst precursor forms an adduct. The equilibrium constants *K*₁ calculated for acetic acid, oxalic acid, and 2,3-PDCA were 127±8, (7±2)×10⁴, and 1250±50 M^{−1}, respectively. The same kinetic scheme was applied for the cyclohexanol oxidation catalyzed by the complex in the presence of oxalic acid. The oxidation of cyclohexane in water solution using oxalic acid as a co-catalyst gave cyclohexanol and cyclohexanone, which were rapidly transformed into a mixture of over-oxidation products. In the oxidation of cyclohexanol to cyclohexanone, varying the concentrations of the reactants and the reaction time we were able to find optimal conditions and to obtain the cyclohexanone in 94% yield based on the starting cyclohexanol. Oxidation of acetone to acetic acid by the system containing oxalic acid was also studied.

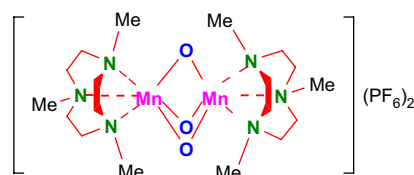
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1. Introduction

Complexes of transition metals catalyze oxidations of hydrocarbons (see reviews¹) and some other organic compounds, for example, alcohols with molecular oxygen and peroxides, especially with hydrogen peroxide. Manganese derivatives containing in many cases chelating N-ligands are among the

most active catalysts in various oxidations as well as H₂O₂ decomposition processes.² The dinuclear manganese(IV) complex [LMn(O)₃MnL](PF₆)₂ (complex 1; L is 1,4,7-trimethyl-1,4,7-triazacyclononane, TMTACN), which has been synthesized and characterized by Wieghardt and co-workers,³ and similar



Complex 1

[☆] For Parts 1–9, see Refs. 5a–i, respectively. Electronic Supplementary data (Figs. S1–S12) are available.

* Corresponding author. Tel.: +7 495 9397317; fax: +7 495 1376130/9397417/6512191.

E-mail addresses: gbsb@mail.ru, shulpin@chph.ras.ru (G.B. Shul’pin).

compounds are known to catalyze some oxidations of organic compounds, such as olefins and phenols (see reviews^{4a–c} and very recent original publications^{4d–g}).

In 1998, we discovered^{5a,6a} that the oxidizing power of catalyst **1** in the H_2O_2 oxidation can be dramatically increased if a small amount of a carboxylic acid is added to the reaction solution. Further detailed study of our system has been published in subsequent papers.^{5,6} Thus, we found^{5a–g,i,6a,c,h–j} that the combination '1/ $\text{CH}_3\text{COOH}/\text{H}_2\text{O}_2$ ' in acetonitrile solution very efficiently oxidizes inert alkanes to afford primarily the corresponding alkyl hydroperoxide, which is transformed further into the more stable ketone (aldehyde) and alcohol. Some other acids have been employed as co-catalysts instead of acetic acid. It turned out that the system oxidizes not only alkanes but also epoxidizes olefins,^{5c,e–g,6f,j} transforms alcohols into ketones (aldehydes),^{5c,h,6e} and sulfides into sulfoxides.^{5c} The reaction with olefins gave rise to products of dihydroxylation^{5e} in addition to the corresponding epoxides. Alkanes,^{5f} olefins,^{5f} and alcohols^{5h} were oxidized also in the absence of acetonitrile. A relevant soluble polymer-bound Mn(IV) complex with *N*-alkylated 1,4,7-triazacyclononane was used as a catalyst in the H_2O_2 oxygenation of alkanes.^{6d} Bosch and Veghini^{7a} prepared insoluble salts of formula $[\text{LMn}(\mu\text{-O})_3\text{MnL}]_n[\text{XM}_{12}\text{O}_{40}]_m$ (X is P or Si and M is Mo or W), which are active catalysts in the oxidation of alcohols^{5h,7a} and olefins.^{7a} It is important that almost no oxidation reaction can be observed in the absence of a carboxylic acid as a co-catalyst in all cases mentioned above. Recently our '1/carboxylic acid/ H_2O_2 ' system has been used by other authors^{7b} for the cis-hydroxylation and epoxidation of olefins. We have also demonstrated that alkanes and olefins can be oxidized by *tert*-butyl hydroperoxide^{5c,6b,1} or peroxyacetic acid^{5a,6a,k} using complex **1** as a catalyst. The reaction with *tert*-butyl hydroperoxide is significantly accelerated in the presence of a small amount of a carboxylic acid.^{5c,6b,1}

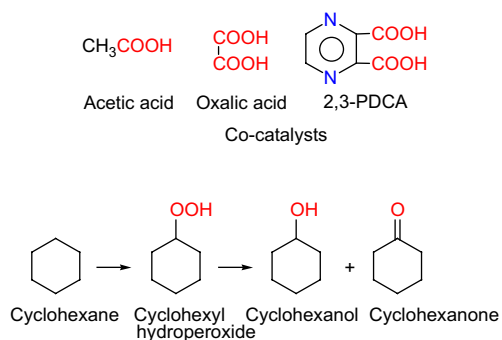
In continuation of studies of our '1/carboxylic acid/ H_2O_2 ' oxidizing system, in the present work we carried out a comparative kinetic investigation of the cyclohexane oxidation in acetonitrile in the presence of three co-catalysts of the different nature: acetic acid, oxalic acid, and pyrazine-2,3-dicarboxylic acid (2,3-PDCA). Another aim of the present work was an exploration of the possibility to use alternative solvents for the oxidation of alkanes and alcohols. Attempting to employ water instead of acetonitrile we have found an extensive over-oxidation of the formed products. This fact prompted us to vary the conditions in order to find optimal concentrations, temperature, and reaction time. When we tried to replace acetonitrile with acetone as a solvent in the alkane oxidations we discovered that acetone can be easily oxidized by our system to produce acetic acid. This reaction has been also studied in the present work.

2. Results and discussion

2.1. Cyclohexane oxidation in acetonitrile solution

We studied oxidation of cyclohexane in acetonitrile solution with hydrogen peroxide catalyzed by complex **1** in the presence of the following carboxylic acids: acetic acid, oxalic

acid, and pyrazine-2,3-dicarboxylic acid (2,3-PDCA). The oxygenation of cyclohexane gives rise to the formation of the corresponding alkyl hydroperoxide as the main primary product. To demonstrate the formation of cyclohexyl hydroperoxide in this oxidation and to estimate its concentration in the course of the reaction we used a simple method developed by us earlier.^{6c,g,8} If an excess of solid PPh_3 is added to the sample of the reaction solution ca. 10 min before the GC analysis, the alkyl hydroperoxide present is completely reduced to the corresponding alcohol. As a result, the chromatogram differs from that of a sample not subjected to the reduction (the alcohol peak rises, while the intensity of the ketone peak decreases). Comparing the intensities of peaks attributed to the alcohol and ketone before and after the reduction, it is possible to estimate the real concentrations of the alcohol, ketone, and alkyl hydroperoxide present in the reaction solution. If an oxidation is carried out in water solution, other than PPh_3 reducing reagents can be used, for example, NaBH_4 . In recent years, our method was employed by other chemists for the analysis of reaction products and detection of alkyl hydroperoxides in various oxidations of C–H compounds by molecular oxygen, hydrogen peroxide, and other peroxides.⁹



The kinetic curves of the cyclohexane oxidation in the presence of the three acids are shown in Figures 1–3. It can be seen that the addition of oxalic acid gives the most efficient conversion of cyclohexane into the cyclohexyl hydroperoxide with the formation of only small amounts of the cyclohexanol and cyclohexanone. The usage of acetic acid and especially pyrazine-2,3-dicarboxylic acid as co-catalysts gives rise to noticeably lower yields. Although in the cases of the three co-catalysts in the beginning of the process only the cyclohexyl hydroperoxide is formed, the reaction in the presence of acetic acid or 2,3-PDCA proceeds with simultaneous transformation of the cyclohexyl hydroperoxide into the more stable cyclohexanone and cyclohexanol. Relative concentrations of the latter products become substantial in the end of the oxidation process.

We studied dependencies of initial rates of the cyclohexane oxidation and total yield of oxygenates after 6 h on initial concentrations of catalyst **1**, co-catalyst, the cyclohexane and the hydrogen peroxide for the reactions carried out in the presence of acetic acid (Figs. 4–7), oxalic acid (Figs. 9–12), and 2,3-PDCA (Figs. 14–17). For the reactions with participation of acetic and oxalic acids the influence of water was also

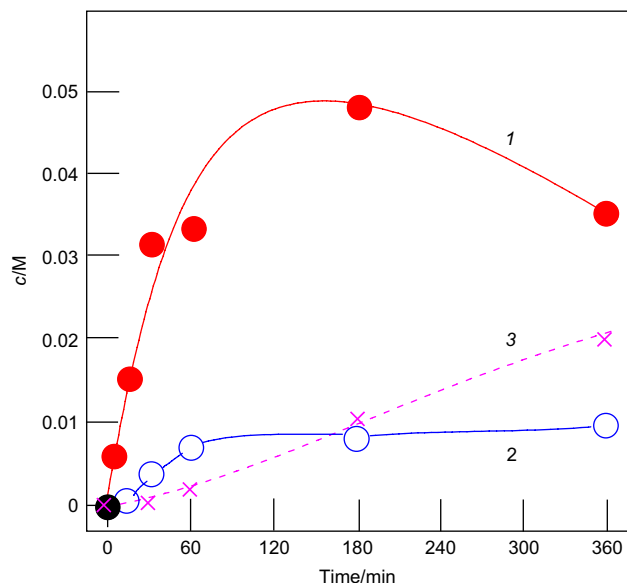


Figure 1. Oxidation of cyclohexane (0.25 M) in MeCN at 25 °C with H_2O_2 (0.75 M) catalyzed by complex **1** (5×10^{-5} M) in the presence of acetic acid (0.11 M). Concentrations of cyclohexyl hydroperoxide (curve 1), cyclohexanol (curve 2), and cyclohexanone (curve 3) are shown. Concentrations in Figures 1–3 were measured by injecting the reaction samples before and after reduction of the reaction mixture with PPh_3 (for this method, see Refs. 6c, g, and 8).

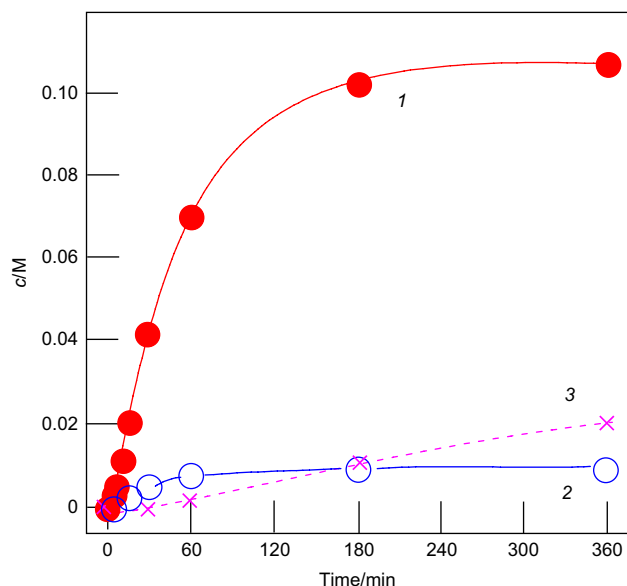


Figure 2. Oxidation of cyclohexane (0.25 M) in MeCN at 25 °C with H_2O_2 (0.75 M) catalyzed by complex **1** (5×10^{-5} M) in the presence of oxalic acid (0.11 M). Concentrations of cyclohexyl hydroperoxide (curve 1), cyclohexanol (curve 2), and cyclohexanone (curve 3) are shown.

investigated (Fig. 8 and 13, respectively). In the kinetic data analysis (see below, Section 2.3), we operated with ‘initial reaction rates’, which are the maximum stationary rates of product accumulation attained in a few minutes after mixing the reagents. A sum of product (cyclohexanol and cyclohexanone) concentrations was determined for the certain time interval after the reduction of the reaction aliquots with solid triphenylphosphine.

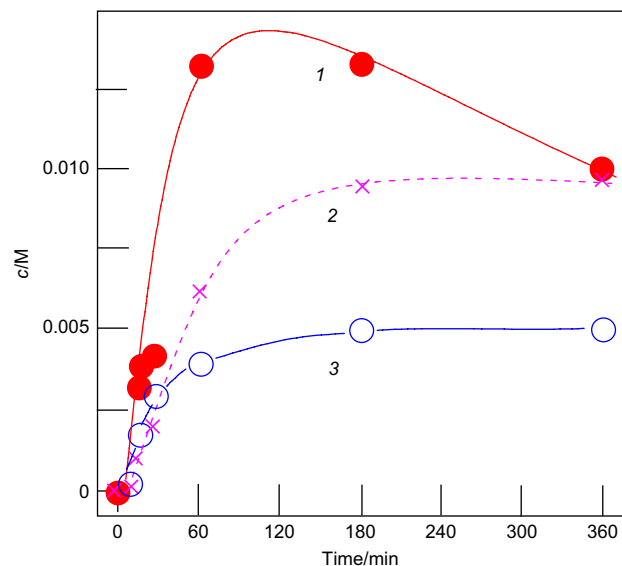


Figure 3. Oxidation of cyclohexane (0.25 M) in MeCN at 25 °C with H_2O_2 (0.25 M) catalyzed by complex **1** (5×10^{-5} M) in the presence of 2,3-PDCA (1×10^{-3} M). Concentrations of cyclohexyl hydroperoxide (curve 1), cyclohexanol (curve 2), and cyclohexanone (curve 3) are shown.

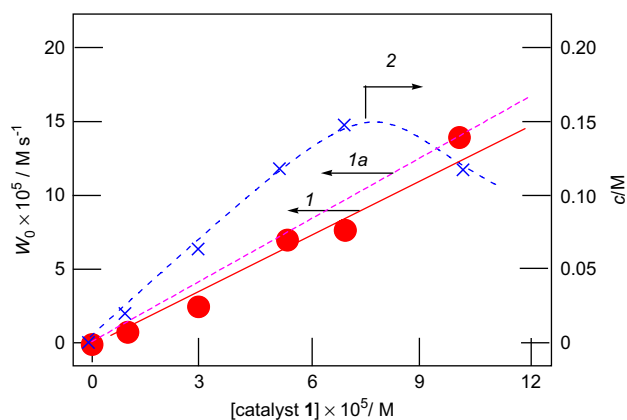


Figure 4. Oxidation of cyclohexane (0.25 M) with hydrogen peroxide (70% aqueous; 0.75 M; the content of water in the reaction mixture was 0.6 M) catalyzed by **1** and acetic acid (0.11 M) in MeCN at 25 °C. Total volume of the reaction solution was 5 mL. Dependences of the initial rate of formation of oxygenates W_0 (curve 1) and the total yield of oxygenates after 6 h c (curve 2) on initial concentration of catalyst **1** are shown. Curve 1a is a theoretical line (see Section 2.3).

For the three co-catalysts the initial rate of the oxidation is proportional to concentration of the catalyst **1** in the interval of its concentrations 0 – 10^{-4} M and the yields of the oxygenates (after 6 h) become a bit lower for acetic acid and 2,3-PDCA at $[\text{I}] = 10^{-4}$ M (Figs. 4 and 14). The yield does not depend on the catalyst concentration when $[\text{I}] > 0.5 \times 10^{-4}$ M (Fig. 9) in the case of oxalic acid. Each curve for dependence of the initial rate on concentration of either the co-catalyst or the cyclohexane has a plateau at relatively high concentration of this reactant. Initial rates of the oxidation are proportional to initial concentration of hydrogen peroxide (Figs. 7, 12, and 17). It follows from Figures 12 and 17 that the yield of products after

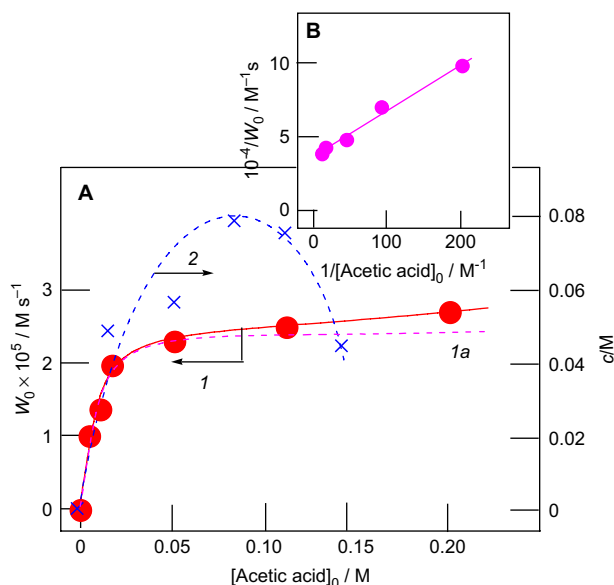


Figure 5. Oxidation of cyclohexane (0.25 M) with hydrogen peroxide (70% aqueous; 0.25 M; the content of water in the reaction mixture was 0.2 M) catalyzed by **1** (5×10^{-5} M) and acetic acid in MeCN at 25 °C. Total volume of the reaction solution was 5 mL. Graph A: dependences of the initial rate of formation of oxygenates W_0 (curve 1) and the total yield of oxygenates after 6 h c (curve 2) on initial concentration of acetic acid are shown. Curve 1a is a theoretical line (see Section 2.3). Graph B: dependence of $1/W_0$ versus $1/[\text{Acetic acid}]_0$ (derived from curve 1a).

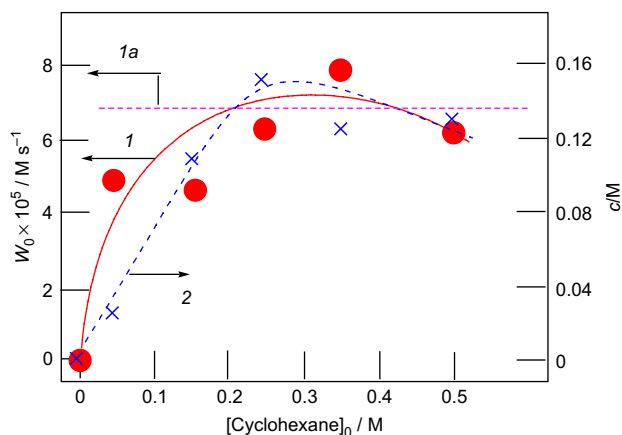


Figure 6. Oxidation of cyclohexane with hydrogen peroxide (70% aqueous; 0.75 M; the content of water in the reaction mixture was 0.6 M) catalyzed by **1** (5×10^{-5} M) and acetic acid (0.11 M) in MeCN at 25 °C. Total volume of the reaction solution was 5 mL. Dependences of the initial rate of formation of oxygenates W_0 (curve 1) and the total yield of oxygenates after 6 h c (curve 2) on initial concentration of the cyclohexane are shown. Curve 1a is a theoretical line (see Section 2.3).

6 h does not practically depend on initial concentration of the used hydrogen peroxide. Addition of water does not also affect dramatically initial oxidation rate and the product yield (Figs. 8 and 13). It is, however, interesting that in the case of co-catalysis by acetic acid in the presence of relatively high concentration of water the cyclohexanol/cyclohexanone ratio (after 6 h) obtained after the reduction with PPh_3 becomes four times lower. Enhanced concentration of the ketone after reduction with PPh_3 testifies that in the presence of water

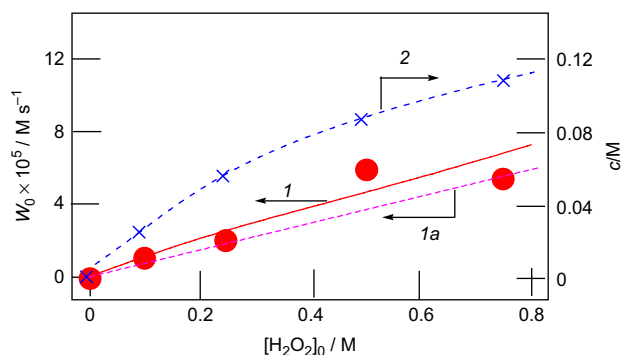


Figure 7. Oxidation of cyclohexane (0.25 M) with hydrogen peroxide (70% aqueous) catalyzed by **1** (5×10^{-5} M) and acetic acid (0.05 M) in MeCN at 25 °C. Total volume of the reaction solution was 5 mL. Dependences of the initial rate of formation of oxygenates W_0 (curve 1) and the total yield of oxygenates after 6 h c (curve 2) on initial concentration of the hydrogen peroxide are shown. Curve 1a is a theoretical line (see Section 2.3). In all experiments water was added to maintain the total concentration of water equal to 0.89 M.

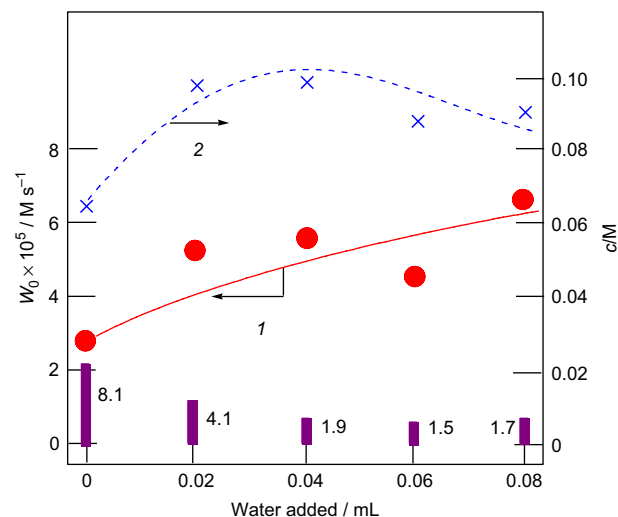


Figure 8. Oxidation of cyclohexane (0.25 M) with hydrogen peroxide (70% aqueous; 0.75 M) catalyzed by **1** (5×10^{-5} M) and acetic acid (0.11 M) in MeCN at 25 °C. Total volume of the reaction solution was 5 mL. Dependences of the initial rate of formation of oxygenates W_0 (curve 1) and the total yield of oxygenates after 6 h c (curve 2) on the volume of added water are shown. The bars in the bottom of the graph correspond to the cyclohexanol/cyclohexanone ratio (after 6 h) obtained after the reduction with PPh_3 .

the cyclohexyl hydroperoxide decomposes to afford the cyclohexanone more intensively than when no additional water was used (see Fig. 8). Under these conditions water concentration (from 70% hydrogen peroxide) $[\text{H}_2\text{O}] = 0.6$ M and the cyclohexanol/cyclohexanone ratio attained 8.1.

2.2. Cyclohexanol oxidation in acetonitrile solution

In the present work we have also studied the oxidation of cyclohexanol into cyclohexanone by the ' H_2O_2 /1/oxalic acid' system in homogeneous acetonitrile solution. Figure 18 shows typical kinetic curves for consumption of the alcohol and accumulation of the ketone at different concentrations of oxalic acid. It can be clearly seen that no oxidation reaction occurs in the absence of oxalic acid.

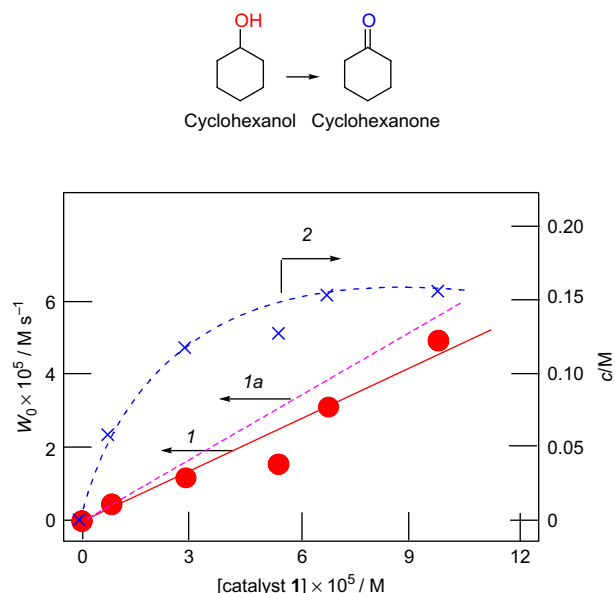


Figure 9. Oxidation of cyclohexanol (0.25 M) with hydrogen peroxide (70% aqueous; 0.75 M; the content of water in the reaction mixture was 0.6 M) catalyzed by **1** and oxalic acid (0.11 M) in MeCN at 25 °C. Total volume of the reaction solution was 5 mL. Dependences of the initial rate of formation of oxygenates W_0 (curve 1) and the total yield of oxygenates after 6 h c (curve 2) on initial concentration of catalyst **1** are shown. Curve 1a is a theoretical line (see Section 2.3).

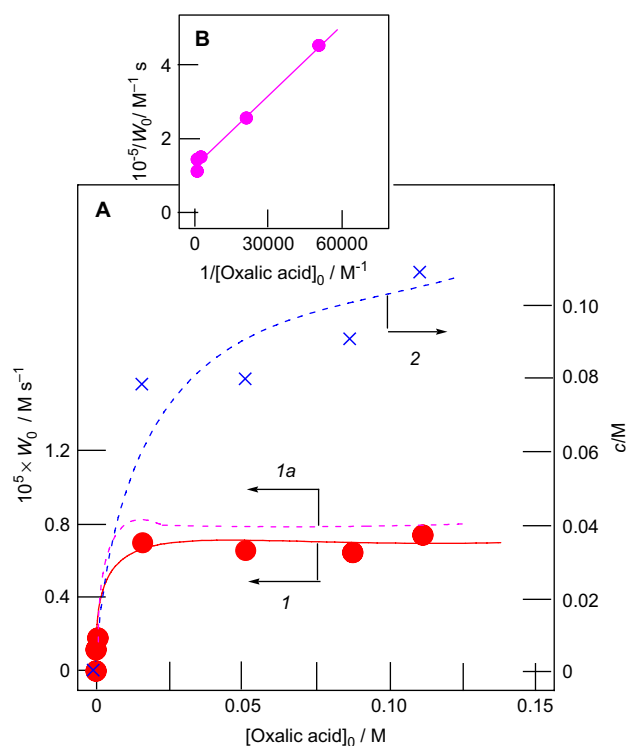


Figure 10. Oxidation of cyclohexane (0.25 M) with hydrogen peroxide (70% aqueous; 0.25 M; the content of water in the reaction mixture was 0.2 M) catalyzed by **1** (5×10^{-5} M) and oxalic acid in MeCN at 25 °C. Total volume of the reaction solution was 5 mL. Graph A: dependences of the initial rate of formation of oxygenates W_0 (curve 1) and the total yield of oxygenates after 6 h c (curve 2) on initial concentration of oxalic acid are shown. Curve 1a is a theoretical line (see Section 2.3). Graph B: dependence of $1/W_0$ versus $1/[\text{Oxalic acid}]_0$ (derived from curve 1a).

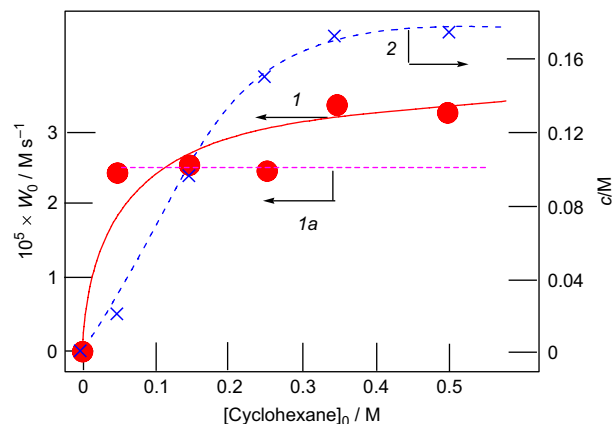


Figure 11. Oxidation of cyclohexane with hydrogen peroxide (70% aqueous; 0.75 M; the content of water in the reaction mixture was 0.6 M) catalyzed by **1** (5×10^{-5} M) and oxalic acid (0.11 M) in MeCN at 25 °C. Total volume of the reaction solution was 5 mL. Dependences of the initial rate of formation of oxygenates W_0 (curve 1) and the total yield of oxygenates after 6 h c (curve 2) on initial concentration of cyclohexane are shown. Curve 1a is a theoretical line (see Section 2.3).

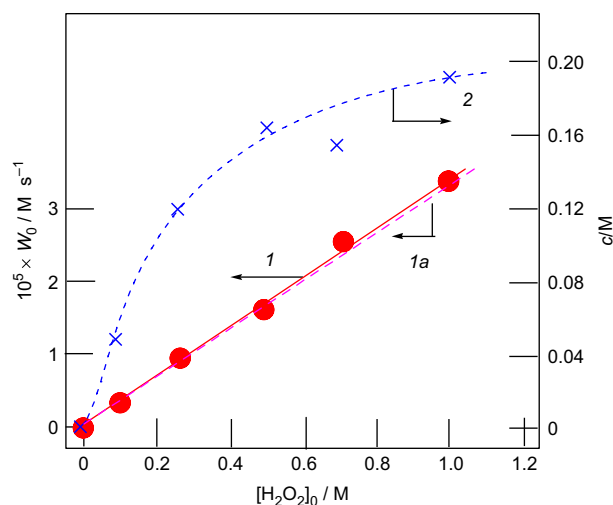


Figure 12. Oxidation of cyclohexane (0.25 M) with hydrogen peroxide (70% aqueous) catalyzed by **1** (5×10^{-5} M) and oxalic acid (0.05 M) in MeCN at 25 °C. Total volume of the reaction solution was 5 mL. Dependences of the initial rate of formation of oxygenates W_0 (curve 1) and the total yield of oxygenates after 6 h c (curve 2) on initial concentration of hydrogen peroxide are shown. Curve 1a is a theoretical line (see Section 2.3).

The reaction rate linearly depends on concentration of catalyst **1** (Fig. 19). Dependences of the initial reaction rate on concentration of oxalic acid and initial concentrations of cyclohexanol and hydrogen peroxides are shown in Figures 20–22. It can be seen that at relatively high concentrations of oxalic acid and cyclohexane initial rate does not depend on concentration of these reactants. Such a behavior is similar to that found by us for the oxidation of cyclohexane (see Section 2.1; compare Figs. 20 and 21 with Figs. 10 and 11). Dependences of W_0 on initial concentrations of catalyst **1** and hydrogen peroxide are also similar for oxidations of both cyclohexanol and cyclohexane (compare Figs. 19 and 22 with

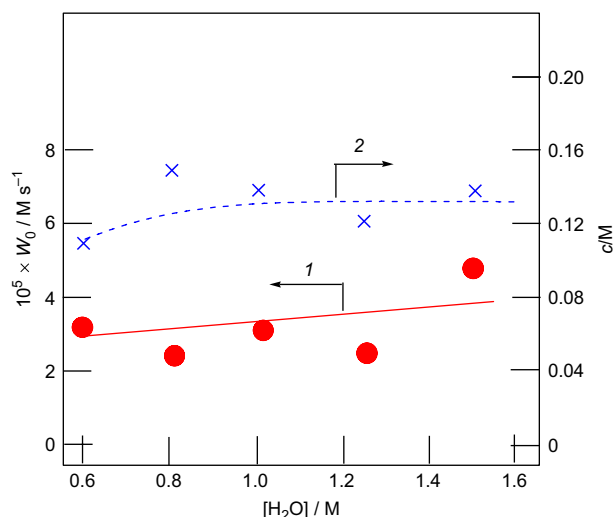


Figure 13. Oxidation of cyclohexane (0.25 M) with hydrogen peroxide (70% aqueous; 0.75 M) catalyzed by **1** (5×10^{-5} M) and oxalic acid (0.11 M) in MeCN at 25 °C. Total volume of the reaction solution was 5 mL. Dependences of the initial rate of formation of oxygenates W_0 (curve 1) and the total yield of oxygenates after 6 h c (curve 2) on concentration of water are shown.

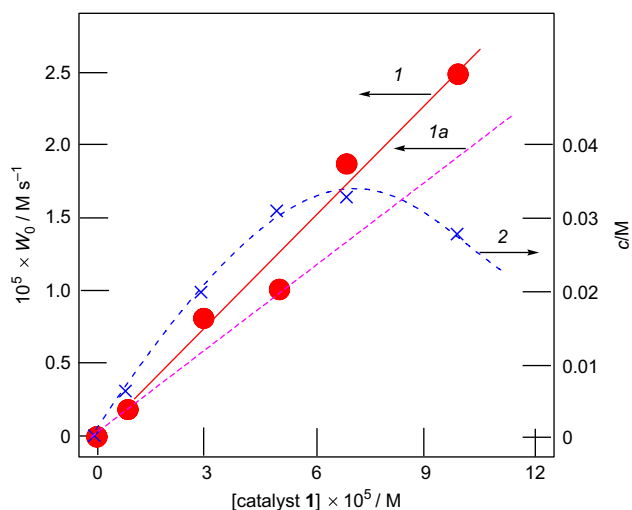


Figure 14. Oxidation of cyclohexane (0.25 M) with hydrogen peroxide (70% aqueous; 0.25 M; the content of water in the reaction mixture was 0.2 M) catalyzed by **1** and 2,3-PDCA (1×10^{-3} M) in MeCN at 25 °C. Total volume of the reaction solution was 5 mL. Dependences of the initial rate of formation of oxygenates W_0 (curve 1) and the total yield of oxygenates after 6 h c (curve 2) on initial concentration of catalyst **1** are shown. Curve 1a is a theoretical line (see Section 2.3).

Figs. 10 and 12). At relatively high concentration (>0.75 M) water insignificantly decreases the yield of the cyclohexanone (Fig. S1, see Supplementary data).

2.3. A kinetic scheme for the cyclohexane and cyclohexanol oxidation in acetonitrile solution

It has been mentioned above that in the absence of a carboxylic acid the rate of cyclohexane or cyclohexanol oxidation is negligible (see Figs. 5, 10, 15, and 20). This fact allows us to propose the following general kinetic scheme for the oxidation

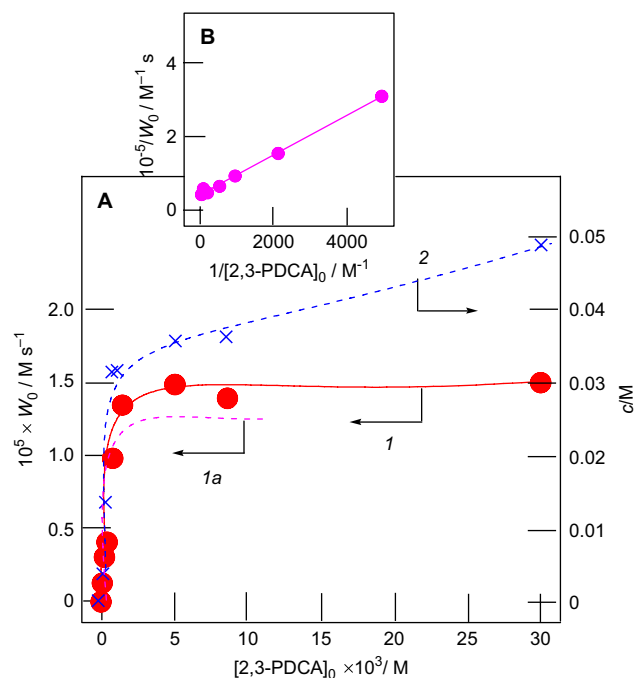


Figure 15. Oxidation of cyclohexane (0.25 M) with hydrogen peroxide (70% aqueous; 0.25 M; the content of water in the reaction mixture was 0.2 M) catalyzed by **1** (5×10^{-5} M) and 2,3-PDCA in MeCN at 25 °C. Total volume of the reaction solution was 5 mL. Graph A: dependences of the initial rate of formation of oxygenates W_0 (curve 1) and the total yield of oxygenates after 6 h c (curve 2) on initial concentration of 2,3-PDCA are shown. Curve 1a is a theoretical line (see Section 2.3). Graph B: dependence of $1/W_0$ versus $1/[\text{2,3-PDCA}]_0$ (derived from curve 1a).

of cyclohexane as well as cyclohexanol (Cy-one and Cy-ol are cyclohexanone and cyclohexanol, respectively).

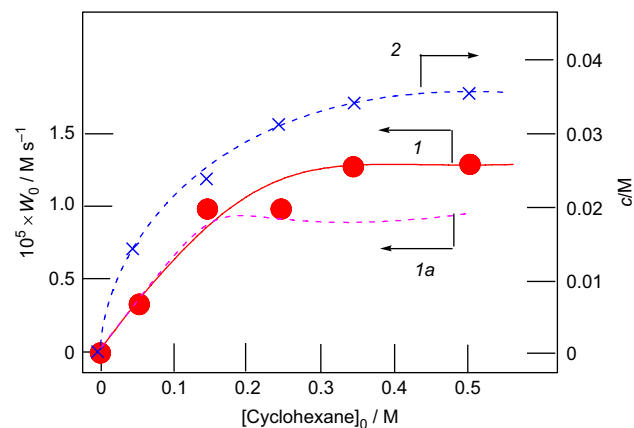
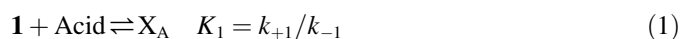


Figure 16. Oxidation of cyclohexane with hydrogen peroxide (70% aqueous; 0.25 M; the content of water in the reaction mixture was 0.2 M) catalyzed by **1** (5×10^{-5} M) and 2,3-PDCA (1×10^{-3} M) in MeCN at 25 °C. Total volume of the reaction solution was 5 mL. Dependences of the initial rate of formation of oxygenates W_0 (curve 1) and the total yield of oxygenates after 6 h c (curve 2) on initial concentration of cyclohexane are shown. Curve 1a is a theoretical line (see Section 2.3).

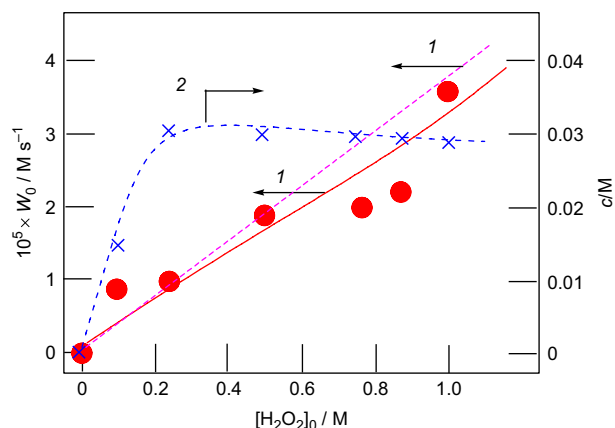
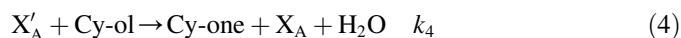
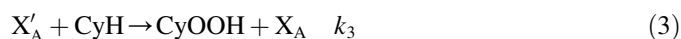


Figure 17. Oxidation of cyclohexane (0.25 M) with hydrogen peroxide (70% aqueous) catalyzed by **1** (5×10^{-5} M) and 2,3-PDCA (1×10^{-3} M) in MeCN at 25 °C. Total volume of the reaction solution was 5 mL. Dependences of the initial rate of formation of oxygenates W_0 (curve 1) and the total yield of oxygenates after 6 h c (curve 2) on initial concentration of hydrogen peroxide are shown. In all experiments water was added to maintain the total concentration of water equal to 0.89 M. Curve 1a is a theoretical line (see Section 2.3).



The first step of the scheme is an equilibrium leading to the formation of an adduct X_A , which in the second step in the presence of hydrogen peroxide is converted to an active

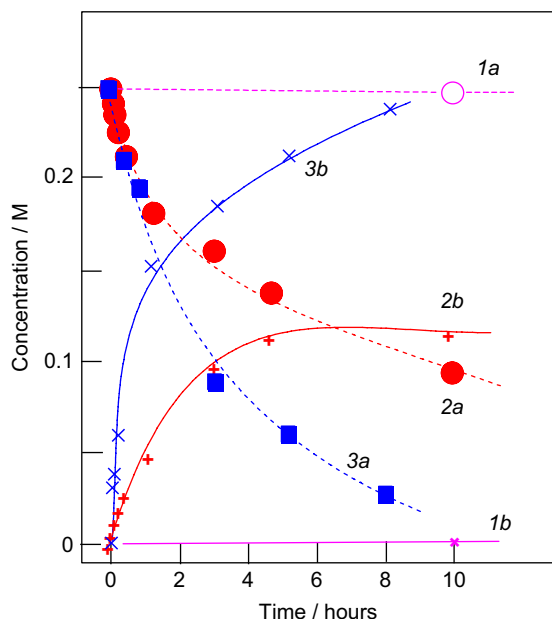


Figure 18. Oxidation of cyclohexanol (0.25 M; curves a) to cyclohexanone (curves b) with 70% aqueous H_2O_2 catalyzed by complex **1**. Consumption of cyclohexanol and accumulation of cyclohexanone with time are shown. The temperature was 25 °C and the solvent was acetonitrile. Conditions: curves 1: complex **1**, 5×10^{-5} M; oxalic acid, 0 M; H_2O_2 , 0.25 M. Curves 2: complex **1**, 5×10^{-5} M; oxalic acid, 0.05 M; H_2O_2 , 0.25 M. Curves 3: complex **1**, 10×10^{-5} M; oxalic acid, 0.11 M; H_2O_2 , 0.5 M.

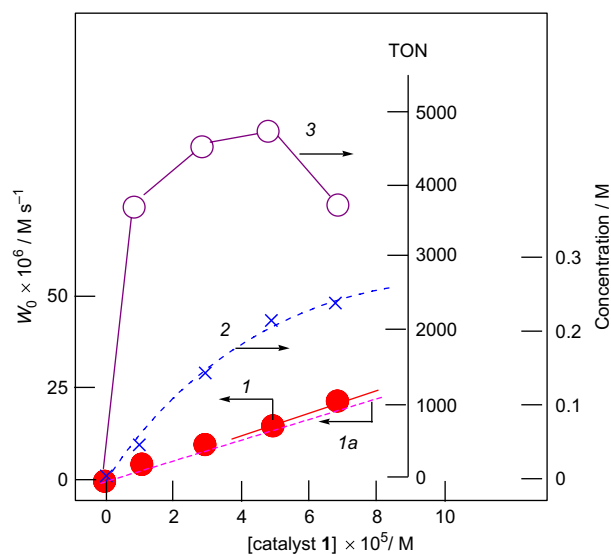


Figure 19. Dependences of the initial rate (curve 1) and the yield of cyclohexanone after 8 h (M, curve 2) as well as TON on concentration of **1** in the oxidation of cyclohexanol (0.25 M) with 70% aqueous H_2O_2 (0.50 M) in the presence of oxalic acid (0.11 M). The temperature was 25 °C and the solvent was acetonitrile. Curve 1a is a theoretical line (see Section 2.3).

species X'_A . The right part of Eqs. 3–5 contains the main reaction products that can be also achievable via a series of consecutive steps. However, we found that these steps do not affect the total reaction rate under conditions in use. Indeed, when $[\text{CyH}]_0 > 0.15$ M the initial reaction rate is independent on the cyclohexane concentration (Figs. 6, 11, and 16)

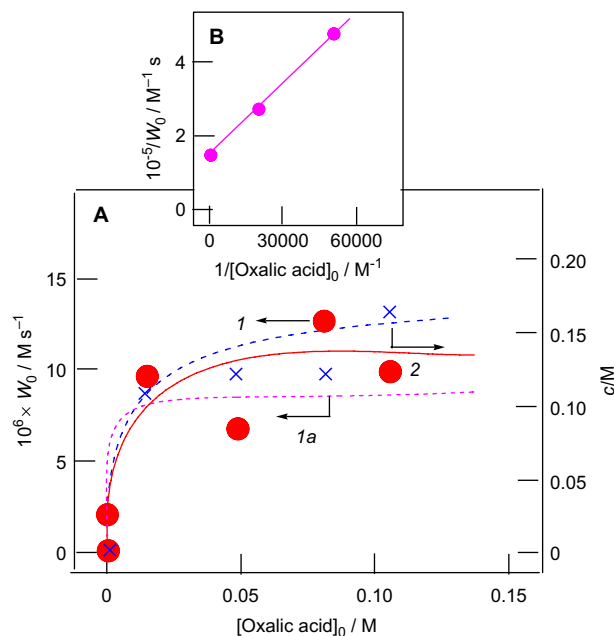


Figure 20. Graph A: dependences of the initial rate (curve 1) and the yield of cyclohexanone after 8 h (M, curve 2) in the oxidation of cyclohexanol (0.25 M) with 70% aqueous H_2O_2 (0.25 M) catalyzed by **1** (5×10^{-5} M) on concentration of added oxalic acid. The temperature was 25 °C and the solvent was acetonitrile. Curve 1a is a theoretical line (see Section 2.3). Graph B: dependence of $1/W_0$ versus $1/[\text{Oxalic acid}]_0$ (derived from curve 1a).

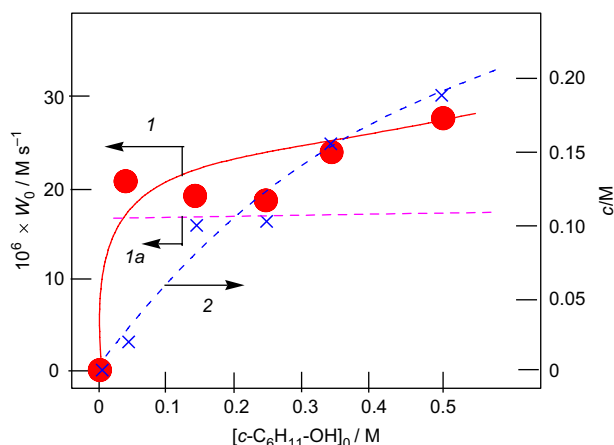


Figure 21. Dependence of the initial rate (curve 1) and the yield of cyclohexanone after 8 h (M, curve 2) in cyclohexanol oxidation with 70% aqueous H_2O_2 (0.5 M) catalyzed by **1** (5×10^{-5} M) and oxalic acid (0.11 M) on initial concentration of cyclohexanol. The temperature was 25 °C and the solvent was acetonitrile. Curve 1a is a theoretical line (see Section 2.3).

resulting in $W_3 > W_2$, the cyclohexyl hydroperoxide being the major reaction product. By analogy, the initial rate of cyclohexanol oxidation measured in the separate experiment (Fig. 21) is independent on the cyclohexanol concentration, therefore $W_4 > W_2$.

Thus, reaction 2 can be regarded as the rate-limiting step of the overall process: we observed the first-order dependences of the initial reaction rates on concentration of hydrogen peroxide (Figs. 7, 12, 17, and 22). Assuming that the concentration of species X_A is quasi-stationary and the rate of reverse reaction 1 is much lower than a sum of the rates of reactions 3–5, the analysis gave rise to Eq. 6:

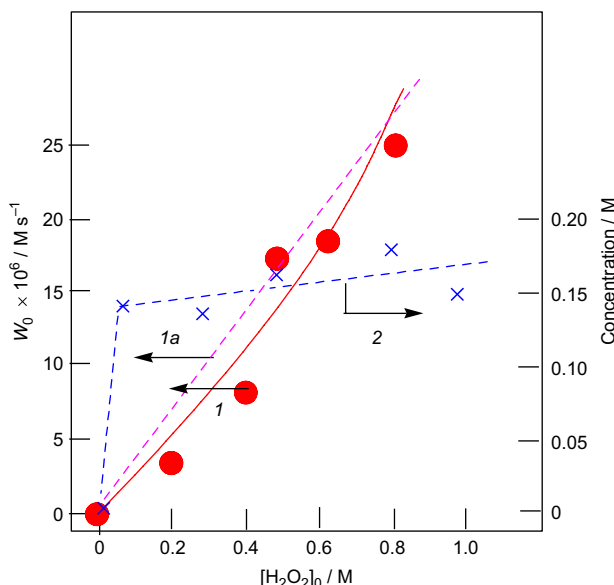


Figure 22. Dependence of the initial rate (curve 1) and the yield of cyclohexanone after 8 h (M, curve 2) in the oxidation of cyclohexanol (0.25 M) with 70% aqueous H_2O_2 catalyzed by **1** (5×10^{-5} M) and oxalic acid (0.05 M) on concentration of H_2O_2 . The temperature was 25 °C and the solvent was acetonitrile. Curve 1a is a theoretical line (see Section 2.3).

Table 1

Parameters for the catalytic oxidation of cyclohexane

Constant	Acetic acid	Oxalic acid	2,3-PDCA
K_1 (M^{-1})	127 ± 8	$70,000 \pm 20,000$	1250 ± 50
k_2 ($\text{M}^{-1} \text{s}^{-1}$)	2.0 ± 0.2	0.67 ± 0.07	1.4 ± 0.1
k_3 ($\text{M}^{-1} \text{s}^{-1}$)	Not determined	Not determined	2.3 ± 0.2

$$\frac{d[\text{CyOOH}]}{dt} = W_2 = k_2[X_A][\text{H}_2\text{O}_2] \approx \frac{k_2 K_1 [\mathbf{1}]_0 [\text{Acid}]_0 [\text{H}_2\text{O}_2]_0}{(1 + K_1 [\text{Acid}]_0)} \quad (6)$$

when $[\text{H}_2\text{O}_2] \approx [\text{H}_2\text{O}_2]_0$ and $[\text{Acid}] \approx [\text{Acid}]_0 \gg [\mathbf{1}]_0$.

Parameters k_2 and K_1 can be determined from the data of Figures 5, 10, 15, and 20 using the regression analysis of Eq. 6 in its linear form 6a (see graphs B in Figs. 5, 10, 15, and 20). The results are shown in Table 1.

$$\frac{1}{W} = \frac{1}{W_2} = \frac{1}{k_2 K_1 [\mathbf{1}]_0 [\text{H}_2\text{O}_2]_0} \times \frac{1}{[\text{Acid}]_0} + \frac{1}{k_2 [\mathbf{1}]_0 [\text{H}_2\text{O}_2]_0} \quad (6a)$$

In the case of 2,3-PDCA, when $[\text{CyH}]_0 < 0.15$ M, the initial rate of the reaction is proportional to cyclohexane concentration (Fig. 16) and we can estimate k_3 from Eq. 7:

$$\frac{d[\text{CyOOH}]}{dt} = W_3 = k_3[X_A][\text{CyH}] \approx \frac{k_3 K_1 [\mathbf{1}]_0 [\text{Acid}]_0 [\text{CyH}]_0}{(1 + K_1 [\text{Acid}]_0)} \quad (7)$$

The same kinetic scheme can be applied for the cyclohexanol oxidation catalyzed by **1** in the presence of oxalic acid. The parameters $70,000 \pm 20,000 \text{ M}^{-1}$ for K_1 and $0.6 \pm 0.2 \text{ M}^{-1} \text{s}^{-1}$ for k_2 were obtained by analogy from the analysis of dependences shown in Figures 20 (graph B) and 22. These parameters are close to those obtained for the cyclohexane oxidation. Thus, we can assume that the rate-limiting step for the cyclohexane and cyclohexanol oxidations is the same, that is, the formation of active oxidizing species can be described by Eq. 2. Finally, we can see that our theoretic calculations are in good agreement with experimental data (compare experimental points and theoretical curves in Figs. 4–7, 9–12, 14–17, and 19–22).

2.4. Cyclohexane and cyclohexanol oxidation in the absence of organic solvent

It is interesting to explore the possibility of the oxidation in the absence of acetonitrile. We found that the cyclohexane oxidation in water solution when oxalic acid is used as a co-catalyst gives cyclohexanol and cyclohexanone. Concentrations of these products decrease at time > 15 min due to the formation of over-oxidation products (Fig. S2). According to the GC analysis the reaction gives rise to the non-selective formation of many products, and adipic acid is only a minor component of the mixture. Due to this fact we did not study in detail the oxidation of cyclohexane in water.

The kinetic curves of the cyclohexanol oxidation in water under certain conditions also have a maximum (see Figs.

S3–S7, graphs A). We studied the reaction under different conditions and evaluated the optimal conditions when the cyclohexanone yield attains 94% based on starting cyclohexanol (see Fig. S5, curve 1b). It should be noted that at relatively high amounts of catalyst **1**, oxalic acid, cyclohexanol, and hydrogen peroxide the initial rate of cyclohexanone formation as well as its yield after 6 h do not depend on initial amounts of these reactants (see Figs. S3–S6, graphs B). The kinetic curves of cyclohexanone accumulation at various temperatures and dependences of W_0 and the yield of cyclohexanone after 6 h on temperature are presented in Figure S7.

2.5. Oxidation of acetone to acetic acid

The oxidation of cyclohexanol in the absence of acetonitrile showed that the cyclohexanone formed in this reaction can be easily oxidized further to afford a complex mixture of products. We decided to study in more detail the oxidation of acetone as a model substrate. Acetone played also the role of a solvent (it is known that acetone forms adducts with hydrogen peroxide¹⁰). This reaction at 40 °C in the presence of oxalic acid gives rise to the formation of acetic acid as a sole product (a typical kinetic curve is shown in Fig. S8). The initial rate of acetic acid accumulation and its yield after 3 h linearly depend on concentration of catalyst **1** (Fig. S9). At relatively high concentration of oxalic acid or hydrogen peroxide the yield of acetic acid does not depend on the concentrations of these reactants (Figs. S10 and S11). The initial rate of acetic acid accumulation and its yield after 3 h only slightly depend on temperature in the interval 10–50 °C (Fig. S12).

3. Conclusions

Our kinetic study showed that the first stage of the cyclohexane oxygenation with the '1/carboxylic acid/H₂O₂' system begins from the formation of an adduct of species **1** and the carboxylic acid. The equilibrium constants K_1 differ drastically for different acids: acetic acid, oxalic acid, and 2,3-PDCA. The difference in values K_1 can explain a quantitative difference in the behavior of the three acids as co-catalysts. We have also demonstrated in this work that using very carefully chosen reaction conditions (concentrations, time, and temperature) it is possible to avoid an extensive over-oxidation of cyclohexanone in the cyclohexanol oxidation in the absence of acetonitrile. The yield of cyclohexanone obtained under optimal conditions attained 94% based on starting cyclohexanol.

4. Experimental section

4.1. General

The oxidations of cyclohexane in acetonitrile were carried out in air in thermostated (25 °C) Pyrex cylindrical vessels with vigorous stirring. The total volume of the reaction solution was 5 mL. In our experiments, 70% aqueous solution of hydrogen peroxide ('Peróxidos do Brasil') was used. Typically, catalyst **1** (for the preparation, see Ref. 3), and the

co-catalyst (a carboxylic acid, acetic, oxalic acid or 2,3-PDCA) were introduced into the reaction mixture in the form of stock solutions in acetonitrile or water. A substrate was then added and the reaction started when hydrogen peroxide was added in one portion. Samples of the reaction solutions were usually analyzed by GC (instrument 'HP 5890 Serie-II'; fused silica capillary columns Hewlett–Packard; the stationary phase was polyethylene glycol: INNOWAX with parameters 25 m×0.2 mm×0.4 μm; carrier gas was N₂ with column pressure of 15 psi) twice, before and after addition of an excess of solid triphenylphosphine.^{6c,g,8}

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2007.12.033.

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