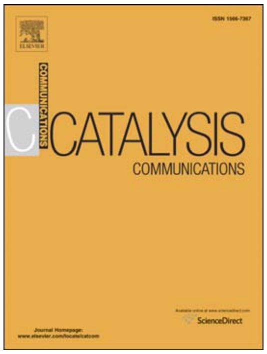

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*Catalysis Communications*

# Mild oxidative alkane functionalization with peroxides in the presence of ferrocene

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ABSTRACT

Ferrocene in an unexpected *emploi*: alkanes can be efficiently oxygenated by $H_2O_2$ in the presence of catalytic amounts of this well-known organometallic compound in combination with pyrazine-2-carboxylic acid or 2,2'-bipyridine. Saturated hydrocarbons, RH, are also transformed into carboxylic acids, RCOOH, when reacted with the ferrocene/CO/$S_2O_8^{2-}$/$H_2O$ system in acetonitrile solution.

## 1. Introduction

Soluble iron compounds are known to catalyze various processes (see reviews [1–11]) including oxidation of C–H compounds with peroxides (see selected papers [11–23]). However, organometallic complexes are very rarely used as (pre)catalysts in oxidations of aromatic and saturated hydrocarbons [24–30]. In particular, it is surprising that ferrocene has never been applied in oxidation catalysis in spite of being one of the most common organometallic compounds.

In the present work we have discovered, for the first time, that catalytic amounts of ferrocene (compound **1**) very efficiently induce several types of oxidative transformations of alkanes, namely (i) the oxidation by $H_2O_2$ or *tert*-butyl hydroperoxide and (ii) the hydrocarboxylation with the $CO/S_2O_8^{2-}/H_2O$ system.

## 2. Results and discussion

The oxidation of gaseous (Tables 1 and 2) and liquid alkanes to the corresponding alkyl hydroperoxides by $H_2O_2$ in the presence of catalytic amounts of ferrocene proceeds in MeCN at 50 ºC. An obligatory component of the catalytic system is pyrazine-2-carboxylic acid (PCA). In the cyclohexane oxidation the yield and turnover number (TON) after 1.5 h (Fig. 1) attained 32% and 1200, respectively. In the ethane oxidation TON reached 970. Maximum yield (58% based on the alkane) was obtained for the *n*-butane oxidation after 4 h (Table 1). These values can be considered as very high taking into account the known inertness of alkanes.

Table. 1 here

Table 2 here

Fig. 1 here

Parameters of regio- and bond selectivity (1:7:7:6 for *n*-heptane, 1:10:33 for methylcyclohexane) indicate that the reaction occurs with the participation of hydroxyl radicals. In accordance with this assumption, the oxidation of *cis*- and *trans*-isomers of 1,2-dimethylcyclohexane is not stereospecific

(Appendix A. Supplementary data, Table S1). In the alkane oxidation, samples of the reaction solutions were analyzed by GC by applying a simple method developed earlier by some of us [8,27,28] which uses $PPh_3$ (see Experimental). Fig. 1 and Tables 1 and 2 demonstrate that the ferrocene-catalyzed oxidation of alkanes, RH, affords predominantly the alkyl hydroperoxides, ROOH, whereas the ketones and alcohols are formed in lower concentrations.

The rate dependence of cyclohexane oxygenation in the presence of the ferrocene/PCA combination is first-order in hydrogen peroxide and second-order in the initial ferrocene (Fig. 2). The dependence of the initial oxidation rate $W_0$ is second-order in PCA at its low ($< 2 \times 10^{-3}$ M) concentrations. This dependence has maximum (Fig. 3), thus suggesting the possible formation of adducts with PCA. The mode of dependence of the initial cyclohexane oxidation rate on the initial cyclohexane concentration ($W_0$ is approaching to a plateau at high concentrations of cyclohexane, see Fig. 4) indicates that hydroxyl radicals as oxidizing species competitively interact both with cyclohexane (CyH) and acetonitrile [13, 23]. Indeed, it follows from Fig. 4 that the ratio of constants $k_{\mathrm{MeCN}}$ and $k_{\mathrm{CyH}}$ for the interaction of oxidizing species with MeCN and CyH, respectively, is equal to $k_{\mathrm{MeCN}}[\mathrm{MeCN}]/k_{\mathrm{CyH}} = 0.011$ M which is the typical for hydroxyl radicals value [13, 23].

The simplest kinetic scheme of the alkane oxygenation which is in agreement with obtained in our work kinetic data (see Figs. 2–4) is shown below. In the first stage ferrocene is oxidized to ferricenium cation $(FeCp_2)^+$ which in turn is transformed into species ***Fe***, where ***Fe*** 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 (see Fig. S1).

$$\mathrm{FeCp_2} + \mathrm{H_2O_2} \xrightarrow{\mathrm{H^+}} (\mathrm{FeCp_2})^+$$

$$(\mathrm{FeCp_2})^+ \rightarrow \boldsymbol{Fe}$$

Two reactions written above are the fast stages of the generation from $FeCp_2$ and $H_2O_2$ the main species active in the catalytic process. Fragment ***Fe*** produced in these two consecutive reactions interacts with a PCA molecule to form complex ***Fe***(PCA):

$$\boldsymbol{Fe} + \mathrm{PCA} \rightleftharpoons \boldsymbol{Fe}(\mathrm{PCA}) \qquad (K_1)$$

Here (PCA) is a PCA fragment (possibly pyrazinecarboxylate). The formed complex can react with the second PCA molecule giving in this case an adduct containing two PCA fragments per one Fe ion:

$$\boldsymbol{Fe}(\mathrm{PCA}) + \mathrm{PCA} \rightleftharpoons \boldsymbol{Fe}(\mathrm{PCA})_2 \qquad (K_2)$$

Two adducts ***Fe***(PCA) can dimerize to afford the *dinuclear* complex $\boldsymbol{Fe}_2(\mathrm{PCA})_2$:

$$\boldsymbol{Fe}(\mathrm{PCA}) + \boldsymbol{Fe}(\mathrm{PCA}) \rightleftharpoons \boldsymbol{Fe}_2(\mathrm{PCA})_2 \qquad (K_3)$$

Dinuclear iron complexes are known to take part in alkane oxygenations with hydrogen peroxide [12,13]. We assume that complex $\boldsymbol{Fe}_2(\mathrm{PCA})_2$ is a catalytically active species which produces hydroxyl radicals from $H_2O_2$:

$$\boldsymbol{Fe}_2(\mathrm{PCA})_2 + H_2O_2 \rightarrow \mathrm{HO}\bullet \qquad (k_4)$$

Hydroxyl radicals react in parallel routes with solvent (acetonitrile) and substrate (cyclohexane, RH):

$$\mathrm{HO}\bullet + \mathrm{MeCN} \rightarrow \mathrm{products} \qquad (k_5)$$

$$\text{HO}\bullet + \text{RH} \rightarrow \ldots \rightarrow \text{ROOH} \qquad (k_6)$$

The last reaction is the rate limiting step in the sequence of alkane transformations into cyclohexyl hydroperoxide. Assuming that concentration of HO• is steady-state and concentrations of iron all complexes are in quasi-equilibrium and taking into account conditions [***Fe***(PCA)] << $[\text{FeCp}_2]_0$ and $[\boldsymbol{Fe}_2(\text{PCA})_2]$ << $[\text{FeCp}_2]_0$ (that is $K_1$ and $K_2$ are low values) we come to the equation for the initial reaction rate:

$$W_0 = \frac{k_4[\boldsymbol{Fe}_2(\text{PCA})_2][\text{H}_2\text{O}_2]_0}{1 + k_5[\text{MeCN}]/k_6[\text{RH}]_0}$$

where $[\boldsymbol{Fe}_2(\text{PCA})_2] = K_3[\boldsymbol{Fe}(\text{PCA})]^2$

and $[\boldsymbol{Fe}(\text{PCA})] = \dfrac{K_1[\text{FeCp}_2]_0[\text{PCA}]_0}{1 + K_1K_2[\text{PCA}]_0^2}$

We can rewrite the equation for the initial reaction rate in the following form:

$$W_0 = \frac{\alpha[\text{PCA}]_0^2}{(1 + \beta[\text{PCA}]_0^2)^2}$$

here $\alpha = \dfrac{k_4[\text{H}_2\text{O}_2]_0(K_1[\text{FeCp}_2]_0)^2}{1 + k_5[\text{MeCN}]/k_6[\text{RH}]_0}$

and $\beta = K_1K_2$

For conditions of our experiments values $\alpha = 30\ M^{-1}\ s^{-1}$ and $\beta = 1.1 \times 10^5\ M^{-2}$. Using these values of parameters $\alpha$ and $\beta$ the initial reaction rates (presented by a dotted curve) have been calculated at different concentrations of PCA under conditions described in the caption to Fig. 3. It can be seen that the simulated curve coincides closely with the experimental curve. This testifies that our kinetic scheme adequately reflects the real reaction.

*tert*-Butyl hydroperoxide (0.58 M; 70% aqueous) oxidizes cyclohexane (0.92 M) in MeCN at 50 ºC in the presence of ferrocene ($1 \times 10^{-3}$ M) and PCA ($25 \times 10^{-3}$ M) affording (after reduction with $PPh_3$) cyclohexanol (0.02 M) and cyclohexanone (0.001 M) after 4.5 h.

It is noteworthy that pyridine-2,3-dicarboxylic acid is substantially less efficient whereas picolinic acid is almost inactive as co-catalysts in the oxidation induced by ferrocene. In the presence of 2,2'-bipyridine ($3 \times 10^{-3}$ M) instead of PCA and ferrocene ($5 \times 10^{-4}$ M) the oxidation of cyclohexane (0.37 M) with $H_2O_2$ (1.2 M) occurs with a long induction period affording the oxygenates (0.028 M) after 200 min.

We have also found the first example of alkane hydrocarboxylation with the $CO/S_2O_8^{2-}/H_2O$ system promoted by an iron complex, i.e., ferrocene. In contrast to the alkane oxidation, this transformation does not require the presence of PCA. Thus, the reaction of an alkane (RH) with CO and $H_2O$ in the presence of $K_2S_2O_8$ in neutral $H_2O$–$CH_3CN$ medium at 60 ºC affords the corresponding carboxylic acid (RCOOH). Linear alkanes (propane, *n*-butane, *n*-pentane, *n*-hexane and *n*-heptane) containing primary and secondary carbon atoms lead to the formation of two to four isomeric acids (Table 3, Fig. S2). The carboxylation reactions at secondary carbon atoms give branched acids which are formed in higher concentrations than linear acids. This is reflected by the C(1) : C(2) : C(3) : C(*n*) regioselectivity parameters (normalized for the relative number of hydrogen atoms) of 1 : 15: 14 (for *n*-$C_5H_{12}$), 1 : 15: 15 (for *n*-$C_6H_{14}$) and 1 : 18 : 18 : 18 (for *n*-$C_7H_{16}$). Only one carboxylic acid product is detected in the hydrocarboxylation of alkanes bearing a single type of carbon atom, e.g., ethane and cyclohexane (Table 3). In the latter case, a small amount of cyclohexanone and cyclohexanol (total yield of 1.1% after reduction of the reaction solution with $PPh_3$) is also obtained due to the partial oxidation of alkane. In the hydrocarboxylation reactions promoted by ferrocene, the maximum total yield of carboxylic acid products attains 60% (based on alkane) for propane, followed by the 21% yield for *n*-butane. Other tested alkanes result in inferior yields of carboxylic acids, namely 18.3% (for cyclohexane), 15% (for ethane), 12.6% (for *n*-pentane), 9.2% (for *n*-heptane) and 8.3% (for *n*-hexane). Taking into consideration the previous background [31–35] and the obtained herein experimental data (i.e., selectivity parameters typical for free-radical transformations with the participation of a sulfate radical derived from $K_2S_2O_8$), the present hydrocarboxylation reactions are believed to proceed *via* a free-radical mechanism.

Table 3 here

## 3. Conclusions

We have discovered that alkanes can be easily oxidized with $H_2O_2$ or *tert*-BuOOH under mild homogeneous conditions to the corresponding alkyl hydroperoxides in the presence of catalytic amounts of ferrocene and pyrazine-2-carboxylic acid (PCA). Ferrocene has been also found to be a promoter of the alkane hydrocarboxylation with the $CO/S_2O_8^{2-}/H_2O$ system in aqueous acetonitrile. This work opens new horizons in applications of organometallic compounds in oxidation catalysis.

## 4. Experimental

Ferrocene and co-catalyst were used in the form of stock solutions in MeCN. Aliquots of these solutions were added to the reaction mixtures in alkane oxidations. The reactions of alkanes with $H_2O_2$ (50% aqueous) were typically carried out in air in thermostated (50 ºC) Pyrex cylindrical vessels with vigorous stirring (**CAUTION**: the combination of air or molecular oxygen and $H_2O_2$ with organic compounds at elevated temperatures may be explosive!). The reactions were stopped by cooling, and typically analyzed twice, i.e., before and after the addition of an excess of solid $PPh_3$. This method was developed previously by some of us [8,27,28] for the analysis of reaction mixtures obtained from various alkane oxidations. In the case of the formation of the corresponding alkyl hydroperoxides as the main products, if an excess of solid $PPh_3$ is added to a sample of the reaction solution, ca. 10 min before 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. A Fisons Instruments GC 8000 series gas chromatograph with a capillary column 30 m × 0.22 mm × 25 μm, BP20 (SGE) (helium was the carrier gas; the internal standard was nitromethane) was used.

The oxidations of gaseous alkanes with $H_2O_2$ were carried out in a 13 mL stainless steel autoclave, equipped with a Teflon-coated magnetic stirring bar. In a typical experiment, after additions of all liquid reagents in the form of stock solutions in acetonitrile, the autoclave was closed and pressurized with gaseous alkane (typically 20.0, 6.0 or 0.7 atm of $CH_4$ and $C_2H_6$, $C_3H_8$ or $n$-$C_4H_{10}$, respectively). The reaction mixture was stirred for 4 h at 50 °C using a magnetic stirrer and an oil bath, whereupon it was cooled in an ice bath, degassed, opened and transferred to a flask for GC analysis.

The hydrocarboxylation experiments were performed following the previously developed protocol [31–35]. The reaction mixtures were placed into a 13.0-mL stainless steel autoclave, equipped with a Teflon-coated magnetic stirring bar. Then the autoclave was closed and flushed with CO three times for removing the air and finally pressurized with CO (**CAUTION**: Due to the toxicity of CO, the heating oven should be located in a well-ventilated hood!) The reaction mixture was stirred using a magnetic stirrer and an oil bath, whereupon it was cooled in an ice bath, degassed, opened and the contents transferred to a flask. Diethyl ether and cycloheptanone (GC internal standard) were added. The obtained mixture was vigorously stirred for 10 min, and the organic layer was analyzed typically by GC [a Fisons Instruments GC 8000 series gas chromatograph equipped with 30 m × 0.22 mm × 25 μm, BP20 (SGE) capillary column (helium was the carrier gas) and the Jasco-Borwin v.1.50 software] (see Fig. S2).

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at http://xxxxxxxx

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## *Tables*

**Table 1.** Oxygenation of light alkanes by the **1**/PCA/$H_2O_2$ system [a]

| Alkane (mmol) | Products | before $PPh_3$ (M) | after $PPh_3$ (M) | Total yield (%) | Total TON |
|---|---|---|---|---|---|
| *n*-Butane | MeCOEt | 0.015 | 0.0097 | 58 | 253 |
| (0.22) | EtCH(OH)Me | 0.0034 | 0.0064 | | |
| | $EtCH_2CHO$ | 0.0026 | 0.0015 | | |
| | $EtCH_2CH_2OH$ | 0.0009 | 0.0019 | | |
| | $EtCH_2COOH$ | 0.0005 | 0.0005 | | |
| Propane | MeCOMe | 0.0097 | 0.0029 | 7 | 267 |
| (1.9) | MeCH(OH)Me | 0.0022 | 0.0145 | | |
| | $MeCH_2CHO$ | 0.0046 | 0.000 | | |
| | $MeCH_2CH_2OH$ | 0.001 | 0.0081 | | |
| Ethane | MeCHO | 0.0585 | 0.0169 | 8 | 970 |
| (6.5) | EtOH | 0.0273 | 0.065 | | |
| | MeCOOH | 0.014 | 0.015 | | |

[a] Conditions. Concentrations: ferrocene, $1 \times 10^{-4}$ M; $H_2O_2$, 1.28 M; PCA, $25 \times 10^{-4}$ M. Solvent was acetonitrile, 50 °C, 4 h. Total volume of the reaction solution was 5 mL. Volume of the autoclave was 13 mL. Concentrations of the products were measured before and after reduction with $PPh_3$. Yield is based on the alkane.

**Table 2.** Oxygenation of ethane by the **1**/PCA/$H_2O_2$ system [a]

| Time (h) | Products | before $PPh_3$ (M) | after $PPh_3$ (M) |
|---|---|---|---|
| 1 | MeCHO | 0.0012 | 0.000 |
| | EtOH | 0.000 | 0.0015 |
| | MeCOOH | 0.0024 | 0.002 |
| 2 | MeCHO | 0.018 | 0.002 |
| | EtOH | 0.0046 | 0.015 |
| | MeCOOH | 0.0016 | 0.002 |
| 4 | MeCHO | 0.0585 | 0.0169 |
| | EtOH | 0.0273 | 0.065 |
| | MeCOOH | 0.014 | 0.015 |
| 20 | MeCHO | 0.067 | 0.053 |
| | EtOH | 0.0146 | 0.0246 |
| | MeCOOH | 0.008 | 0.009 |
| 46 | MeCHO | 0.022 | 0.021 |
| | EtOH | 0.012 | 0.009 |
| | MeCOOH | 0.055 | 0.046 |

[a] Conditions. Concentrations: ferrocene, $1 \times 10^{-4}$ M; $H_2O_2$, 1.28 M; PCA, $25 \times 10^{-4}$ M. Solvent was acetonitrile, 50 °C. Total volume of the reaction solution was 5 mL. Volume of the autoclave was 13 mL. In the absence of ethane (blank experiment) concentration of MeCOOH (formed from MeCN) was 0.002 M after 4 h.

**Table 3.** Hydrocarboxylation of alkanes by the **1**/PCA/CO/$K_2S_2O_8$ system [a]

| Alkane [b] (atm; mmol) | CO (atm) | Products | Yield (%) | Total yield (%) |
|---|---|---|---|---|
| Ethane | | | | |
| 10 | 20 | EtCOOH | 9 | 9 |
| 1 [c] | 10 | EtCOOH | 15 | 15 |
| Propane | | | | |
| 6 | 20 | $Me_2CHCOOH$ | 17 | 19 |
| | | $Me(CH_2)_2COOH$ | 2 | |
| 1 [c] | 10 | $Me_2CHCOOH$ | 51 | 60 |
| | | $Me(CH_2)_2COOH$ | 9 | |
| *n*-Butane | | | | |
| 0.75 [c] | 10 | EtCH(Me)COOH | 19 | 21 |
| | | $Me(CH_2)_3COOH$ | 2 | |
| *n*-Pentane [d] | | | | |
| 1.0 | 20 | $Me(CH_2)_4COOH$ | 0.8 | 12.6 |
| | | $MeCH(COOH)(CH_2)_2Me$ | 8.2 | |
| | | EtCH(COOH)Et | 3.6 | |
| *n*-Hexane [d] | | | | |
| 1.0 | 20 | $Me(CH_2)_5COOH$ | 0.4 | 8.3 |
| | | $MeCH(COOH)(CH_2)_3Me$ | 4.0 | |
| | | $EtCH(COOH)(CH_2)_2Me$ | 3.9 | |
| *n*-Heptane [d] | | | | |
| 1.0 | 20 | $Me(CH_2)_6COOH$ | 0.3 | 9.2 |
| | | $MeCH(COOH)(CH_2)_4Me$ | 3.6 | |
| | | $EtCH(COOH)(CH_2)_3Me$ | 3.5 | |
| | | $Me(CH_2)_2CH(COOH)(CH_2)_2Me$ | 1.8 | |
| Cyclohexane [e] | | | | |
| 1.0 | 20 | *cyclo*-$C_6H_{11}COOH$ | 18.3 | 19.4 |
| | | *cyclo*-$C_6H_{11}OH$ | 0.8 | |
| | | *cyclo*-$C_6H_{10}O$ | 0.3 | |

[a] Conditions. Amounts: ferrocene, $4 \times 10^{-3}$ mmol; $K_2S_2O_8$, 1.5 mmol; Solvent was MeCN, 4 mL; $H_2O$, 2 mL; 60 °C, 4 h. Volume of the autoclave was 13 mL. Yield is based on the alkane. [b] Amounts as pressure for gaseous ethane, propane and *n*-butane and as mmol for other alkanes are given. [c] $K_2S_2O_8$, 1.0 mmol. [d] Regioselectivity parameters C(1):C(2):C(3):C(4) for pentane, hexane and heptane are 1:15:14; 1:15:15 and 1:18:18:18, respectively. [e] At 50 °C; $CH_3CN$, 3 mL; $H_2O$, 3 mL.

## *Figures*

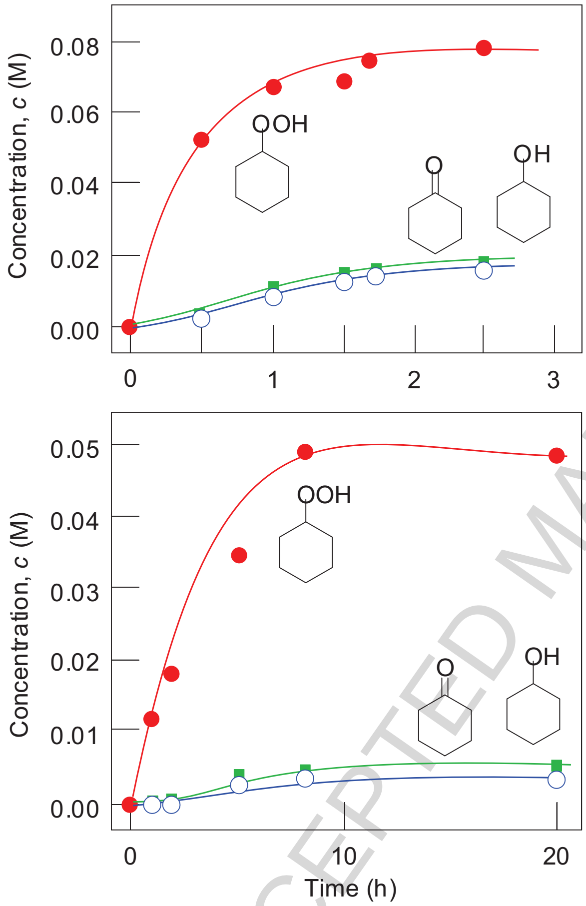


**Fig. 1**. Oxidation of cyclohexane (0.37 M) with $H_2O_2$ (0.64 M; 50% aqueous) in the presence of ferrocene ($1 \times 10^{-4}$ M) and PCA ($25 \times 10^{-4}$ M) in MeCN at 50 ºC (top) and 20 ºC (bottom). Concentrations of the three products (cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone) were calculated from the concentrations of cyclohexanol and cyclohexanone measured before and after reduction with $PPh_3$ (for this method, see [8,27,28]).

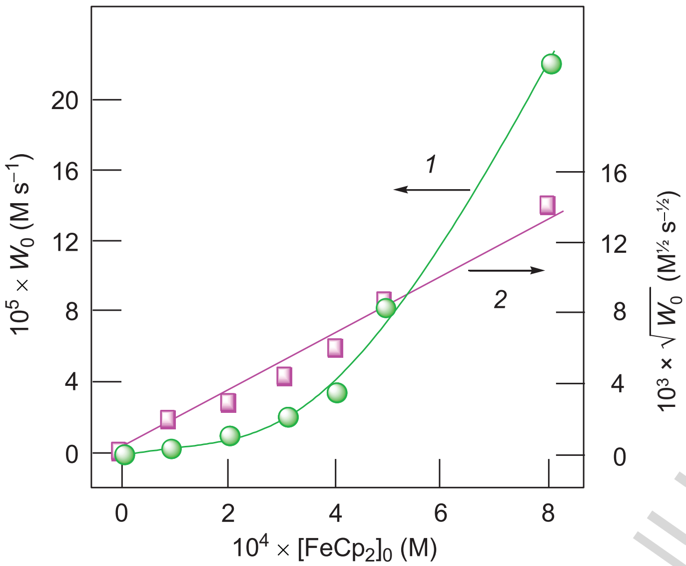


**Fig. 2.** Dependence of the initial rate $W_0$ of oxygenates accumulation in the cyclohexane oxidation with $H_2O_2$ in the presence of ferrocene in MeCN on the initial concentration of ferrocene (curve *1*). Conditions: $[PCA]_0 = 3 \times 10^{-3}$ M, $[H_2O_2]_0 = 0.32$ M, $[\text{cyclohexane}]_0 = 0.37$ M, 50 °C. Curve *2*: linearization of curve *1* in coordinates $[FeCp_2]_0$–$W_0^{1/2}$.

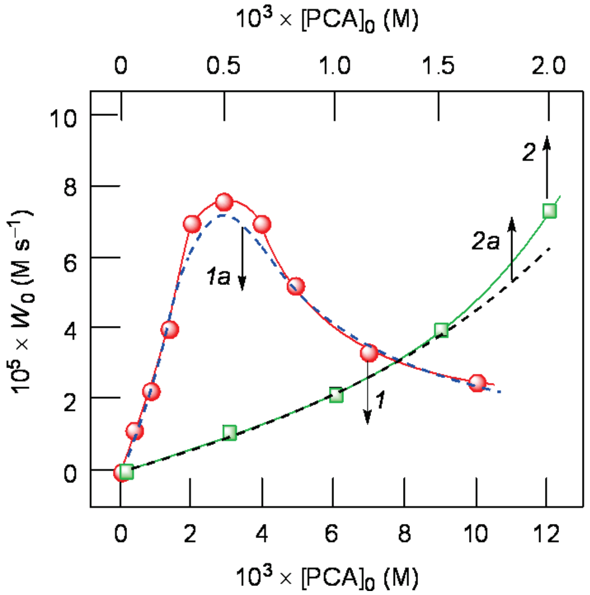


**Fig. 3** Dependence of the initial rate $W_0$ of oxygenates accumulation in the cyclohexane oxidation with $H_2O_2$ in the presence of ferrocene in MeCN on the initial concentration of PCA in the intervals 0–10 × $10^{-3}$ M (curves *1* and *1a*) and 0–2 × $10^{-3}$ M (curves *2* and *2a*). Conditions: $[FeCp_2]_0 = 5.0 \times 10^{-4}$ M, $[H_2O_2]_0 = 0.32$ M, $[\text{cyclohexane}]_0 = 0.37$ M, 50 °C. Dotted curves *1a* and *2a* present the simulated dependence.

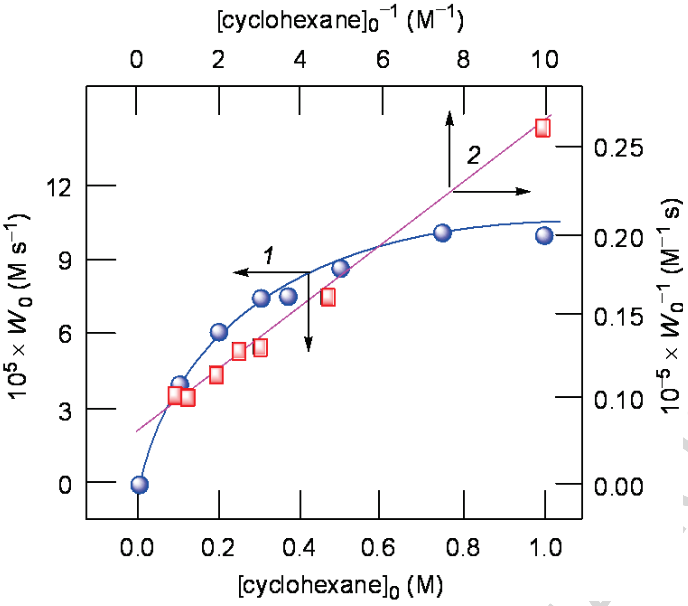


**Fig. 4.** Curve *1*: dependence of the initial rate $W_0$ of oxygenates accumulation in the cyclohexane oxidation with $H_2O_2$ in the presence of ferrocene in MeCN on the initial concentration of cyclohexane. Conditions: $[FeCp_2]_0 = 5.0 \times 10^{-4}$ M, $[PCA]_0 = 3.0 \times 10^{-3}$ M, $[H_2O_2]_0 = 0.32$ M, 50 °C. Straight line *2*: linearization of the dependence presented by curve *1* in coordinates $(1/W_0)$–$(1/[PCA]_0)$.

**Captions to Figures:**

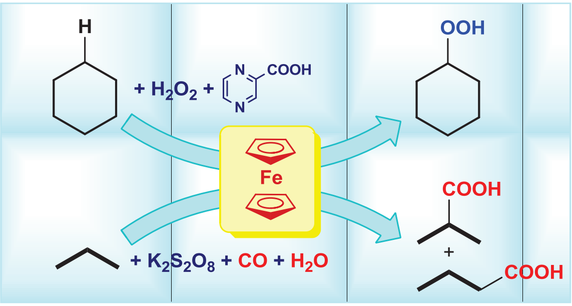
**Fig. 1**. Oxidation of cyclohexane (0.37 M) with $H_2O_2$ (0.64 M; 50% aqueous) in the presence of ferrocene ($1 \times 10^{-4}$ M) and PCA ($25 \times 10^{-4}$ M) in MeCN at 50 ºC (top) and 20 ºC (bottom). Concentrations of the three products (cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone) were calculated from the concentrations of cyclohexanol and cyclohexanone measured before and after reduction with $PPh_3$ (for this method, see [8,27,28]).

**Fig. 2.** Dependence of the initial rate $W_0$ of oxygenates accumulation in the cyclohexane oxidation with $H_2O_2$ in the presence of ferrocene in MeCN on the initial concentration of ferrocene (curve *1*). Conditions: $[PCA]_0 = 3 \times 10^{-3}$ M, $[H_2O_2]_0 = 0.32$ M, $[\text{cyclohexane}]_0 = 0.37$ M, 50 °C. Curve *2*: linearization of curve *1* in coordinates $[FeCp_2]_0$–$W_0^{1/2}$.

**Fig. 3** Dependence of the initial rate $W_0$ of oxygenates accumulation in the cyclohexane oxidation with $H_2O_2$ in the presence of ferrocene in MeCN on the initial concentration of PCA (in the intervals $0–10 \times 10^{-3}$ M and $0–2 \times 10^{-3}$ M). Conditions: $[FeCp_2]_0 = 5.0 \times 10^{-4}$ M, $[H_2O_2]_0 = 0.32$ M, $[\text{cyclohexane}]_0 = 0.37$ M, 50 °C. Dotted curves present the simulated dependence.

**Fig. 4.** Curve *1*: dependence of the initial rate $W_0$ of oxygenates accumulation in the cyclohexane oxidation with $H_2O_2$ in the presence of ferrocene in MeCN on the initial concentration of cyclohexane. Conditions: $[FeCp_2]_0 = 5.0 \times 10^{-4}$ M, $[PCA]_0 = 3.0 \times 10^{-3}$ M, $[H_2O_2]_0 = 0.32$ M, 50 °C. Straight line *2*: linearization of the dependence presented by curve *1* in coordinates $(1/W_0)$–$(1/[PCA]_0)$.

**Graphical Abstract:**



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*Catalysis Communications*

# Mild oxidative alkane functionalization with peroxides in the presence of ferrocene

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## Highlights

- ▶ Combination $H_2O_2$/ferrocene/pyrazinic acid oxygenates alkanes.
- ▶ Turnover numbers were up to 1200.
- ▶ The ferrocene/CO/$S_2O_8^{2-}$/$H_2O$ system transforms RH into RCOOH.
- ▶ The oxidation proceeds with the participation of free radicals.