

# Oxidations by the system “hydrogen peroxide– $[\text{Mn}_2\text{L}_2\text{O}_3][\text{PF}_6]_2$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane)–oxalic acid”. Part 6. Oxidation of methane and other alkanes and olefins in water <sup>☆</sup>

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## Abstract

Oxidation of alkanes with hydrogen peroxide in water solution at 10–50 °C is efficiently catalyzed by the cationic dinuclear manganese (IV) derivative  $[\text{Mn}_2\text{L}_2\text{O}_3]^{2+}$  (**1**, with L = 1,4,7-trimethyl-1,4,7-triazacyclononane, TMTACN) in the form of the hexafluorophosphate salt ( $[\text{1}][\text{PF}_6]_2$ ) if oxalic acid is present as a co-catalyst. Methane gives methanol and formaldehyde (turnover numbers, TONs, were 7 and 2, respectively, after reduction of the reaction mixture with ascorbic acid) whereas cyclohexane was oxidized with TONs up to 160 affording cyclohexyl hydroperoxide, cyclohexanone and cyclohexanol (the ketone was the main product, although at room temperature almost pure alkyl hydroperoxide was formed). In contrast to the oxidation in acetonitrile, the reaction with linear *n*-alkanes in water exhibits an unusual distribution of oxygenates. For example, in the oxidation of *n*-heptane the normalized reactivity of the methylene group in position 4 of the chain is 3–7 times higher than that of the CH<sub>2</sub> group in position 2. Dec-1-ene is epoxidized by hydrogen peroxide in water (a biphasic system) catalyzed by  $[\text{1}][\text{PF}_6]_2$  and oxalic acid in the presence of a small amount of acetonitrile with TONs up to 1000 (no epoxidation has been detected in the absence of MeCN).

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## 1. Introduction

Selective oxidation of saturated hydrocarbons (which may be called “noble gases of organic chemistry” due to their very high inertness) under mild conditions is a chal-

lenging goal of contemporary metal-complex catalysis [1–3]. It should be noted that use of metals and metal oxides as heterogeneous catalysts requires usually relatively high (>200 °C) temperature and proceeds with low regio- and bond-selectivity.

Earlier, we have found a very efficient unique system for oxidations of various organic compounds at room (and even lower) temperature [4–15]. This system (Fig. 1) consists of the catalyst – cationic dinuclear manganese (IV) derivative  $[\text{Mn}_2\text{L}_2\text{O}_3]^{2+}$  (**1**, with L = 1,4,7-trimethyl-1,4,7-triazacyclononane, TMTACN) in the form of the hexafluorophosphate salt ( $[\text{1}][\text{PF}_6]_2$ ), obligatory carboxylic acid (co-catalyst, present in a low concentration) and hydrogen peroxide (oxidant).

<sup>☆</sup> For parts 1–5, see [5–9], respectively. See also our relevant publications [10–15]. This work was reported at the 14th International Symposium on Homogeneous Catalysis, Munich, 2004, as well as published on the Chemistry Preprint Server (<http://preprint.chemweb.com/orgchem/0402003> and <http://preprint.chemweb.com/orgchem/0405002>).

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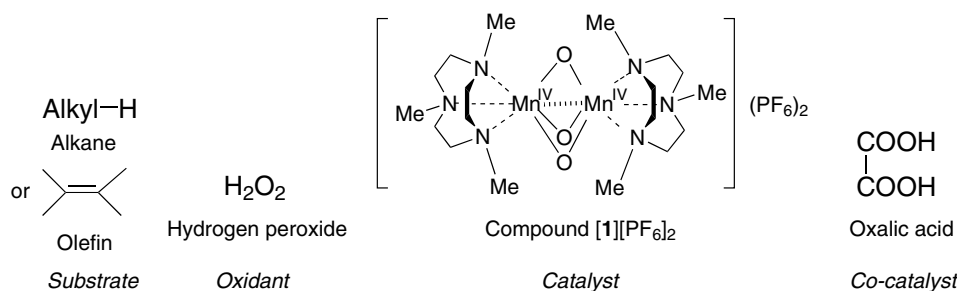


Fig. 1. Oxidizing system described in the present article.

Compound  $[\mathbf{1}][\text{PF}_6]_2$  has been synthesized by Wiegardt and co-workers [16]. The X-ray analysis showed that the complex contains an unprecedented short  $\text{Mn} \cdots \text{Mn}$  distance of 2.296(2) Å which “seems to indicate a direct bonding interaction between the two  $\text{Mn}^{\text{IV}}$  centers” [16]. Hage et al. [17] used cation **1** as a catalyst in  $\text{H}_2\text{O}_2$  oxidations of certain substrates. Later many authors applied this catalyst for the oxidations of olefins, alcohols and some other organic compounds [18–28]. It is noteworthy that cationic complex **1** is absolutely inefficient in the  $\text{H}_2\text{O}_2$  oxidation of saturated hydrocarbons if no carboxylic acid is present in the solution.

Complexes of unknown structure have been prepared in situ by mixing a  $\text{Mn}(\text{II})$  salt and the TMTACN and used in the  $\text{H}_2\text{O}_2$  oxidations of olefins, alcohols and even alkylaromatics in the presence of certain (e.g., oxalate and ascorbate) buffers [29–41]. It is necessary to emphasize that such in situ prepared systems cannot oxidize saturated hydrocarbons and their nature is very probably different from that of our system consisting of compound  $[\mathbf{1}][\text{PF}_6]_2$  and a carboxylic acid.

In the present article, we report first results obtained in the study of a new version of previously described system. We applied the “ $[\mathbf{1}][\text{PF}_6]_2$ –oxalic acid– $\text{H}_2\text{O}_2$ ” system to the oxidation of some alkanes and olefins in water solution (both in biphasic systems and in “true” solutions). Oxalic acid has been recently shown by us to be the most efficient co-catalyst in the olefin epoxidations in acetonitrile [9,15]. It is well-known that various metal complexes are widely used as catalysts in olefin epoxidation with hydrogen peroxide [42–48] including the reactions in biphasic systems which contain water [49–55] (see also relevant publications [56,57]). Water is attractive solvent because it is a cheap and ecologically friendly liquid.

## 2. Experimental

Aqueous 35% hydrogen peroxide solution (solution in water, “Fluka”, stabilized; measured by titration concentration was  $11.5 \text{ mol dm}^{-3}$ ) was used as received. The

experiments on higher alkane oxidations were carried out in water in thermostated Pyrex cylindrical vessels (total volume 10 mL) with vigorous stirring. The total volume of the reaction mixture usually consisting of two phases was about 2 mL. In a typical experiment, initially, a portion of the aqueous solution of  $\text{H}_2\text{O}_2$  was added to the mixture of a higher alkane and a solution of the catalyst  $[\mathbf{1}][\text{PF}_6]_2$  and oxalic acid water. After certain period, the reaction mixture was extracted with ether and analyzed by GC (LKhM-80-6, columns 2 m with 5% Carbowax 1500 on 0.25–0.315 mm Inerton AW-HMDS; carrier gas argon) twice: before and after the addition of triphenylphosphine to the organic extract. Usually samples were analyzed twice, i.e. before and after the addition of the excess of solid  $\text{PPh}_3$ . This very simple method (solid triphenylphosphine is added to the samples 10–15 min before the GC analysis and the chromatogram obtained is compared with the chromatogram prepared for the sample untreated with  $\text{PPh}_3$ ) was proposed and described by us earlier [2–10,13,14,58–65].

Since alkyl hydroperoxides, which are transformed in the GC injector into a mixture of the corresponding ketone and alcohol, are quantitatively reduced with  $\text{PPh}_3$  to give the corresponding alcohol, this method allows to calculate the real concentrations not only of the hydroperoxide but of the alcohols and ketones present in the solution at a given moment. Authentic samples of all oxygenated products were used to attribute the peaks in chromatograms (comparison of retention times was carried out for different regimes of GC-analysis).

The oxidation of methane was carried out in a glass inlet tube put in a stainless steel autoclave with intensive stirring (volume of the reaction solution was 2 mL and total volume of autoclave was 5 mL). The autoclave was charged with air (under atmospheric pressure) and then, consecutively, with the solution of  $[\mathbf{1}][\text{PF}_6]_2$ , oxalic acid and  $\text{H}_2\text{O}_2$  in water, and finally with methane. The reaction was quenched by addition of solid ascorbic acid to decompose an excess of hydrogen peroxide and to reduce formed methyl hydroperoxide to methanol. The solution was analyzed by GC (LKhM-80-6, columns 2 m with 5% Carbowax 1500 on 0.25–0.315 mm Inerton

AW-HMDS; carrier gas argon) to determine the methanol concentration. The formaldehyde concentration was determined by the reaction with the Nash reagent.

The experiments on dec-1-ene epoxidation were carried out in biphasic system at 40 °C in thermostated Pyrex cylindrical vessels (total volume 12 mL) with vigorous stirring. Aqueous 70% hydrogen peroxide solution ("Peróxidos do Brasil") was used as received. In a typical experiment, initially, a portion of the 70% aqueous solution of H<sub>2</sub>O<sub>2</sub> containing catalyst [1][PF<sub>6</sub>]<sub>2</sub> and oxalic acid was stirred vigorously with dec-1-ene. The reaction was quenched by addition of solid MnO<sub>2</sub> to decompose an excess of hydrogen peroxide. The solution was filtered and extracted twice with ether. Concentration of the dec-1-ene epoxide was determined by GC (the 'HP Series 6890' instrument). Oxalic acid was introduced into the reaction solution as a solid and catalyst was used as a stock solution either in water or in acetonitrile (or nitrobenzene).

### 3. Results and discussion

#### 3.1. Oxidation of alkanes including methane

In the course of our detailed study of H<sub>2</sub>O<sub>2</sub> oxidations catalyzed by complex [1][PF<sub>6</sub>]<sub>2</sub> in the presence of a carboxylic acid we decided to explore the possibility to oxidize methane and higher alkanes using water as a reaction medium. We chose oxalic acid as a co-catalyst because we demonstrated previously that this is a reagent of choice for the olefin epoxidation in acetonitrile [9,15]. We have found that stirring a solution of [1][PF<sub>6</sub>]<sub>2</sub> (2 × 10<sup>-7</sup> mol), oxalic acid (1 × 10<sup>-4</sup> mol), hydrogen peroxide (1 × 10<sup>-3</sup> mol), and methane (6 bar) in water at 50 °C during 2 h and then at 20 °C during 10 h gave rise to the formation of formaldehyde (4 × 10<sup>-7</sup> mol) and (after

reduction with ascorbic acid) methanol (1.4 × 10<sup>-6</sup> mol). Thus the turnover number (TON) attained 9.

The oxidation of higher alkanes have been studied in more detail. Vigorous stirring of the emulsion consisting of cyclohexane (0.2 mL) and aqueous solution of complex [1][PF<sub>6</sub>]<sub>2</sub> (1 × 10<sup>-7</sup> mol), oxalic acid (1 × 10<sup>-4</sup> mol) and hydrogen peroxide (1 × 10<sup>-3</sup> mol) at 50 °C during 3 h gave a mixture of the oxygenates (total amount was 1.6 × 10<sup>-5</sup> mol which corresponded to TON = 160). The reaction mixture consisted of cyclohexanone and cyclohexyl hydroperoxide with the 10:1 ratio. When the reaction was carried out at low temperature (11 °C; 30 min), the yield of the products was lower (6 × 10<sup>-7</sup> mol; TON = 6), however in this case cyclohexyl hydroperoxide was obtained as a sole product.

Further, surprisingly, it turned out that the reaction rate did not practically depend on the shaking frequency. Thus the reduction of the number of vibrations per one min from a maximum to the quarter of this maximum value did not reduce the yield of oxygenates.

Another surprising finding has been discovered in the oxidation of linear higher alkanes. The oxidation of *n*-heptane by the system under discussion gave (after the reduction of the ether extract with PPh<sub>3</sub>) a mixture of all possible isomeric alcohols and ketones (aldehyde). Fig. 2 demonstrates selectivity parameters C(2):C(3):C(4) which are normalized (i.e., calculated taking into account the number of hydrogen atoms at each position) relative reactivities of hydrogen atoms at positions 2, 3 and 4 of the hydrocarbon chain, respectively, calculated for both obtained alcohols and ketones (the reactivity of the CH<sub>2</sub> hydrogens at position 2 is accepted to be equal 1.0). It can be clearly seen that hydrogens at position 3

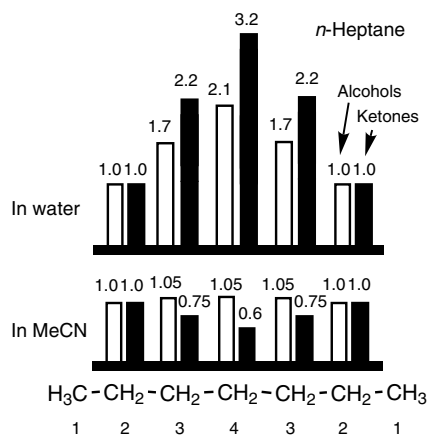


Fig. 2. Selectivity parameters C(2):C(3):C(4) for the oxidation of *n*-heptane by the "[1][PF<sub>6</sub>]<sub>2</sub>-oxalic acid-H<sub>2</sub>O<sub>2</sub>" system in water and acetonitrile.

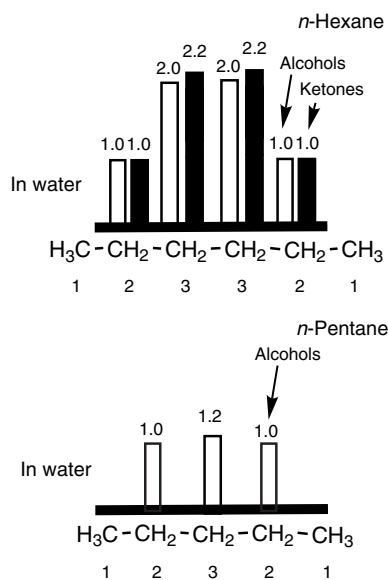


Fig. 3. Selectivity parameters C(2):C(3) for the oxidation of *n*-hexane and *n*-pentane by the "[1][PF<sub>6</sub>]<sub>2</sub>-oxalic acid-H<sub>2</sub>O<sub>2</sub>" system in water.

and especially at position 4 are much more reactive than hydrogen atoms in position 2. Analogous profiles have been obtained for the selectivities in oxidations of *n*-hexane and *n*-pentane, although it can be noted that the shorter the alkane chain (on going from *n*-heptane to *n*-hexane and to *n*-pentane) the less pronounced maximum (Fig. 3) is observed. Such a profile having the pronounced maximum for the central CH<sub>2</sub> groups is in a striking contrast with the corresponding profiles for the reactions in acetonitrile (an example for *n*-heptane is shown in Fig. 2).

It was interesting to compare regio-selectivities for the oxidation of *n*-heptane in water on the one hand and in acetonitrile on the other hand relative to the reactivity of the terminal methyl group (accepted as 1). We followed these parameters (the relative normalized reactivities of the hydrogen atoms at carbon atoms 1, 2, 3, and 4 taking into account the number of hydrogen atoms in each position) only for the isomeric alcohols (Fig. 4). It can be concluded from the data of Fig. 4 that the reaction in water is less selective in respect to the terminal methyl groups. Indeed, in the case of acetonitrile all hydrogens of CH<sub>2</sub> groups are 74–78 times more reactive than the hydrogens of CH<sub>3</sub> groups. In the reaction in water CH<sub>2</sub> group are only 29 times more reactive than terminal hydrogen atoms. It is noteworthy that the oxidation of *n*-heptane in biphasic system containing a small amount of acetonitrile (water/acetonitrile = 40:1) occurred with “usual” selectivity, i.e., the reactivities of CH<sub>2</sub> groups in positions 2, 3 and 4 were approximately equal.

Selectivity parameters (parameter 1°:2°:3° is normalized relative reactivities of hydrogen atoms at primary, secondary and tertiary carbons, respectively) obtained from the oxidations of branched alkanes in water and acetonitrile are comparable though in this cases the reaction in water is less bond-selective (Table 1). It is impor-

Table 1  
Oxidation of branched alkanes with H<sub>2</sub>O<sub>2</sub> catalyzed by [1][PF<sub>6</sub>]<sub>2</sub> and oxalic acid<sup>a</sup>

Entry	Hydrocarbon	Solvent	1°	2°	3°
1	2,2,4-Trimethylpentane	Water	1	2.6	45
2		Acetonitrile	1	8.7	190
3	Methylcyclohexane	Water	1	11	280
4		Acetonitrile	1	28	250

<sup>a</sup> Parameter 1°:2°:3° is normalized relative reactivities of hydrogen atoms at primary, secondary and tertiary carbons, respectively. Parameters were determined for the isomeric alcohols obtained after reduction with PPh<sub>3</sub>.

tant that the stereoselectivity of the reaction (parameter *trans/cis* = [*trans-ol*]/[*cis-ol*], i.e., the ratio of concentrations of *trans-ol* and *cis-ol* formed in the oxidation of *cis*-1,2-dimethylcyclohexane or *trans*-1,2-dimethylcyclohexane) in acetonitrile is higher when oxalic acid is used instead of acetic acid (Table 2). The stereoselectivity is noticeably lower in water when compared with acetonitrile.

In order to get an understanding of this oxidation process we carried out a few additional experiments. We oxidized by the system under discussion homogeneous aqueous solutions of cyclohexane and *n*-heptane. After vigorous shaking a mixture of *n*-heptane and water, aqueous layer was separated (the solubility of *n*-heptane is known: 0.0052 g in 100 mL of water at 15.5 °C), filtered and an aqueous solution of H<sub>2</sub>O<sub>2</sub>, catalyst [1][PF<sub>6</sub>]<sub>2</sub> and oxalic acid was added. After stirring during 0.5 h at 25 °C this solution contained the oxygenates (ca. 30% of isomeric hydroperoxides) with the ratio C(2):C(3):C(4) = 1:4:7 (normalized using concentrations of isomeric ketones). This ratio is close to the parameter found for the oxidation in the biphasic system (see above). In other experiment, we connected two vessels (one of them contained an aqueous solution of [1][PF<sub>6</sub>]<sub>2</sub>, oxalic acid and H<sub>2</sub>O<sub>2</sub>, the second vessel contained only *n*-heptane) with a tube at room temperature. Both solutions were agitated with stirring bars to allow *n*-heptane vapors to penetrate through the tube to the catalyst solution. We found the oxygenates in the catalyst solution and the selectivity was the following: C(2):C(3):C(4) = 1:4:7.

Unlike the oxidation in water catalyzed by [1][PF<sub>6</sub>]<sub>2</sub> and oxalic acid, the oxidations of *n*-heptane in the biphasic system with the reagents which are known to generate hydroxyl radicals gave a different C(2):C(3):C(4) ratio. Thus, the oxidation with the Fe(ClO<sub>4</sub>)<sub>3</sub>-H<sub>2</sub>O<sub>2</sub> system [66] led to a very small amount of isomeric ketones with almost “usual” selectivity C(2):C(3):C(4) = 1:1.5:1.5 (based on the ratio of ketones). The selectivity in the oxidation of *n*-heptane in water by the “vanadate anion-pyrazine-2-carboxylic acid-H<sub>2</sub>O<sub>2</sub>” system [61, 64, 67] was also close to “usual”, C(2):C(3):C(4) = 1:1.8:1.6.

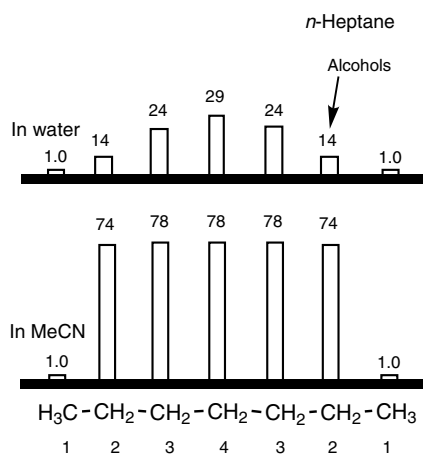


Fig. 4. Selectivity parameters C(1):C(2):C(3):C(4) for the oxidation of *n*-heptane by the “[1][PF<sub>6</sub>]<sub>2</sub>-oxalic acid-H<sub>2</sub>O<sub>2</sub>” system in water and acetonitrile.

Table 2  
Oxidation of isomeric dimethylcyclohexanes (DMCH) with H<sub>2</sub>O<sub>2</sub> catalyzed by [1][PF<sub>6</sub>]<sub>2</sub> and carboxylic acid<sup>a</sup>

Entry	Hydrocarbon	Solvent	Acid	<i>trans/cis</i>
1	<i>cis</i> -1,2-Dimethylcyclohexane	Water	Oxalic	0.7
2		Acetonitrile	Oxalic	0.11
3			Acetic	0.35
4	<i>trans</i> -1,2-Dimethylcyclohexane	Acetonitrile	Oxalic	8
5			Acetic	4
6	<i>cis</i> -1,4-Dimethylcyclohexane	Acetonitrile	Oxalic	0.43
7	<i>trans</i> -1,4-Dimethylcyclohexane	Acetonitrile	Oxalic	2.6

<sup>a</sup> Parameter *trans/cis* = [*trans*-ol]/[*cis*-ol], i.e., the ratio of concentrations of *trans*-ol and *cis*-ol formed in the oxidation of *cis*-DMCH or *trans*-DMCH. Parameters were determined for the isomeric alcohols obtained after reduction with PPh<sub>3</sub>.

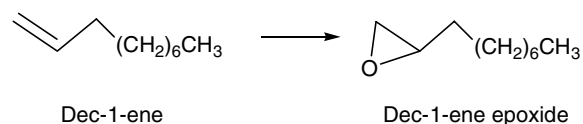
Taking into account all data described above, we can propose the following scheme of the oxidation process which does not include free radicals as intermediates. The interaction of an active Mn<sub>2</sub>-containing species (which is probably a manganyl derivative [8]) with the alkane molecule can proceed either in the interface between two phases (organic and water solutions) or in the aqueous solution (and possibly also in the organic phase: we cannot exclude the capability of an active metal-centered species to penetrate to the organic phase). The reaction in aqueous solution can predominate because we did not found a noticeable dependence of the reaction rate on the shaking intensity and demonstrated that the oxidation in “true” aqueous solution occurs in reality and its regioselectivity is the same as for the case of the biphasic system. We can accept that dissolution of *n*-heptane in water is not a rate-limiting stage of the process.

At the moment, we cannot give a reliable explanation of predominance of alcohols obtained by the substitution at CH<sub>2</sub> groups in the middle of the hydrocarbon chain. One may assume that hydrocarbon chains exist in aqueous solution in the folded conformation and in this case position 4 of *n*-heptane is more accessible for the attack than position 2 (see <http://preprint.chemweb.com/orgchem/0402003>). Alternatively, the found phenomenon could be due to the over-oxidation of formed isomers of alkyl hydroperoxides or/and ketones. The HOO-group in 4-hydroperoxidated *n*-heptane can prevent a further attack at neighboring positions, and as a consequence concentration of this isomer will be higher. Similarly, the 4-ketone can be over-oxidized less easily than the 2-isomer. Indeed, in a special experiment we demonstrated that a competitive oxidation by the system under discussion of a 1:1 mixture of heptan-4-one and heptan-2-one gave rise to a some predominance of heptan-4-one. A special study is required to elucidate the reason for an unusual selectivity in the described oxygenation.

### 3.2. Epoxidation of dec-1-ene

We carried out also the reaction between dec-1-ene (2.225 mL) and hydrogen peroxide (0.075 mL,

$2.175 \times 10^{-3}$  mol; used as 70% aqueous solution) in biphasic system. Catalyst [1][PF<sub>6</sub>]<sub>2</sub> was introduced into the reaction mixture as a stock solution in water ( $7.5 \times 10^{-7}$  mol in 0.05 mL of water) and oxalic acid ( $3.75 \times 10^{-4}$  mol; 0.035 g) was added as a solid. Stirring the biphasic mixture during 5 min at 40 °C followed by quenching with MnO<sub>2</sub> and extraction with ether gave no epoxide. It is interesting that the reaction under the same conditions but in the presence of small amount of acetonitrile (only 0.3 mL) yielded corresponding epoxide with high yield ( $2.8 \times 10^{-4}$  mol; TON = 373).



In further experiments, we used catalyst [1][PF<sub>6</sub>]<sub>2</sub> as a stock solution in acetonitrile ( $7.5 \times 10^{-7}$  mol in 0.3 mL of MeCN) in order to avoid addition of water. Nitrobenzene (0.05 mL) was added as an internal standard for the GC analysis. Other conditions were similar with described above: H<sub>2</sub>O<sub>2</sub> (used as 70% aqueous solution),  $2.175 \times 10^{-3}$  mol (0.075 mL); oxalic acid,  $3.75 \times 10^{-4}$  mol; 0.0346 g; dec-1-ene, 2.1 mL, 25 °C. This oxidation gave after 4 h the epoxide ( $7.19 \times 10^{-4}$  mol, TON = 960) and the diol ( $2.17 \times 10^{-5}$  mol, TON = 30). It is noteworthy that when we used the catalyst as a stock solution in nitrobenzene instead of acetonitrile ( $7.5 \times 10^{-7}$  mol in 0.05 mL of nitrobenzene), that is in the absence of acetonitrile, we obtained neither the epoxide nor the diol. The dependence of the epoxide yield on the amount of added acetonitrile is shown on Fig. 5. The epoxide yield after 5 min does not practically depend on the amount of dec-1-ene used (Fig. 6). The dependence of the epoxide yield on concentration of oxalic acid has a maximum (Table 3).

Discussing a possible role of added acetonitrile which dramatically rises the epoxide yield we can assume that acetonitrile not only simply enhances the solubility of dec-1-ene in aqueous solution but disturbs a compact clew conformation of dec-1-ene molecule. In the interface between water and organic phases, dec-1-ene

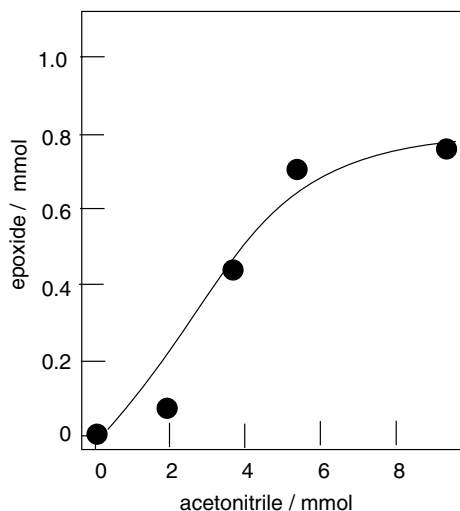


Fig. 5. Dependence of the yield of dec-1-ene epoxide (after 5 min; 40 °C) in the oxidation of dec-1-ene (5.3 mmol) with H<sub>2</sub>O<sub>2</sub> (2.2 mmol; used as 70% aqueous solution) catalyzed by [I][PF<sub>6</sub>]<sub>2</sub> (7.5 × 10<sup>-4</sup> mmol) and oxalic acid (0.375 mmol) on the amount of added acetonitrile.

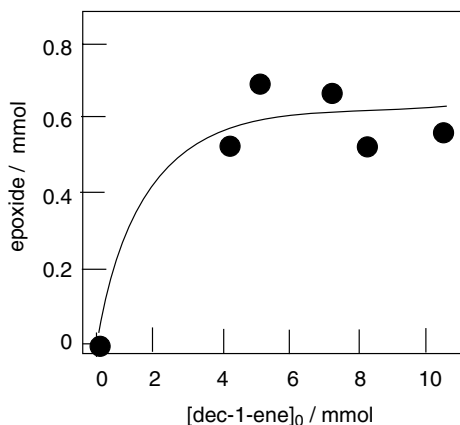


Fig. 6. Dependence of the yield of dec-1-ene epoxide (after 5 min; 40 °C) in the oxidation of dec-1-ene with H<sub>2</sub>O<sub>2</sub> (2.2 mmol; used as 70% aqueous solution) catalyzed by [I][PF<sub>6</sub>]<sub>2</sub> (7.5 × 10<sup>-4</sup> mmol) and oxalic acid (0.375 mmol) in the presence of acetonitrile (5.7 mmol) on the initial amount of dec-1-ene.

Table 3

Epoxidation of dec-1-ene (5.3 mmol) with H<sub>2</sub>O<sub>2</sub> (2.2 mmol) catalyzed by [I][PF<sub>6</sub>]<sub>2</sub> (7.5 × 10<sup>-4</sup> mmol) in the presence of acetonitrile (5.75 mmol) at different concentrations of carboxylic acid<sup>a</sup>

Entry	Oxalic acid (mmol)	Epoxide			TON (after 5 min)
		1 min	3 min	5 min	
1	0			0.01	13
2	0.011		0.29	0.63	853
3	0.375	0.18	0.41	0.73	552
4	0.660	0.31	0.72	0.67	960
5	0.940		0.039	0.60	524
6	1.210	0.47	0.48	0.50	666

<sup>a</sup> Temperature 40 °C.

molecules exist in the form of clews due to hydrophobic interactions. The double bond is unable to react with the catalyst reaction center. Acetonitrile molecules destroy the olefin globules and solvate the double bonds. This facilitates direct contact between the double bond and the catalyst reaction center. Acetonitrile molecules can interact also with the catalytic active species enhancing its activity.

#### 4. Conclusions

We have demonstrated in this work for the first time that hydrogen peroxide can oxidize saturated hydrocarbons in biphasic system without organic solvent if complex [I][PF<sub>6</sub>]<sub>2</sub> is used as a catalyst and oxalic acid as a co-catalyst. Alkyl hydroperoxides are the primary products which are decomposed in the course of the reaction to the corresponding ketones as well as (in small amounts) alcohols. Analogous oxidation (epoxidation) of dec-1-ene occurs only if a small amount of acetonitrile is added to the reaction mixture.

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