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Oxidations by the system “hydrogen peroxide–dinuclear manganese(IV) complex–carboxylic acid”[☆]

Part 5. Epoxidation of olefins including natural terpenes

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Abstract

Dinuclear manganese(IV) complex $[LMn(O)_3MnL](PF_6)_2$ (**1**, L = 1,4,7-trimethyl-1,4,7-triazacyclononane) efficiently catalyzes epoxidation of sterically accessible olefins, including natural compounds by hydrogen peroxide in acetonitrile at room temperature if a small amount of a carboxylic acid is present in the solution. The kinetics of dec-1-ene epoxidation and accompanying dioxygen evolution (catalase activity) under the action of this system in the presence of acetic acid has been studied. The initial rates of both epoxidation and O_2 evolution are proportional to the catalyst initial concentration. First order has been found for catalyst **1** for both processes, whereas the rate dependences of the dec-1-ene epoxidation is first order and the O_2 evolution is second order for H_2O_2. The epoxidation rate increases and the O_2 evolution rate decreases with growing of acetic acid concentration. Zero order has been found for dec-1-ene in its epoxidation. The reaction proceeds with an induction period for a few minutes during which changes in the electronic spectra of the reaction solution are observed. It has been proposed that the processes of the alkane oxidation and dioxygen evolution on the one hand and of the olefin epoxidation on the other hand are induced by different intermediate species. An assumption has been made that the epoxidation occurs with participation of oxo-hydroxy Mn(V) derivative $[LMn^{V}(=O)(O)_2(HO)Mn^{IV}L]^{2+}$, whereas di(hydroperoxy) complex $[LMn^{III}(OOH)(O)_2(HOO)Mn^{IV}L]^{+}$ is responsible for the alkane oxidation with simultaneous dioxygen evolution. The following equations for the initial rates were proposed for $[CH_3CO_2H] = 0.25\,\mathrm{mol\,dm^{-3}}$: $d[\mathrm{epoxide}]/dt = k_{\mathrm{eff}}(\mathrm{epoxide})[\mathbf{1}][H_2O_2]$ with $k_{\mathrm{eff}}(\mathrm{epoxide}) = 2.8–3.7\,\mathrm{mol^{-1}\,dm^{3}\,s^{-1}}$; $d[\mathrm{CyOOH}]/dt = k_{\mathrm{eff}}(\mathrm{CyOOH})[\mathbf{1}][H_2O_2]^2[\mathrm{CyH}]$ with $k_{\mathrm{eff}}(\mathrm{CyOOH}) = 4.1–6.2\,\mathrm{mol^{-3}\,dm^{9}\,s^{-1}}$; $d[O_2]/dt = k_{\mathrm{eff}}(O_2)[\mathbf{1}][H_2O_2]^2$ with $k_{\mathrm{eff}}(O_2) = 2.8–7.0\,\mathrm{mol^{-2}\,dm^{6}\,s^{-1}}$. Many different carboxylic acids were checked as cocatalysts and it has been found that oxalic acid acts with the highest efficiency in the epoxidation whereas the accompanying catalase activity of the system is very low in this case. It has been also demonstrated that complex **1** is unique catalyst because similar compounds containing only one Mn(IV) center (**2**) or dinuclear complex with bridging phenylboronic acid (**3**) are very poor catalysts in the olefin epoxidation. No epoxidation has been found when hydrogen peroxide was replaced by *tert*-butyl hydroperoxide. The system based on **1**, H_2O_2 and acetic and/or oxalic acid was employed for the efficient epoxidation of terpenes limonene, citral, carvone and linalool, while other terpenes containing sterically hindered double bonds (citronellal, α- and β-isomers of pinene) were epoxidized only with <15% yield. Using limonene as example, it has been demonstrated that regioselectivity of the epoxidation (predominant formation of product with addition of the O atom either to internal ring or external double bond) can be controlled by replacing acetic acid by oxalic acid.

Keywords: Carvone; Citral; Citronellal; Epoxidation; Epoxides; Homogeneous catalysis; Hydrogen peroxide; Kinetics; Limonene; Linalool; Manganese complexes; Olefins; Pinene; Terpenes

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[☆] For parts 1–4 see [31–34], respectively. For preliminary communications and applications, see [35–39].

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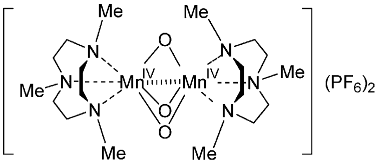
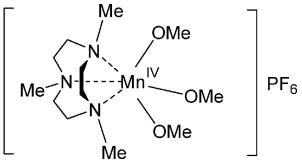
1. Introduction

In 1988, Wieghardt et al. described [1] the synthesis and the crystal structure of binuclear manganese(IV) complex $[LMn^{IV}(\mu\text{-}O)_3Mn^{IV}L](PF_6)_2\cdot H_2O$ (**1**) where L is 1,4,7-trimethyl-1,4,7-triazacyclononane (TMTACN). X-ray crystallography showed that the complex contains an unprecedented short Mn–Mn distance of 2.296(2) Å, which “seems to indicate a direct bonding interaction between the two Mn^{IV} centers” [1]. It is interesting to compare **1** with a molecule containing undisputed bond between the two manganese ions, $Mn_2(CO)_{10}$, in which the Mn–Mn distance is 2.93 Å. Two years later an analogous binuclear (μ-peroxo)dimanganese(IV) derivative, $[LMn^{IV}(\mu\text{-}O)(\mu\text{-}O)_2Mn^{IV}L](ClO_4)_2$, was synthesized and characterized [2]. More recently an improved synthesis of complex **1** and analogous derivatives has been reported [3] as well as an efficient synthesis of binucleating 1,4,7-triazacyclononane (TACN) ligands [4].



Complex **1**

Hage et al. [5] were the first to demonstrate that manganese complexes derived from TMTACN and related ligands are effective catalysts for the bleaching of stains by hydrogen peroxide. It was also shown that mononuclear Mn(IV) complex $[LMn^{IV}(OMe)_3](PF_6)$ (**2**) catalyzes in aqueous solution the H_2O_2 oxidation of 4-vinylbenzoic acid to the corresponding epoxide and of styrilacetic acid to a mixture of the epoxide, diol and a ring-closed lactone [6].



Complex **2**

Complex **1** and relative compounds with various *N*-substituted 1,4,7-triazacyclononanes (TACN) were used as catalysts by Gilbert and Lindsay Smith and their co-workers [7,8] for the H_2O_2 oxidation of phenols in water, by Barton et al. [9] for the oxidation of sulfides to sulfones by periodic acid in pyridine and by Koek et al. [10] for the epoxidation of styrene with hydrogen peroxide in a two phase system (H_2O–CH_2Cl_2). It has been demonstrated that complexes of such type can catalyze the H_2O_2 oxidations of benzyl alcohols to corresponding benzaldehydes [11] and oxidations of phenolic compounds modeling lignin [12]. Manganese complexes with similar structure and with similar ligands were used for epoxidations with H_2O_2 in acetone solution. Thus, Bolm et al. [13] found that the reaction of styrene catalyzed by $[L'_2Mn^{III}(\mu\text{-}O)(\mu\text{-}AcO)_2](PF_6)_2$ (L′ is an enantiopure C_3-symmetric TACN derived from L-proline) proceeds at −25 °C with 28% conversion and gives the S-enantiomer of the epoxide with 24% ee; Brinksma et al. [14] described the olefin epoxidation catalyzed with complex $[L''Mn_2(O)(OAc)_2](ClO_4)_2$ (L″ is *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)propane-1,3-diamine). Recently Feringa, Alsters and co-workers reported *cis*-hydroxylation and epoxidation of olefins with H_2O_2 catalyzed by complex **1** in combination with glyoxalic acid methylester methyl hemiacetal [15]. Complex **1** was shown to initiate oxidation of cyclohexanecarboxaldehyde with air to produce cyclohexanecarboxylic acid and considerable amounts of oxidative decarboxylation products (cyclohexane, cyclohexanol, and cyclohexanone) [16]. Finally, in a very recent publication Gilbert et al. [17] carried out a kinetic and mechanistic study of the H_2O_2 oxidation of a number of azonaphthol dyes in aqueous solution, catalyzed by **1** and related compounds.

It is interesting that alternative systems have been reported which used a catalyst prepared by mixing in the reaction solution both TMTACN or its analogue and a simple manganese(II) salt (sulfate or acetate) and H_2O_2 as an oxidant. De Vos, Bein and Jacobs with co-workers described in a series of publications [18–23] olefin epoxidations, Bolm et al. [24] were able to epoxidize olefins enantioselectively catalyzing the reaction with the combination of $Mn(OAc)_2$ and chiral *N*-substituted TACNs. Fish and co-workers [25] invented the “fluorous biphasic catalysis”: allylic oxidation with *tert*-BuOOH and oxygen catalyzed by R_fTACN–$[R_f(CH_2)_2COO]_2Mn$. Efficient systems for olefin epoxidations based on a manganese(II) salt and a TACN derivative were proposed by De Vos and co-workers [26] (see also [27]) and Berkessel et al. [28] and contained an oxalate buffer or ascorbate buffer, respectively, as a co-catalyst. Feringa, Rossini and their co-workers described oxidation of sulfides to sulfoxides in acetone using hydrogen peroxide under catalysis by in situ prepared manganese complexes with *N*-containing ligands [29]. Recently, Srinivas and co-workers studied benzylic oxidation and revealed the formation of terminal oxo– and μ-oxo-Mn(IV)–TMTACN complexes during the reaction [30].

In 1998, a principally new system [31–39] was discovered by us in cooperation with Lindsay Smith [31,35]. This system operating at room or even lower temperature uses complex **1** as a catalyst, hydrogen peroxide as an oxidant and a carboxylic acid in a relatively low concentration as a co-catalyst. Saturated hydrocarbons were employed as substrates and acetonitrile or nitromethane were used as solvents. It was also shown [31,35] that *m*-chloroperbenzoic acid and peroxyacetic acid are capable of oxidizing alkanes if complex **1** is used as a catalyst of these processes, however the most interesting was alkane hydroperoxidation with the “H_2O_2–compound **1**–$MeCO_2H$” system. It is important to emphasize that no alkane oxidation occurred in the absence of carboxylic (usually acetic) acid. Turnover numbers (TONs) attained 3300 after 2 h, the yield of oxygenated products was

46% based on the alkane. Higher alkanes (cyclohexane, *n*-pentane, *n*-heptane, methylbutane, 2- and 3-methylpentanes, 3-methylhexane, *cis*- and *trans*-decalins) were oxidized at 20 °C in acetonitrile (or nitromethane) solution to afford initially the corresponding alkyl hydroperoxides as the predominant products. In the course of the reaction these compounds decomposed to produce the corresponding ketones and alcohols. Light alkanes (methane, ethane, propane, normal butane and isobutane) can also be easily oxidized by the same reagent in acetonitrile solution. The "H_2O_2–compound **1**–carboxylic acid" system transforms secondary alcohols into the corresponding ketones with quantitative yields at room temperature within a few minutes [33,39]. Preliminary results have been also obtained [33], which demonstrated that terminal aliphatic olefins are quantitatively epoxidized by this system. Finally, dimethylsulfide was quantitatively and selectively converted [33] into dimethylsulfoxide within 3 h at room temperature.

The aim of the present work is to study the kinetics and mechanism of the dec-1-ene epoxidation with our "H_2O_2–compound **1**–carboxylic acid" system and to expand this system to the epoxidation of natural terpenes containing C=C double bonds. Some experiments on oxidation of saturated hydrocarbons were also carried out in order to compare various systems and make mechanistic conclusions.

It is reasonable to note here that various manganese complexes, containing Mn ions in low oxidation states (II or III) are known to catalyze epoxidation of olefins [40–59] including natural compounds [60–65]. Complexes of such type catalyze also relatively efficient oxidations of other organic substrates including saturated hydrocarbons [66–85]. It is noteworthy that $MnSO_4$ catalyzes epoxidation with H_2O_2 in the presence of aqueous sodium hydrogen carbonate buffer [86] (see also [87,88]).

2. Experimental

Syntheses of compounds **1** [1,3], **2** [6], and **3** [89,90] were described in the literature. Dec-1-ene ("Aldrich"), (−)-citronellal ("Merck"), citral (a mixture of *cis*- and *trans*-isomers; "Merck"), linalool (a mixture of enantiomers; "Merck"), (−)- and (+)-limonenes ("Aldrich"), (−)-α-pinene ("Aldrich"), β-pinene (a mixture of enantiomers; "Eucatex Química, Brazil"), (+)-carvone ("Fluka") were used as received.

A stock solution of anhydrous H_2O_2 was prepared by the following method: 2.8 mL of 70% hydrogen peroxide ("Peróxidos do Brasil") was dissolved in 60 mL of MeCN and anhydrous $MgSO_4$ (4.6 g) was added to the solution. After 3 h the solution was filtered and used in further oxidations.

The experiments on olefin and alkane oxidations were carried out in MeCN usually at 25 °C in thermostated Pyrex cylindrical vessels with vigorous stirring. The total volume of the reaction solution was 5 mL. In a typical experiment, initially, a portion of 30% aqueous solution of H_2O_2 ("Merck") was added to the solution of the catalyst, co-catalyst and a hydrocarbon substrate in acetonitrile (was distilled over P_2O_5 before the reaction).

After certain time intervals samples (about 0.2 mL) were taken, the reaction was typically quenched by addition of solid MnO_2 to decompose an excess of hydrogen peroxide. The solutions were filtered and the concentrations of epoxides, diols and starting olefins were determined by GC (HP Series 6890). In order to determine the concentrations of all cyclohexane oxidation products the samples of reaction solutions were typically analyzed twice (before and after their treatment with PPh_3) by GC (HP Series 5890-II, Carbowax 20M, $25\,m \times 0.2\,mm \times 0.2\,\mu m$; helium as a carrier gas) measuring concentrations of cyclohexanol and -hexanone. This simple and convenient method (an excess of solid triphenylphosphine is added to the samples 10–15 min before the GC analysis) which was invented and described by us earlier [91–100] allows us to detect alkyl hydroperoxides and to measure also the real concentrations of all three products (alkyl hydroperoxide, alcohol and aldehyde or ketone) present in the reaction solution, because usually alkyl hydroperoxides are decomposed in the gas chromatograph to produce mainly the corresponding alcohol and ketone. In the experiments on competitive oxidation of dec-1-ene and cyclohexane concentrations of all products were determined only after the reduction with PPh_3 because in this case we were interested only in relative oxidation rates.

The volume of dioxygen evolved was measured using a thermostated burette. The reaction system was connected to a manometric burette with water, which was saturated with oxygen prior to use. After certain time intervals, the pressure was equilibrated using a separation funnel by adjusting the water level to the same heights.

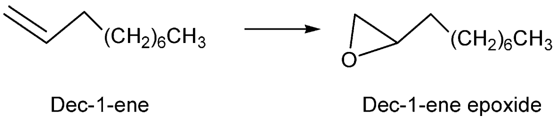
3. Results and discussion

3.1. Mechanistic studies of dec-1-ene epoxidation

We used dec-1-ene as a model compound in our mechanistic studies of olefin epoxidation with the "H_2O_2–compound **1**–carboxylic acid" system. We investigated first of all some general features of the reaction and then kinetic behaviour of the epoxidation in the presence of acetic acid. A number of publications have been devoted to mechanisms of olefin epoxidations catalyzed by various manganese complexes [101–110]. The "productive" usage of hydrogen peroxide for the olefin epoxidation proceeds simultaneously with the "non-productive" decomposition to form molecular oxygen and water (so-called catalase activity of the catalyst; see the most recent publications on dimanganese catalases and their models [111–113], as well as references in our previous paper [34]).

3.2. General features and kinetics of the dec-1-ene epoxidation in the presence of acetic acid

The oxidation of dec-1-ene with the “H_2O_2–compound **1**–acetic acid” system gives rise predominantly to the formation of the corresponding epoxide (Eq. (1)) whereas the diol is formed only in much smaller amount.



(1)

Fig. 1 demonstrates the kinetic curves for epoxidation and accompanying dioxygen evolution at various concentrations of the catalyst (complex **1**) as well as the initial rate dependences on the concentration of the catalyst used. As both processes occur with an auto-acceleration we measured maximum rate (slope of a dotted line) of the reaction in the initial period. Since the dependences are depicted as straight lines the epoxidation and the O_2 evolution are first order in respect to the manganese catalyst.

The character of the rate dependences on the initial hydrogen peroxide concentration is different from the dependence on the Mn concentration and different for the epoxidation and the O_2 evolution (Fig. 2). It can be seen that the rate dependency of the dec-1-ene epoxidation catalyzed by **1** is first order for hydrogen peroxide at $[H_2O_2]_0 < 0.5\,\text{mol dm}^{-3}$. It is interesting that simultaneous dioxygen evolution is second order for H_2O_2 at $[H_2O_2]_0 < 0.7\,\text{mol dm}^{-3}$.

The rate dependency of the dec-1-ene epoxidation is zero order for the initial dec-1-ene. The initial rate of O_2 evolution rises only slightly with growing the initial dec-1-ene concentration (Fig. 3).

The initial rate of the epoxidation is proportional to the added acetic acid concentration at $[CH_3CO_2H] < 0.15\,\text{mol dm}^{-3}$ and is practically independent on the changes in its concentration at $[CH_3CO_2H] > 0.15\,\text{mol dm}^{-3}$ (Fig. 4). At the same time the initial rate of O_2 evolution decreases with growing the added acetic acid concentration.

The concentration of water present in the reaction mixture only very slightly affects the epoxidation whereas the curve for the corresponding O_2 evolution has a maximum at $[H_2O]_{\text{added}} \approx 3\,\text{mol dm}^{-3}$ (Fig. 5).

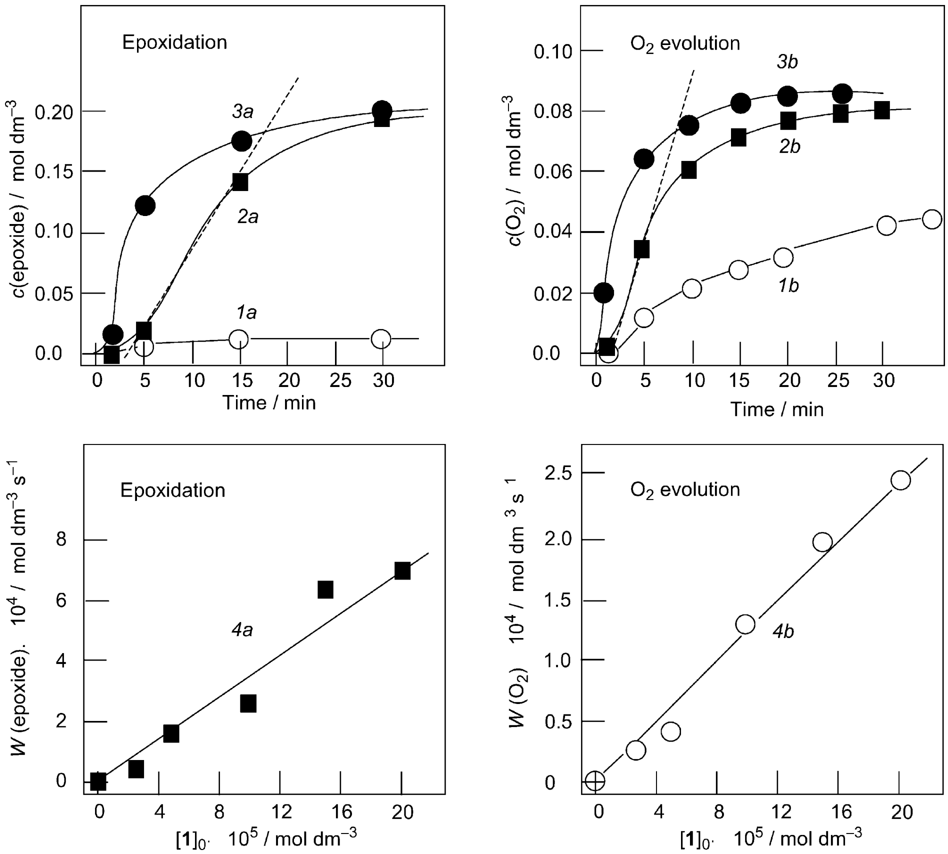


Fig. 1. Epoxidation of dec-1-ene ($0.25\,\text{mol dm}^{-3}$; curves a) and simultaneous dioxygen evolution (curves b) in the reaction with H_2O_2 ($0.65\,\text{mol dm}^{-3}$) catalyzed by complex **1** at different concentrations (mol dm^{-3}) of the catalyst: 2.5×10^{-5} (curves 1), 10×10^{-5} (curves 2) and 20×10^{-5} (curves 3). Dependences of the maximum reaction rates (two examples of measuring are shown for curves 2a and 2b: the rate was determined from the slop of a dotted straight line) on initial concentration of catalyst **1** are depicted by curves 4. The reactions were carried out at 25 °C, in the presence of acetic acid ($0.25\,\text{mol dm}^{-3}$), solvent acetonitrile, total volume of the reaction solution was 5 mL. Hydrogen peroxide was used as 30% solution in water (concentration of water in the reaction was $2.6\,\text{mol dm}^{-3}$) prepared by dilution of 70% aqueous H_2O_2.

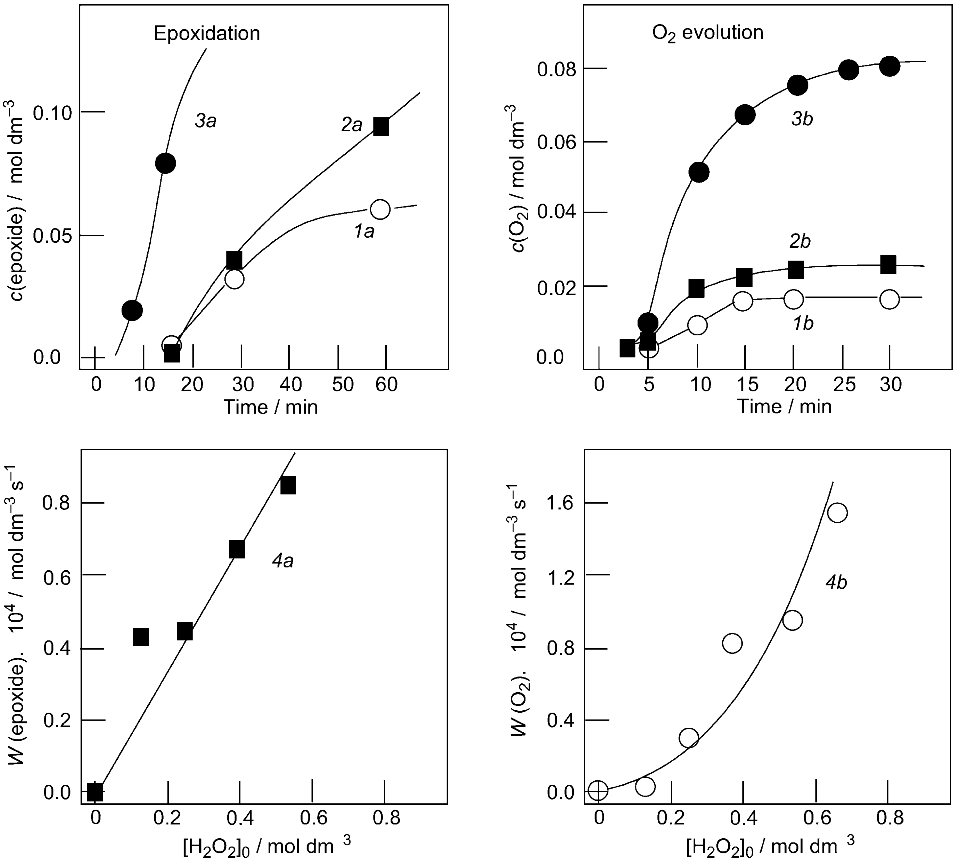


Fig. 2. Epoxidation of dec-1-ene (0.25 mol dm^{-3}; curves a) and simultaneous dioxygen evolution (curves b) in the catalyzed by complex **1** (5 × 10^{-5} mol dm^{-3}) reaction with H_2O_2 at its different concentrations (mol dm^{-3}): 0.13 (curves 1), 0.26 (curves 2) and 0.52 (curves 3). Dependences of the maximum reaction rates on initial concentration of hydrogen peroxide are depicted by curves 4. The reactions were carried out at 25 °C, in the presence of acetic acid (0.25 mol dm^{-3}), solvent acetonitrile, total volume of the reaction solution was 5 mL. Anhydrous hydrogen peroxide was used and water (concentration of water in the reaction was 5.56 mol dm^{-3}) was added to the reaction solution.

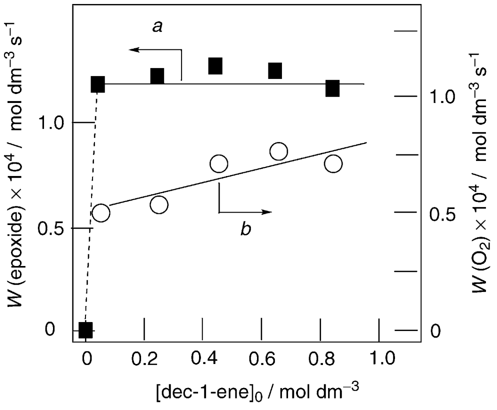


Fig. 3. Dependences of the reaction rates on initial concentration of dec-1-ene in epoxidation of dec-1-ene (curve a) and simultaneous dioxygen evolution (curve b) in the reaction with H_2O_2 (0.65 mol dm^{-3}) catalyzed by complex **1** (5 × 10^{-5} mol dm^{-3}). The reactions were carried out at 25 °C, in the presence of acetic acid (0.25 mol dm^{-3}); solvent acetonitrile, total volume of the reaction solution was 5 mL. Hydrogen peroxide was used as 30% solution in water (concentration of water in the reaction was 2.6 mol dm^{-3}) prepared by dilution of 70% aqueous H_2O_2.

A study of the reaction at different temperatures showed that the higher the temperature the lower final yield of epoxide although at low temperature the initial rate is less and a pronounced induction period can be observed (Fig. 6). From measuring the initial reaction rates at different temperatures effective activation energy for epoxidation ($E_a \approx$ 7 kcal mol^{-1}) and O_2 evolution ($E_a \approx$ 5 kcal mol^{-1}) were estimated.

Changes in UV–vis spectra in the course of dec-1-ene epoxidation are shown in Fig. 7. Just after the addition of hydrogen peroxide to the reaction mixture its spectrum exhibits some changes: after a few minute induction period the absorptions at 404 and 500 nm grow until 4 or 30 min depending on the concentration of catalyst **1**. It is important that the induction period in the epoxidation coincides with the induction period in the changes in absorption spectra (compare graphs B and C, as well as D and E in Fig. 7). After approximately 30 min the absorptions at 404 and 500 nm begin to decrease rather sharply and the epoxidation stops. In special experiments, we added to such a reaction solution a new portion of dec-1-ene and hydrogen peroxide after 60 min, however almost no addition in the epoxide concentration was detected. This testifies that a catalytically active form of the

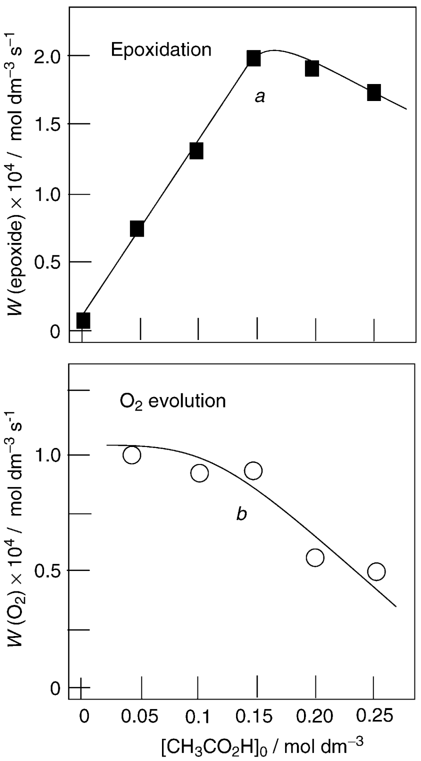


Fig. 4. Dependences of the reaction rates on initial concentrations of acetic acid in epoxidation of dec-1-ene (0.25 mol dm^{-3}; curve a) and simultaneous dioxygen evolution (curve b) in the reaction with H_2O_2 (0.65 mol dm^{-3}) catalyzed by complex **1** (5×10^{-5} mol dm^{-3}). The reactions were carried out at 25 °C, solvent acetonitrile, total volume of the reaction solution was 5 mL. Hydrogen peroxide was used as 30% solution in water (concentration of water in the reaction was 2.6 mol dm^{-3}) prepared by dilution of 70% aqueous H_2O_2.

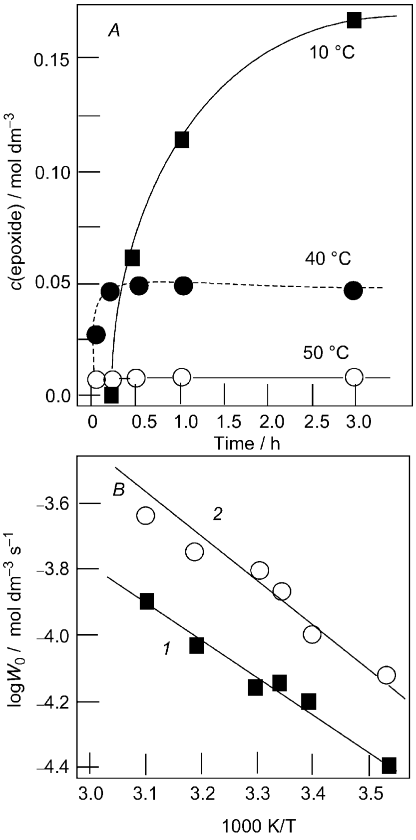


Fig. 6. Epoxidation of dec-1-ene (0.25 mol dm^{-3}) with H_2O_2 (0.65 mol dm^{-3}) catalyzed by complex **1** (5×10^{-5} mol dm^{-3}) at different temperatures (graph A). Dependences of the maximum reaction rates of epoxidation (curve 1, corresponds E_a = 7.0 ± 2 kcal mol^{-1}) and simultaneous O_2 evolution (curve 2, corresponds E_a = 5.2 ± 2 kcal mol^{-1}) on temperature are shown on graph B. The reactions were carried out in the presence of acetic acid (0.25 mol dm^{-3}), solvent acetonitrile, total volume of the reaction solution was 5 mL. Hydrogen peroxide was used as 30% solution in water (concentration of water in the reaction was 2.6 mol dm^{-3}) prepared by dilution of 70% aqueous H_2O_2.

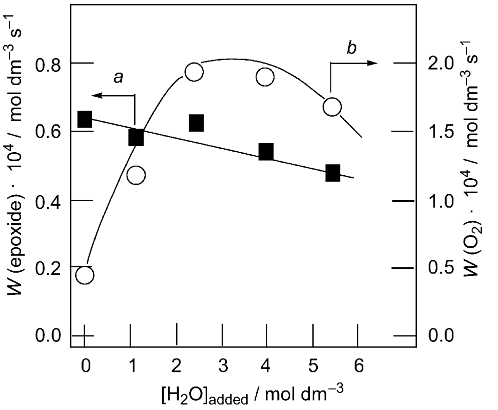


Fig. 5. Dependences of the rates of epoxidation of dec-1-ene (0.25 mol dm^{-3}; curve a) and dioxygen evolution (curve b) in the catalyzed by complex **1** (5×10^{-5} mol dm^{-3}) reaction with H_2O_2 on concentration of added water. The reactions were carried out at 25 °C, in the presence of acetic acid (0.25 mol dm^{-3}), solvent acetonitrile, total volume of the reaction solution was 5 mL. Anhydrous hydrogen peroxide was used and water was added to the reaction solution.

Mn-containing species is formed within first minutes of the reaction and then this catalyst works during approximately 40 min after which the catalyst completely decomposes. Thus three different processes compete in the course of this reaction: olefin epoxidation, dioxygen evolution, and catalyst decomposition.

3.3. On the epoxidation mechanism

Previously we concluded [34] on the basis of our data on selectivities and kinetics of cyclohexane oxidation according to Eq. (2) that a species which induces the oxidation of saturated hydrocarbons, RH, is not hydroxyl radical, $HO^{\bullet}$. We assumed that the alkane hydroperoxidation is due to the formation of a mixed-valent oxo-peroxy Mn(V)Mn(IV) complex.

In the present work we demonstrated that experimentally determined kinetic features of the olefin epoxidation are distinct from that found for the case of cyclohexane hydroperox-

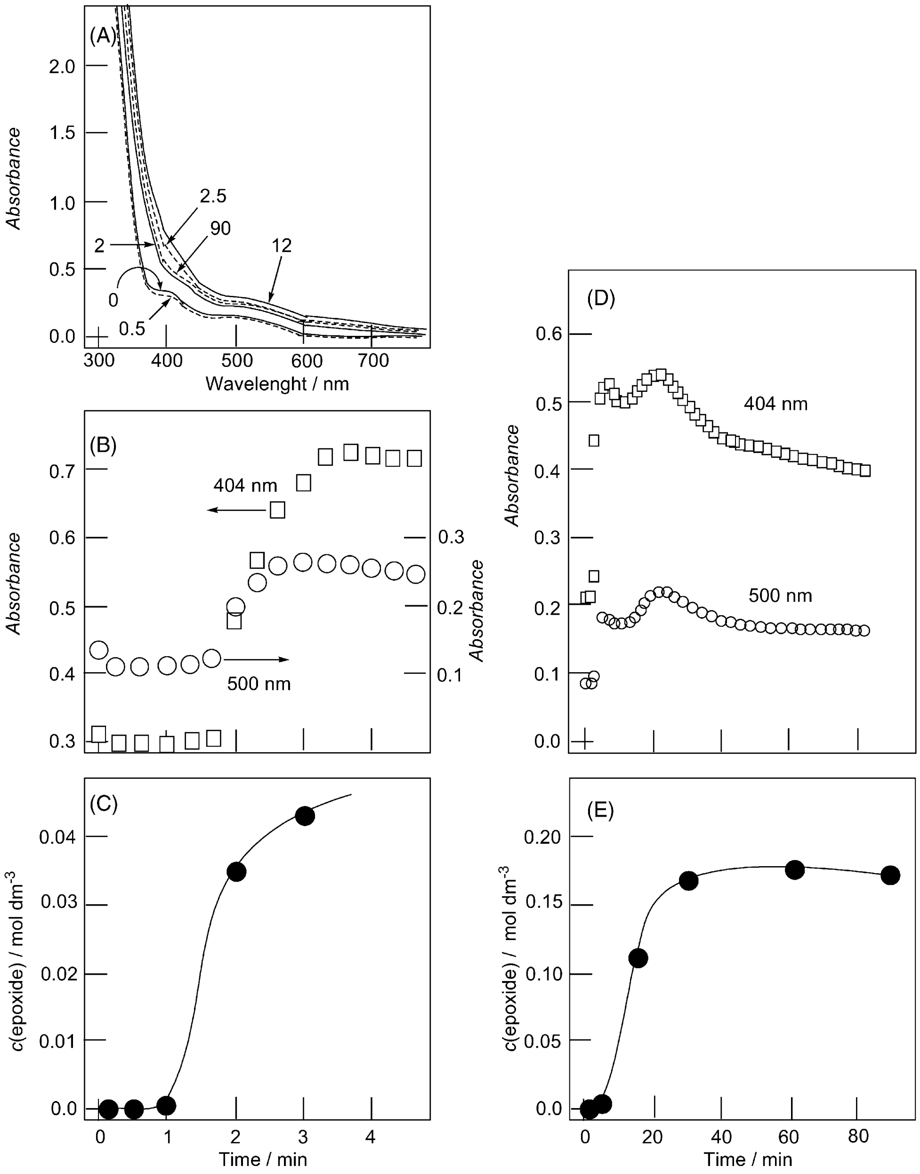
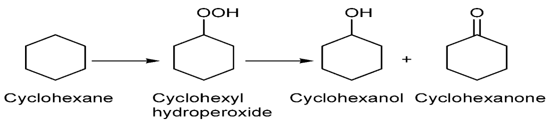


Fig. 7. Epoxidation of dec-1-ene (0.25 mol dm^{-3}) with H_2O_2 (0.65 mol dm^{-3}) catalyzed by complex **1** (20 × 10^{-5} mol dm^{-3} for graphs A, B and C; 5 × 10^{-5} mol dm^{-3} for graphs D and E) in the presence of acetic acid (0.25 mol dm^{-3}). Solvent acetonitrile, 25 °C. Absorbance of the reaction mixture after 0, 0.5, 2, 2.515 and 90 min is shown on graph A. Kinetics of the absorbance changes at 404 and 500 nm are shown on graph B. Kinetics of dec-1-ene epoxide accumulation are shown in graphs C and E.

idation [34]. Due to this fact we assumed that the processes of alkane oxidation and olefin epoxidation are induced by different intermediate species generated during catalytic hydrogen peroxide decomposition catalyzed by complex **1** in the presence of acetic acid.

Linear dependence of the cyclohexane (CyH) oxidation (Eq. (2)) rate on its initial concentration (see Fig. 4, plot C in [34]) testifies that only small portion of generated by the system oxidizing species X interact with the alkane. On the contrary, the mode of the initial rate dependence on the initial dec-1-ene concentration in its epoxidation (see Fig. 3, curve a in the present paper) shows that even at relatively low olefin concentration all generated species which are capable of epoxidizing react with the olefin. If we assume that in both cases the same oxidizing species operates we need to accept that the reaction rate constant for the interaction between X and the olefin is much higher than that for the analogous interaction of X with the alkane. In accordance with such an assumption we might expect that added olefin would depress the cyclohexane oxidation whereas added alkane cannot affect the epoxidation rate.



(2)

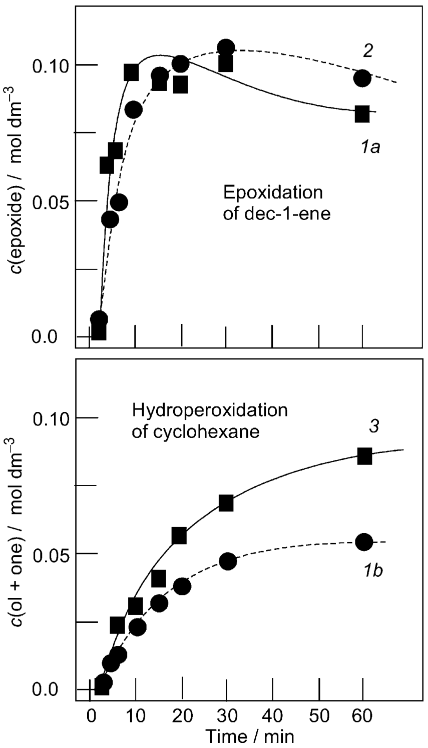


Fig. 8. Accumulation of dec-1-ene epoxide (curve 1a) and a sum of cyclohexanol and cyclohexanone (curve 1b) in the competitive oxidation of a mixture of dec-1-ene and cyclohexane, as well as (for comparison) accumulation of dec-1-ene epoxide (curve 2) and a sum of cyclohexanol and cyclohexanone (curve 3) in the oxidation of pure dec-1-ene and cyclohexane, respectively. Reaction conditions: dec-1-ene (for curves 1a and 2), 0.15 mol dm^{-3}; cyclohexane (for curves 1b and 3), 0.23 mol dm^{-3}; complex **1**, 1×10^{-4} mol dm^{-3}; H_2O_2 (30% aqueous), 0.65 mol dm^{-3}; acetic acid, 0.25 mol dm^{-3}; 25 °C. Concentrations of all products were measured by GC after the reduction of the reaction samples with PPh_3.

Our experiments on the competitive oxidation of dec-1-ene and cyclohexane (Fig. 8) demonstrated that under identical conditions the epoxidation rate for dec-1-ene concentration 0.15 mol dm^{-3} is approximately five times higher than the rate of the cyclohexyl hydroperoxide formation from cyclohexane at $[CyH]_0$ = 0.23 mol dm^{-3}. Cyclohexane added to the epoxidation reaction solution does not practically affect the epoxidation rate. Finally the most important feature has been found: added to the cyclohexane solution dec-1-ene at its concentration when all oxidation-induced species are accepted by the olefin only weakly decreases the cyclohexane oxidation rate. These results testify that the processes of alkane oxidation and olefin epoxidation are induced by different species generated in the course of hydrogen peroxide decomposition catalyzed by binuclear manganese complex **1**.

Other kinetic data also support the assumption about the different nature of intermediate species, which induce the alkane oxidation and the olefin epoxidation. Thus quadratic dependence of the initial rates for both dioxygen evolution and cyclohexane oxidation on $[H_2O_2]_0$ has been found (see Fig. 5 in [34]) whereas the epoxidation rate is proportional to the initial hydrogen peroxide concentration (Fig. 2, curve 4a in the present paper). The dioxygen evolution rate $W(O_2)$ in the presence of dec-1-ene is proportional to the square of hydrogen peroxide concentration (Fig. 2, curve 4b here). As $W(O_2)$ does not depend practically on the dec-1-ene concentration (Fig. 3, curve b) we can conclude that the epoxidation and the dioxygen evolution reactions are different routes of the process, which are realized with participation of different intermediate active species.

The modes of acetic acid additives influence on the dioxygen evolution rate, $W(O_2)$, the cyclohexyl hydroperoxide formation rate, W(CyOOH), and the epoxide formation rate, W(epoxide), are similar, i.e., the acid affects in common the three processes initial stage of the catalyst, **Cat**, generation from its precursor, complex **1**:

$$\mathbf{1} \overset{CH_3CO_2H,\ H_2O_2}{\rightleftharpoons} \mathbf{Cat} \qquad (3)$$

Taking into account all obtained kinetic data we can propose the following kinetic schemes (4–10) for the three process (the olefin epoxidation, alkane hydroperoxidation and dioxygen evolution), which includes four intermediates, **A**, **B**, **C** and **D**.

$$\mathbf{Cat} + H_2O_2 \rightleftharpoons \mathbf{A} \quad K_4 \qquad (4)$$

$$\mathbf{A} \rightleftharpoons \mathbf{B} \quad K_5 = k_{+5}/k_{-5} \qquad (5)$$

$$\mathbf{A} + H_2O_2 \rightleftharpoons \mathbf{C} \quad K_6 \qquad (6)$$

$$\mathbf{C} \rightleftharpoons \mathbf{D} \quad K_7 \qquad (7)$$

$$\mathbf{B} + \text{olefin} \rightarrow \text{epoxide} \quad k_8 \qquad (8)$$

$$\mathbf{C} \rightarrow O_2 \quad k_9 \qquad (9)$$

$$\mathbf{D} + \text{CyH} \rightarrow \cdots \xrightarrow{O_2} \text{CyOOH} \quad k_{10} \qquad (10)$$

This scheme assumes that intermediates generated in the course of consecutive transformation of complex **1** exhibit different reactivities towards alkane on the one hand and olefin on the other hand. As we proposed previously [34] catalytically active species **Cat** can be generated in the interaction between initial form of complex **1** with acetic acid and one molecule of hydrogen peroxide, and this species could be complex $[LMn^{III}(O)_2(HO)Mn^{IV}L]^{2+}$. An interaction of **Cat** with a hydrogen peroxide molecule according to Eq. (4) can lead to the formation of intermediate **A** which could be a hydroperoxy derivative of binuclear manganese complex, $[LMn^{III}(OOH)(O)_2Mn^{IV}L]^{2+}$. Intermediate **A** is transformed to **B**, for example, oxo-Mn(V) derivative $[LMn^{V}(=O)(O)_2(HO)Mn^{IV}L]^{2+}$. We assume that intermediate **B** can easily react with the olefin to afford the corresponding epoxide as depicted by Eq. (8) (see recent publications devoted to mechanisms of olefin epoxidation by high-valent metal complexes [101–110]). Experimentally found first order for hydrogen peroxide and zero order for the olefin are in accordance with this assumption. In another route, intermediate **A** reacts with one more hydrogen peroxide molecule which gives rise in the presence of acetate anion to the formation of di(hydroperoxy) binuclear complex **C** with apparent structure $[LMn^{III}(OOH)(O)_2(HOO)Mn^{IV}L]^+$. Intermediate **C** reacts in turn via two routes: either it decomposes according catalase Eq. (9) to produce dioxygen or it is transformed in reaction (7) into an active in alkane hydroperoxidation (10) intermediate **D** with possible structure $[LMn^V(=O)(O)_2(HOO)Mn^{IV}L]^{2+}$ which is similar to the structure of intermediate **A**. It is known that a Mn–OOH fragment is present in Mn-superoxide dismutase [114]. Second order for hydrogen peroxide found in both the dioxygen evolution and the alkane hydroperoxidation are in accordance with this hypothesis. We assume that intermediates **B** and **D** react selectively with either alkanes or olefins: **B** is more reactive towards olefins.

A hypothetical catalytic cycle showing the olefin epoxidation and dioxygen evolution as well as the alkane oxidation is presented in Scheme 1. This Scheme proposes that intermediate **B** is formed from **A** *via* formally intramolecular hydroxyl anion transfer from Mn(III) ion to the neighbouring Mn(IV) ion which affords a oxo-Mn(V)-hydroxy-Mn(IV) derivative **B**. A catalytic cycle for the alkane hydroperoxidation was proposed and discussed previously [34], and intermediates **Cat**, **A**, **C** and **D** in the present paper correspond to intermediate species **4**, **5**, **6** and **8** presented in Scheme 2 from Ref. [34].

A kinetic analysis of schemes (4–10) in quasi-stationary approximation for **B** and quasi-equilibrium approximation for **Cat**, **A**, **C** and **D** accepting the following conditions:

$$[\mathbf{Cat}] \gg [\mathbf{N}], \quad \text{where} \quad \mathbf{N} = \mathbf{A},\ \mathbf{B},\ \mathbf{C} \text{ and } \mathbf{D} \tag{11}$$

gives rise to the below shown equations for the initial rates of epoxidation and dioxygen evolution at fixed acetic acid concentration ($0.25\,\mathrm{mol\,dm^{-3}}$):

$$W(\text{epoxide}) = \frac{\mathrm{d[epoxide]}}{\mathrm{d}t} = \frac{k_8 k_{+5} K_4 [\mathbf{Cat}][\mathrm{H_2O_2}][\text{olefin}]}{k_{-5} + k_8[\text{olefin}]} \tag{12}$$

$$W(\mathrm{CyOOH}) = \frac{\mathrm{d[CyOOH]}}{\mathrm{d}t} = k_{10} K_7 K_6 K_4 [\mathbf{Cat}][\mathrm{H_2O_2}]^2[\mathrm{CyH}] \tag{13}$$

$$W(\mathrm{O_2}) = \frac{\mathrm{d[O_2]}}{\mathrm{d}t} = k_9 K_6 K_4 [\mathbf{Cat}][\mathrm{H_2O_2}]^2 \tag{14}$$

It follows from the data presented in Fig. 3; curve a, that $k_{-5} \ll k_8[\text{olefin}]$ at $[\text{olefin}] > 0.05\,\mathrm{mol\,dm^{-3}}$ and thus

$$\frac{\mathrm{d[epoxide]}}{\mathrm{d}t} = k_{+5} K_4 [\mathbf{Cat}][\mathrm{H_2O_2}] \tag{15}$$

Taking into account that, according to Eq. (3):

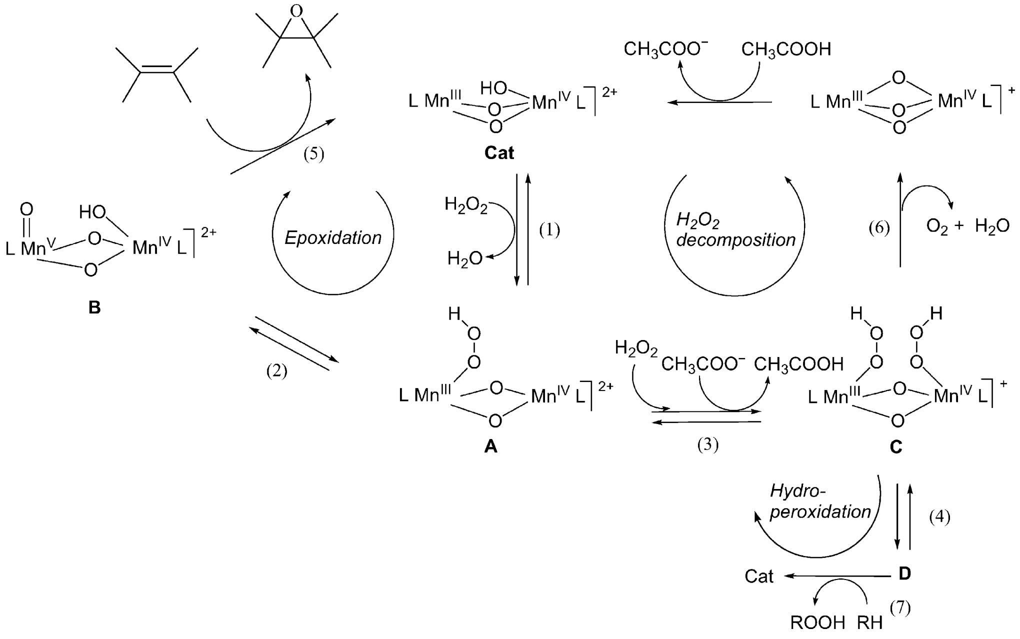
$$[\mathbf{Cat}] = \alpha[\mathbf{1}] \tag{16}$$

where coefficient α depends on the CH_3CO_2H concentration, as well as taking into consideration Eqs. (13)–(15) we were able to calculate effective rate constants for the processes of epoxidation

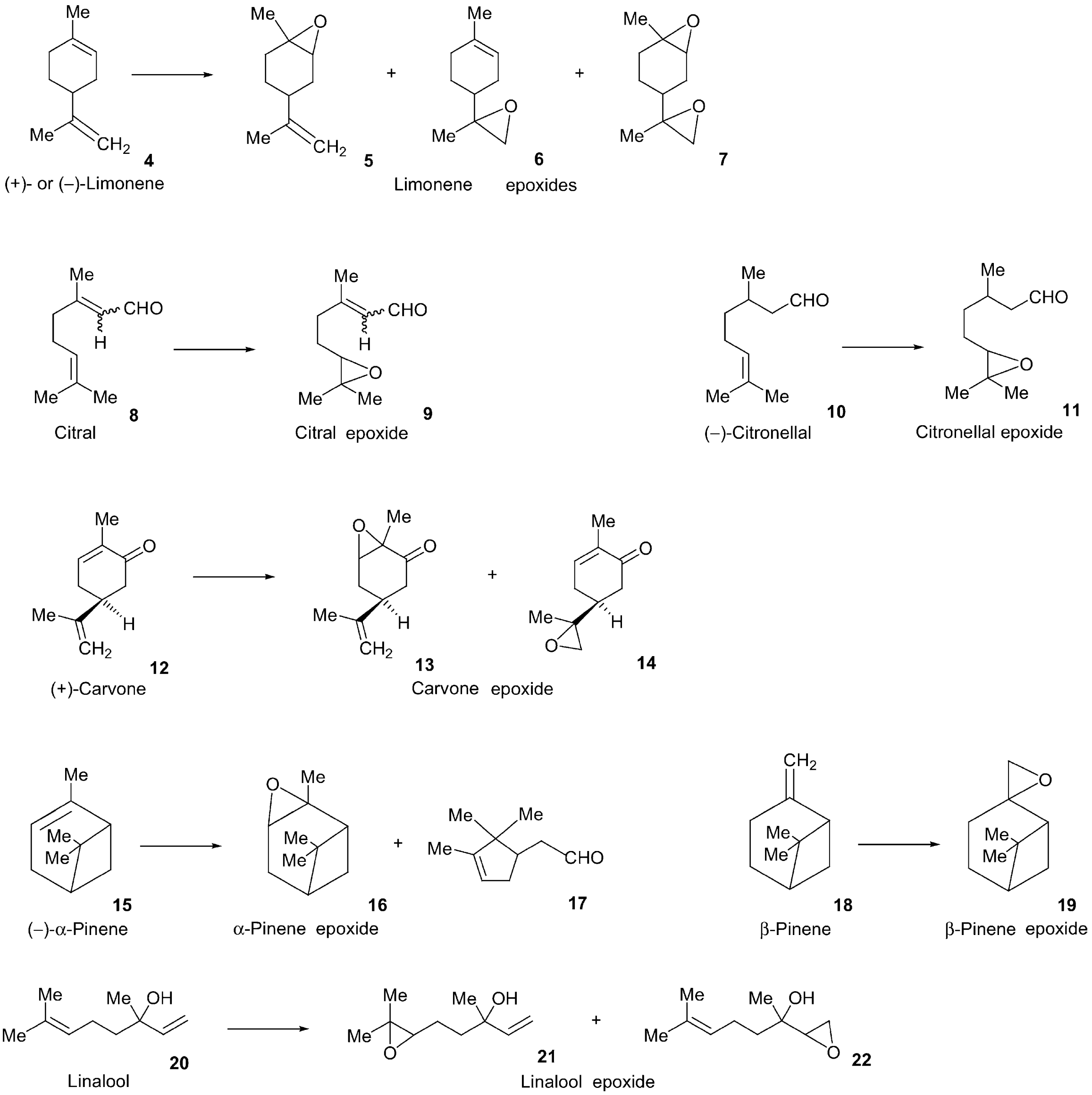
$$k_{\text{eff}}(\text{epoxide}) = k_{+5} K_1 \alpha = 2.8 - 3.7\,\mathrm{mol^{-1}\,dm^3\,s^{-1}} \tag{17}$$

hydroperoxidation

$$k_{\text{eff}}(\mathrm{CyOOH}) = k_{10}\ K_4\ K_6 K_7 \alpha = 4.1 - 6.2\,\mathrm{mol^{-3}\,dm^9\,s^{-1}} \tag{18}$$



Scheme 1.



Scheme 2.

and O_2 formation

$$k_{\text{eff}}(O_2) = k_9 K_4 K_6 \alpha = 2.8 - 7.0\,\text{mol}^{-2}\,\text{dm}^6\,\text{s}^{-1} \qquad (19)$$

In accordance with the obtained kinetic expressions the rates of the three processes are proportional to concentration of the catalyst precursor, i.e., complex **1**. It follows also from the experimental data that the epoxidation efficiency grows with decrease in initial hydrogen peroxide concentration:

$$\frac{W(\text{epoxide})}{W(O_2)} \sim \frac{1}{[H_2O_2]} \qquad (20)$$

Eq. (20) shows that for the most efficient usage of hydrogen peroxide in the olefin epoxidation one should introduce this oxidant into the reaction in low concentration (or portion by portion). On the contrary, in the cyclohexane oxidation, in order to rise a “productively used” H_2O_2 portion we need to introduce high concentration of the hydrogen peroxide though in this case the absolute value of its “non-productive” catalase decomposition to O_2 and H_2O will be also high.

3.4. *Various acids as co-catalysts in the epoxidation*

It was interesting to compare a co-catalytic action of various acids in dec-1-ene epoxidations. The obtained data are summarized in Table 1 and Fig. 9. It can be clearly seen from this table that various carboxylic acids exhibit different initial rates of the epoxidation and final yields of the epoxide. Ascorbic and citric acids do not co-catalyze the process at all. Acids containing electron-withdrawing substituents in benzene ring (*p*-trifluoromethylbenzoic, *p*-cyanobenzoic and *p*-nitrobenzoic acid) turned out to be the most efficient co-

Table 1
Epoxidation of dec-1-ene with H_2O_2 catalyzed by complex **1** in the presence of various acids[a]

Entry	Added acid	Initial rate[b], $W_0 \times 10^5$ mol dm^{-3} s^{-1}	Yield of epoxide[c] (mol dm^{-3})	Yield of diol[c] (mol dm^{-3})	TON[d]
1	Acetic acid	4.7	0.051	0.014	1300
2	Oxalic acid	3.0 (5.6)[f]	0.171 (0.200)[e] (0.198)[f]	0.000 (0.006)[e] (0.000)[f]	3420 (4120)[e] (3960)[f]
3	Succinic acid	3.5	0.081	0.005	1720
4	*p*-Methylbenzoic acid	2.5	0.024	0.013	740
5	Benzoic acid	3.2	0.065	0.070	1440
6	*p*-Chlorobenzoic acid	2.3	0.029	0.005	680
7	*p*-Trifluoromethylbenzoic acid	4.7	0.075	0.022	1940
8	*p*-Cyanobenzoic acid	6.8	0.090	0.032	2440
9	Terephthalic acid	1.5	0.015	0.011	520
10	*p*-Nitrobenzoic acid	5.8	0.095	0.033	2560
11	Phenylboronic acid	0.3	0.014	0.000	280
12	(–)-Camphanic acid	9.2	0.081	0.012	1860
13	Pyrazine-2-carboxylic acid	2.6	0.029	0.010	760
14	Ascorbic acid	0.0	0.000	0.000	0
15	Citric acid	0.0	0.000	0.000	0

[a] Reactions at 25 °C; dec-1-ene, 0.25 mol dm^{-3}; acid, 0.05 mol dm^{-3} (in the case of a dicarboxylic acid, i.e., oxalic, succinic, terephthalic, 0.025 mol dm^{-3}); catalyst, 5×10^{-5} mol dm^{-3}; H_2O_2 (30% aqueous), 0.65 mol dm^{-3}; reaction time, 2 h.

[b] Maximum rate of the epoxide accumulation in the initial period of the reaction (approximately after 10 min).

[c] Concentrations of the epoxide and the diol after 2 h.

[d] Number of moles of the formed epoxide and diol per 1 mol of the catalyst after 2 h.

[e] After 3 h.

[f] H_2O_2 (70% aqueous), 0.65 mol dm^{-3}; 3 h.

catalysts. (−)-Camphanic acid also exhibited high activity, especially at the beginning of the epoxidation. It is interesting that in the presence of this chiral compound hydroperoxidation of ethylbenzene gives a racemic mixture of the enantiomers (the experiments were carried out in cooperation with Prof. Carsten Bolm and Miss Chiara Pavan).

Unexpectedly, the epoxidation in the presence of oxalic acid (Table 1, entry 2) turned out to be very efficient: TONs exceeded 4000 and the selectivity of the reaction was very high (unlike other acids, oxalic acid as a co-catalyst gave very small amounts of decane-1,2-diol). Another interesting feature of the epoxidation in the presence of oxalic acid is the reaction occurring without auto-acceleration in its beginning (see Figs. 9 and 10). Moreover, in the case of oxalic acid the simultaneous dioxygen evolution is depressed in comparison with the reaction co-catalyzed with acetic acid (Fig. 10, graph D). Finally, in the presence of oxalic acid the catalyst is not completely decomposed after long period (many hours) as shown in Fig. 10, graph C. It is noteworthy that enzyme oxalate decarboxylase which converts oxalate to give CO_2 and formate contains two Mn-binding sites [115,116] (see also a recent publication on α-ketocarboxylate derivatives of iron [117]).

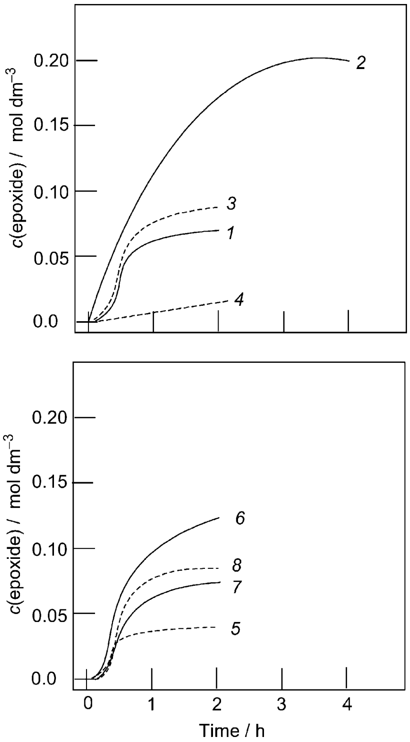


Fig. 9. Epoxidation of dec-1-ene (0.25 mol dm^{-3}) in the reaction with H_2O_2 (0.65 mol dm^{-3}) catalyzed by complex **1** (5×10^{-5} mol dm^{-3}) at 25 °C in the presence of different acids (0.05 mol dm^{-3} for monocarboxylic acids; 0.025 mol dm^{-3} for dicarboxylic acids): acetic (curve 1), oxalic (curve 2), succinic (curve 3), phenylboronic (curve 4), benzoic (curve 5), *p*-nitrobenzoic (curve 6), *p*-trifluoromethylbenzoic (curve 7), camphanic (curve 8) acids.

3.5. *Comparison of manganese complexes in oxidations with different oxidants*

In addition to the study of complex **1**, we checked the activity of mono- and dinuclear manganese complexes **2** and **3** in epoxidation of dec-1-ene as well as in oxidation of cyclohexane. Hydrogen peroxide and *tert*-butyl hydroperoxide were used as oxidants. The results are given in Table 2. It

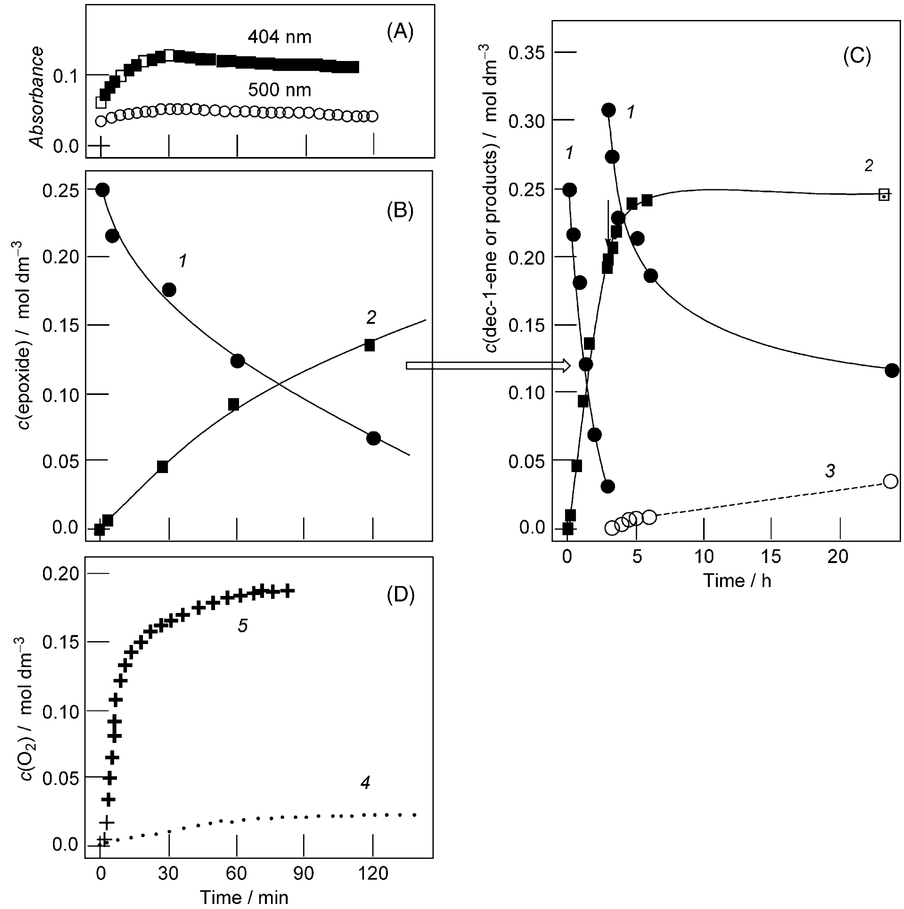
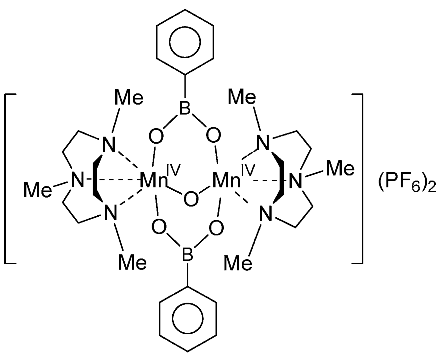


Fig. 10. Epoxidation of dec-1-ene (0.25 mol dm^{-3}; the consumption is shown by curves 1) with H_2O_2 (0.65 mol dm^{-3}) catalyzed by complex **1** (5×10^{-5} mol dm^{-3}) at 25 °C in the presence of oxalic acid (0.025 mol dm^{-3}). Kinetics of the absorbance changes at 404 and 500 nm are shown on graph A. Kinetics of dec-1-ene epoxide (curves 2) and decane-1,2-diol (curve 3) accumulation are shown in graphs B and C. At the moment denoted by arrow (after 3 h) a new portions of dec-1-ene (0.25 mol dm^{-3}) and H_2O_2 (0.65 mol dm^{-3}) were added to the reaction solution. Graph D (curve 4) presents dioxygen evolution under the same conditions (i.e., oxalic acid, 0.025 mol dm^{-3}; dec-1-ene, 0.25 mol dm^{-3}; as well as dioxygen evolution (curve 5) when for comparison oxalic acid is replaced by acetic acid (0.05 mol dm^{-3})).

can be concluded that only compound **1** exhibits a unique activity in both epoxidation and alkane oxidation. Moderate activity was found for the epoxidation of dec-1-ene by *tert*-butyl hydroperoxide under catalysis with complex **3** (TONs up to only 40).



Complex **3**

3.6. Epoxidation of natural terpenes

We also investigated oxidation by the above system of certain natural terpenes shown in Scheme 2. We have found that the olefin is practically inactive in the absence of a small quantity of acetic or oxalic acid.

Epoxidation of limonene, which contains two different double bonds, gives products of addition to both the internal ring double bond (**5**) and the double bond in the side chain (**6**). The obtained results are summarized in Table 3. When acetic acid is used as a co-catalyst product **5** dominates and the ratio **5**/**6** varies from 1.4 (entry 9), to 3.5 (entry 12) depending on the reagent concentrations and the reaction time. The non-optimized maximum yield of both monoepoxides was almost 50% based on starting limonene. In experiments with an excess of hydrogen peroxide the product of double epoxidation at both double bonds (**7**) is produced in significant quantities after long time (entries 11, 12 and 13). The overall yield of epoxides was up to 72% based on starting limonene. It should be noted that another product (GC) of

Table 2
Comparison of certain systems based on Mn–TMTACN complexes as catalysts for oxidations of dec-1-ene and cyclohexane with hydrogen peroxide and *tert*-butyl hydroperoxide[a]

Catalyst	Epoxidation of dec-1-ene with H_2O_2	Epoxidation of dec-1-ene with *tert*-BuOOH	Oxidation of cyclohexane with H_2O_2	Oxidation of cyclohexane with *tert*-BuOOH
1	TONs up to 4000	No epoxide (TON < 0.2)	TONs up to 3300[b]	TONs up to 2000[c]
2	No epoxide (TON < 0.2)	No epoxide (TON < 0.2)	TON = 2[d]	TON = 2
3	No epoxide (TON < 0.2)	TONs up to 40	TON = 4	TON = 9

[a] Reactions at 25 °C; dec-1-ene, 0.25 mol dm^{-3}; cyclohexane, 0.46 mol dm^{-3}; acetic acid, 0.25 mol dm^{-3}; catalyst, 5×10^{-5} mol dm^{-3}; H_2O_2 (30% aqueous) and *tert*-BuOOH (70% aqueous), 0.65 mol dm^{-3}; reaction time, 2 h.

[b] See also [32].

[c] See also [36].

[d] See also [34].

unknown structure was formed in several experiments, however, the amount of it was much less than those of the target epoxides.

It is noteworthy that the limonene epoxidation in the presence of oxalic acid occurs with the opposite selectivity: product **6** dominates and the ratio **5/6** varies from 0.86 (entry 14) to 0.65 (entry 17). This observation is in accordance with an assumption about bulkiness of a reactive complex formed between **1** and oxalic acid.

Epoxidation of a mixture of *cis*- and *trans*-isomers of citral (**8**) in the presence of oxalic acid gives isomeric epoxides **9**, predominant epoxidation of less hindered bond $C{=}CMe_2$ occurs and almost no epoxidation of the second double bond bearing electron-withdrawing CHO group was noticed (Table 4). The reaction with (−)-citronellal (**10**) having similar structure but which does not contain the second double bond gives only very low yield of the two diastereomeric epoxides **11** (Table 5). Lower reactivity of **10** in comparison with **8** can be explained if we take into account that the $C{=}CMe_2$ bond in **10** is connected with less bulky (due to the most compact second double bond) substituent.

The same reason can explain the high yield (up to 90%) of isomeric epoxides **13** and **14** in the oxidation of (+)-carvone (**12**). Concentrations of a mixture of isomers after different times of the reaction are summarized in Table 6.

Epoxidation of both pinene isomers **15** and **18** exhibited low efficiency (Tables 7 and 8, respectively). The yield of the target epoxide was only around 10%. Furthermore, significant quantities of side products appeared (one of them was identified as cyclopentene derivative **17** for oxidation of α-

Table 3
Epoxidation of limonene (4) isomers by the "H_2O_2–complex **1**–carboxylic acid" system[a]

Entry	Acid added (mol dm^{-3})	Complex **1** (× 10^{-5}, mol dm^{-3})	H_2O_2 (mol dm^{-3})[b]	Time (min)	Products (mol dm^{-3})[c]			Total yield (%)[d]
					5	**6**	**7**	
	Acetic acid (0.25)							
1		5	0.25 (anhydrous)	15	0.007	0.004	0.00	
2				60	0.018	0.010	0.00	11
3		5	1.25 (anhydrous)	30	0.017	0.013	0.00	12
4		25	0.25 (anhydrous)	30	0.024	0.014	0.001	16
5		25	1.25 (anhydrous)	30	0.062	0.029	0.080	68
6		5	0.11 (30% aqueous)	60	0.003	0.002	0.00	2
7		5	0.43 (30% aqueous)	60	0.032	0.014	0.005	20
8		5	1.3 (30% aqueous)	60	0.023	0.014	0.00	15
9				120	0.021	0.015	0.00	14
10		20	1.3 (30% aqueous)	15	0.066	0.027	0.042	
11				60	0.082	0.030	0.068	72
12		25	1.25 (30% aqueous)	15	0.094	0.027	0.034	62
13		25	1.25 (70% aqueous)	15	0.083	0.026	0.059	67
	Oxalic acid (0.025)							
14		5	0.65 (70% aqueous)	5	0.006	0.007	0.00	
15				10	0.007	0.009	0.00	
16				15	0.011	0.015	0.00	
17				30	0.032	0.049	0.00	32
18				120	0.026	0.039	0.005	
19				180	0.027	0.041	0.008	

[a] In the oxidation in the presence of acetic or oxalic acids (+)- and (−)-isomers of limonene were used, respectively. Reactions at 25 °C; limonene, 0.25 mol dm^{-3}.

[b] For the preparation of anhydrous hydrogen peroxide, see Section 2.

[c] Two peaks in GC correspond to compounds 5, 6 and 7 because they exist as mixtures of two diastereomers.

[d] Yield of a sum of all identified products based on starting olefin.

Table 4
Epoxidation of citral (**8**) isomers by the "H_2O_2–complex **1**–oxalic acid" system[a]

Entry	Time (min)	Products ($mol\,dm^{-3}$)		Total yield (%)[b]
		9a	**9b**	
1	5	0.006	0.006	
2	10	0.011	0.011	
3	15	0.011	0.011	
4	30	0.024	0.024	
5	60	0.032	0.031	
6	120	0.047	0.045	
7	180	0.055	0.052	43

[a] Reactions at 25 °C; H_2O_2 (30% aqueous), $0.65\,mol\,dm^{-3}$; citral, $0.25\,mol\,dm^{-3}$; catalyst **1**, $5 \times 10^{-5} mol\,dm^{-3}$; oxalic acid, $0.025\,mol\,dm^{-3}$.

[b] Yield of a sum of all identified products based on starting citral.

Table 5
Epoxidation of (−)-citronelal (**10**) by the "H_2O_2–complex **1**–oxalic acid" system[a]

Entry	Time (min)	Products ($mol\,dm^{-3}$)		Total yield (%)[b]
		11a	**11b**	
1	5	0.000	0.005	
2	10	0.000	0.004	
3	15	0.000	0.004	
4	30	0.002	0.006	
5	60	0.002	0.006	
6	120	0.004	0.009	
7	180	0.007	0.011	7

[a] Reactions at 25 °C; H_2O_2 (70% aqueous), $0.65\,mol\,dm^{-3}$; (−)-citronelal, $0.25\,mol\,dm^{-3}$; catalyst **1**, $5 \times 10^{-5} mol\,dm^{-3}$; oxalic acid, $0.025\,mol\,dm^{-3}$.

[b] Yield of a sum of all identified products based on starting citronelal.

pinene). We can propose again that the low efficiency of this system for pinene oxidation is due to extensive steric hindrance by the substituents to approach of the bulky catalyst molecule. This gives additional evidence that the epoxidation occurs via a mechanism that does not involve the formation of free radicals. In contrast, their generation during oxidation of alkanes by *tert*-BuOOH catalyzed by **1** has been assumed previously [33,36]. This oxidation occurs also in the absence of acetic acid although it accelerates oxygenation of saturated hydrocarbons. In accordance with our observation on the reaction between *tert*-BuOOH and dec-1-ene (see Section 3.5 and Table 2), we found that **1** does not catalyze epoxidation of limonene by *tert*-BuOOH even in the presence of acetic acid. This is also consistent with the proposal that oxidation by hydrogen peroxide proceeds without the formation of free radicals.

Oxidation of linalool (**20**), which contains two double bonds and hydroxy group gives rise to the predominant formation of the 6,7-epoxide **21** whereas 1,2-isomer **22** is formed in much lower concentration (Table 9).

Table 6
Epoxidation of (+)-carvone (**12**) by the "H_2O_2–complex **1**–oxalic acid" system[a]

Entry	Time (min)	**13** + **14** ($mol\,dm^{-3}$)	Total yield (%)[b]
1	5	0.023	
2	10	0.049	
3	15	0.062	
4	30	0.092	
5	60	0.156	
6	120	0.202	
7	180	0.226	90

[a] Reactions at 25 °C; H_2O_2 (70% aqueous), $0.65\,mol\,dm^{-3}$; (+)-carvone, $0.25\,mol\,dm^{-3}$; catalyst **1**, $5 \times 10^{-5} mol\,dm^{-3}$; oxalic acid, $0.025\,mol\,dm^{-3}$.

[b] Yield of a sum of all identified products based on starting (+)-carvone.

Table 7
Epoxidation of (−)-α-pinene (**15**) by the "H_2O_2–complex **1**–oxalic acid" system[a]

Entry	Time (min)	Products ($mol\,dm^{-3}$)		Total yield (%)[b]
		16	**17**	
Acetic acid ($0.25\,mol\,dm^{-3}$)[c]				
1	15	0.024	0.007	
2	30	0.019	0.013	13
3	60	0.010	0.017	
Oxalic acid ($0.025\,mol\,dm^{-3}$)[d]				
4	5	0.015	0.000	
5	60	0.027	0.000	11

[a] Reactions at 25 °C; (−)-α-pinene, $0.25\,mol\,dm^{-3}$; catalyst **1**, $5 \times 10^{-5}\,mol\,dm^{-3}$.

[b] Yield of a sum of all identified products based on starting citronelal.

[c] H_2O_2 (30% aqueous), $1.3\,mol\,dm^{-3}$.

[d] H_2O_2 (70% aqueous), $0.65\,mol\,dm^{-3}$.

Table 8
Epoxidation of β-pinene (**18**) by the "H_2O_2–complex **1**–oxalic acid" system[a]

Entry	Time (min)	**19**	Total yield (%)[b]
Acetic acid ($0.25\,mol\,dm^{-3}$)			
1[c]	15	0.005	2
2[d]	30	0.025	10
Oxalic acid ($0.025\,mol\,dm^{-3}$)[e]			
4	30	0.004	2
5	60	0.012	5

[a] Reactions at 25 °C; β-pinene, $0.25\,mol\,dm^{-3}$.

[b] Yield of 19 based on starting citronelal.

[c] Catalyst **1**, $5 \times 10^{-5}\,mol\,dm^{-3}$; H_2O_2 (30% aqueous), $0.43\,mol\,dm^{-3}$.

[d] Catalyst **1**, $25 \times 10^{-5}\,mol\,dm^{-3}$; H_2O_2 (anhydrous), $1.25\,mol\,dm^{-3}$.

[e] Catalyst **1**, $5 \times 10^{-5}\,mol\,dm^{-3}$; H_2O_2 (70% aqueous), $0.65\,mol\,dm^{-3}$.

Table 9
Epoxidation of linaool (**20**) by the "H_2O_2–complex **1**–oxalic acid" system[a]

Entry	Time (min)	**20**	Products ($mol\,dm^{-3}$)	
			21	**22**
1	5	0.234	0.006	0.000
2	10	0.231	0.008	0.003
3	15	0.235	0.008	0.002
4	30	0.194	0.018	0.005
5	60	0.141	0.034	0.008
6	120	0.044	0.048	0.007
7	180	0.047	0.046	0.003

[a] Reactions at 25 °C; H_2O_2 (30% aqueous), $0.65\,mol\,dm^{-3}$; linalool, $0.25\,mol\,dm^{-3}$; catalyst **1**, $5 \times 10^{-5}\,mol\,dm^{-3}$; oxalic acid, $0.025\,mol\,dm^{-3}$. Yield of a sum of both isomeric epoxides (based on starting linalool) was 22% after 2 h.

4. Conclusions

Under the action of the catalytic system described in this paper the processes of the alkane oxidation and dioxygen evolution on the one hand and of the olefin epoxidation on the other hand are induced by different intermediate species. The system is useful for efficient epoxidation of sterically accessible olefins, including natural compounds.

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