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Peroxyacetic Acid Oxidation of Olefins and Alkanes Catalyzed by a Dinuclear Manganese(IV) Complex with 1,4,7-trimethyl-1,4,7-triazacyclononane

Dalmo Mandelli · Yuriy N. Kozlov · Camilla C. Golfeto · Georgiy B. Shul'pin

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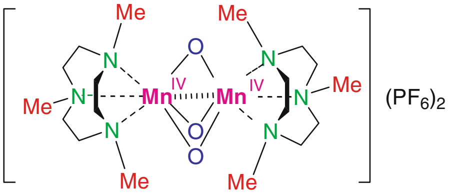
Abstract Natural terpenes, (–)-limonene and (+)-carvone, can be epoxidized by peroxyacetic acid (PAA) at room temperature if a dinuclear manganese(IV) complex with 1,4,7-trimethyl-1,4,7-triazacyclononane (L), $[Mn_2L_2O_3][PF_6]_2$, is used as a catalyst. The total yield of the epoxides based on the consumed olefins are 97 and 95%, respectively. A kinetic study of the dec-1-ene and cyclohexane oxygenations including the investigation of their simultaneous competitive oxidation was carried out. The olefin epoxidation rate does not depend on dec-1-ene concentration and the dec-1-ene concentration does not affect the rate of cyclohexane oxidation. The cyclohexane oxidation rate is proportional to the alkane concentration. The kinetic analysis led to the conclusion that two species X_1 and X_2 are generated in the system, and there is no their mutual interconversion. The rate equation for the dec-1-ene epoxidation was proposed: $W = k_{+1}[cat][\mathrm{PAA}]$, where *cat* is the initial manganese complex or its derivative, and the constant was determined: $k_{+1} = 3.5\ \mathrm{mol^{-1}\ dm^3\ s^{-1}}$. Species X_1 is apparently an effectively epoxidizing manganese peroxo derivative whereas species X_2 is an alkane hydroxylating manganese oxo complex.

Keywords Alkanes · Alkyl hydroperoxides · Carvone · Epoxidation · Homogeneous catalysis · Limonene · Manganese complexes · Olefins · Oxidation · Peroxyacetic acid · Terpenes

1 Introduction

Peroxy acids are known to oxidize olefins [1–3] and alkanes [4–7]. Metal complexes significantly accelerate such processes: olefin epoxidation [8–12] and alkane hydroperoxidation and hydroxylation [13–27]. Earlier we have demonstrated that synthesized and characterized by Wieghardt et al. [28] a dinuclear manganese(IV) complex with 1,4,7-trimethyl-1,4,7-triazacyclononane (complex **1**), is a very efficient catalyst for oxidation of alkanes, olefins, alcohols and sulphides by hydrogen peroxide in the presence of a carboxylic acid as a co-catalyst [15, 16, 29–38]. Usually acetonitrile was used as a solvent and acetic or oxalic acids played the role of the co-catalyst. Compound **1** is also known to catalyze some other oxidations (see reviews [39, 40]). This compound catalyzes bleaching of stains with hydrogen peroxide [41]. It has been recently shown that absorbed on the cotton surface compound **1** exhibits catalase activity [42]. Peroxy acids were also employed as oxidizing reagents in alkane reactions catalyzed by compound **1** [15, 16].



Complex **1**

In the present work, we studied for the first time epoxidation of natural terpenes (limonene and carvone) as well

D. Mandelli · C. C. Golfeto
Faculdade de Química, Pontifícia Universidade Católica de Campinas, Campus I, Rod. D. Pedro I, km 136, Pq. das Universidades, Campinas, SP 13086-900, Brazil

Y. N. Kozlov · G. B. Shul'pin (✉)
Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina 4, Moscow 119991, Russia
e-mail: gbsh@mail.ru

as dec-1-ene by peroxyacetic acid (PAA) under catalysis with complex **1**. The epoxidation and other oxidative transformations of terpenes [43–47] are the important processes from a practical viewpoint because the products are valuable starting materials for the synthesis of fragrances and drugs [48–50]. Molecular oxygen, hydrogen peroxide and TBHP as well have been used as an oxidizing reagent in epoxidations of olefins including terpenes (see reviews [51–53] and recent original papers [54–66]). In order to get additional mechanistic insight we carried out also a kinetic study of the competitive oxidation of dec-1-ene and cyclohexane.

2 Experimental

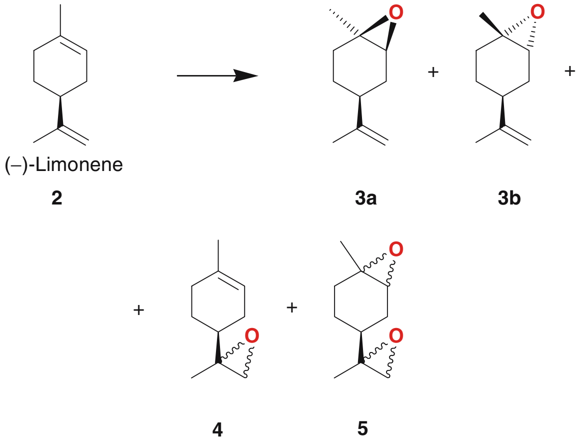
For synthesis and properties of catalyst **1**, see [28]. Peroxyacetic acid (32% solution in acetic acid, “Aldrich”), (–)-limonene, **2**, (“Aldrich”) (+)-carvone, 6; dec-1-ene and cyclohexane (“Fluka”) were used as received. The experiments on olefin oxidations were carried out in MeCN at 25 °C in thermostated Pyrex cylindrical vessels (total volume 12 mL) with vigorous stirring. The total volume of the reaction solution was 5 mL. In a typical experiment, initially, a portion of the PAA solution in acetic acid was added to the solution of the catalyst and terpene in acetonitrile. Nitromethane was used as internal standard for quantification by gas chromatography (GC) analysis. After certain time intervals, samples (about 0.2 mL) were taken, the reaction was typically quenched by addition of solid PPh_3 to reduce an excess of PAA. The concentrations of the terpene epoxide and starting terpene were determined by GC (the ‘HP Series 6890’ instrument; column Hewlett-Packard; the stationary phase was polyethyleneglycol: INNOWAX with parameters 25 m × 0.2 mm × 0.4 μm; carrier gas was N_2 with column pressure of 15 psi). Authentic samples of the epoxides were used to attribute the peaks in chromatograms (comparison of retention times was carried out for different regimes of GC-analysis).

In order to determine 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 measuring concentrations of cyclohexanol and cyclohexanone. 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 [67–76] 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. However, in many experiments on cyclohexane oxygenation and 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 ‘HP Series 5890-II’ instrument was used in this analysis, column Carbowax 20 M, 25 m × 0.2 mm × 0.2 μm; nitrogen as a carrier gas.

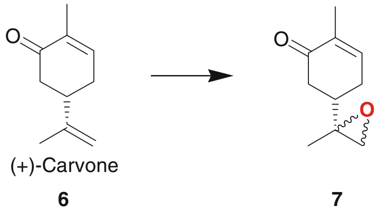
3 Results and Discussion

3.1 Epoxidation of Terpenes

Epoxidation of (–)-limonene, **2**, by peroxyacetic acid (PAA) in the presence of a catalytic amount of complex **1** at room temperature gives rise to the formation of a few products: isomeric internal epoxides **3a** and **3b**, isomers of external epoxide **4** and isomers of diepoxide **5**. The isomer distribution with time is shown in Table 1. It can be seen that diepoxide **5** appears in the reaction mixture only after 15 min, and its highest concentration was attained after 60 min. After this time the total yield of all identified products was 73%.



In the epoxidation of (+)-carvone, **6**, only isomer **7** has been detected, and after 60 min complete consumption of **6** was found (Table 2). The yield of **7** was 85% after 30 min, however some over-oxidation occurred and the concentration of **7** decreased.



Thus, it can be concluded that the system under the discussion can be employed for the epoxidation of natural

Table 1 Epoxidation of (–)-limonene by PAA catalyzed with complex **1**[a]

Time, min	Concentration, mol dm^{-3}					
	2	**3a**	**3b**	**4**	**5**	Total
0	0.125	0	0	0	0	0.125
5	0.121	0.0007	0.0027	0.0065	0	0.124
10	0.106	0.0078	0.0084	0.0065	0	0.129
15	0.073	0.0205	0.015	0.0017	0.0045	0.115
30	0.031	0.029	0.020	0.023	0.019	0.122
60	0.020	0.025	0.021	0.021	0.024	0.111

[a] Conditions: (–)-Limonene (**2**), 0.125 mol dm^{-3}; PAA, 0.72 mol dm^{-3}; complex **1**, 5 × 10^{-5} mol dm^{-3}; 25 °C; solvent acetonitrile. The epoxide concentration was measured after quenching the reaction with PPh_3

Table 2 Epoxidation of (+)-carvone by PAA catalyzed with complex **1**[a]

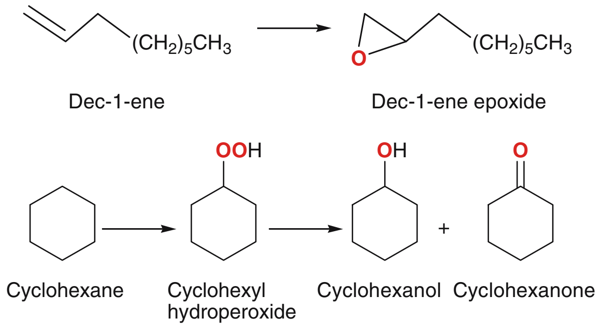
Time, min	Concentration, mol dm^{-3}	
	6	**7**
0	0.127	0
5	0.126	0
10	0.110	0.013
15	0.064	0.062
30	0.013	0.108
60	0	0.087

[a] Conditions: (+)-Carvone (**6**), 0.127 mol dm^{-3}; PAA, 0.72 mol dm^{-3}; complex **1**, 5 × 10^{-5} mol dm^{-3}; 25 °C; solvent acetonitrile. The epoxide concentration was measured after quenching the reaction with PPh_3

terpenes. The yield of products and selectivity is higher in the case of (+)-carvone in comparison with (–)-limonene.

3.2 A Kinetic Study

We studied the epoxidation of dec-1-ene in more detail in order to get some understanding of the mechanism. It was fruitful to carry out the comparative study of the cyclohexane, CyH, oxidation and the competitive simultaneous oxidation of dec-1-ene and cyclohexane.



The kinetic data obtained when the catalyst, substrate and PAA are mixed within a short period of time demonstrate that maximum stationary rates of consumption of the olefins, the epoxide formation from these olefins as well as the formation of oxygenates from the cyclohexane are attained in few minutes after mixing the reagents. Apparently the more active form of the catalyst is formed in the interaction of **1** with PAA during the first few minutes after mixing the reagents. This conclusion is supported by the fact that when the substrate is introduced into the mixture of **1** with PAA (prepared a few minutes before this introduction) we notice in the kinetic curves of the product formation the substantial shortening of the time period which is necessary to attain the stationary process rate. In the following analysis, we operated with 'initial reaction rates' which are maximum stationary rates of product accumulation attained in a few minutes after mixing the reagents. In this work, we studied the dependences of initial reaction rates on initial concentrations of various reactants. Figure 1 demonstrates the kinetics of the epoxide formation in the reaction with dec-1-ene and Figs. 2 and 3 show dependences of initial rates on concentrations of catalyst **1** and PAA in this process. The corresponding kinetic curves and dependences for the oxidation of cyclohexane are depicted in Figs. 4–6. The accumulation of all oxygenates in the simultaneous competitive oxidation of a mixture of dec-1-ene and cyclohexane is presented in Fig. 7. Finally, Figs. 8 and 9 demonstrate the dependences of initial rates in such competitive oxidations on the initial concentrations of dec-1-ene and cyclohexane, respectively.

The decrease of the reaction rates of both dec-1-ene epoxidation and cyclohexane oxidation in the course of the reactions is due not only to the consumption of PAA and the substrate but also to the partial deactivation of the catalyst. Indeed, we have found that if after the epoxidation has deceased to add to the reaction mixture new portions (in the initial concentrations) of PAA and the olefin the reaction starts again but with somewhat lower rate.

Maximum epoxidation rates of the studied olefins under identical conditions are comparable and do not depend on the initial olefin concentration in its concentration interval

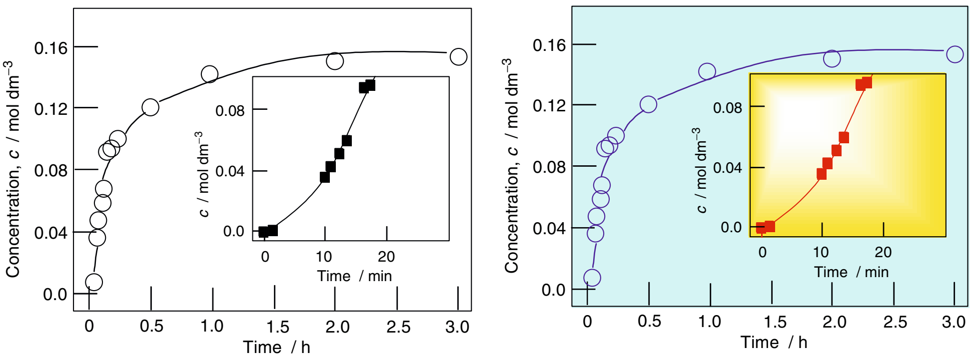


Fig. 1 Accumulation of dec-1-ene epoxide in dec-1-ene (0.25 mol dm^{-3}) epoxidation in MeCN at 25 °C with PAA (0.72 mol dm^{-3}) catalyzed by complex **1** (5×10^{-5} mol dm^{-3}). The epoxide concentration was measured after quenching the reaction with PPh_3

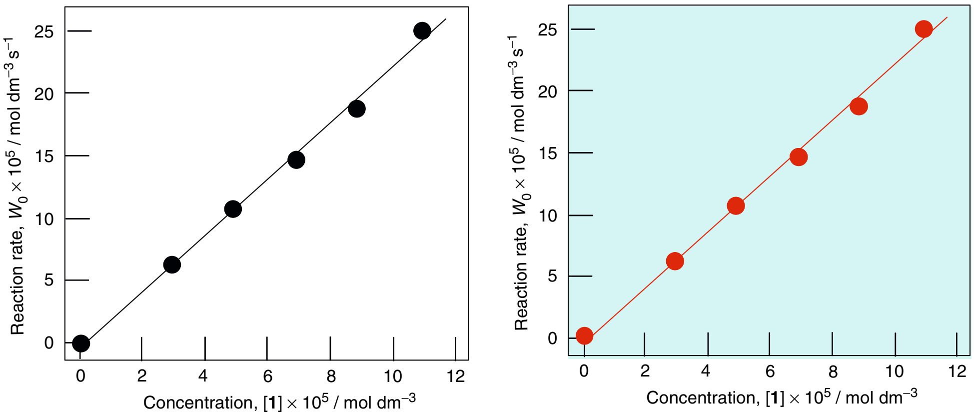


Fig. 2 Initial rates of the dec-1-ene epoxide formation versus concentration of catalyst **1** in dec-1-ene (0.25 mol dm^{-3}) oxidation in MeCN at 25 °C with PAA (0.48 mol dm^{-3})

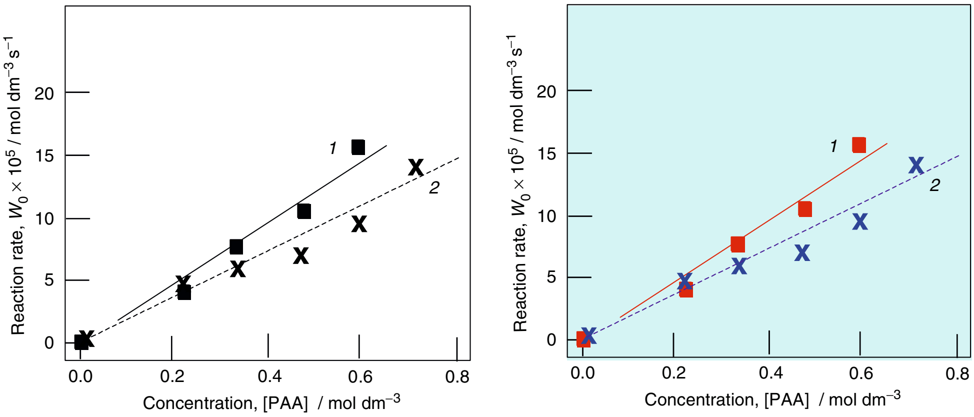


Fig. 3 Initial rates of the formation of dec-1-ene epoxide versus initial concentration of PAA in dec-1-ene oxidation in MeCN at 25 °C catalyzed with **1** (5×10^{-5} mol dm^{-3}). Curve 1: PAA was used as 32% solution in acetic acid, and the PAA concentration increased simultaneously with the increase in the concentration of acetic acid; initial concentration of dec-1-ene was 0.25 mol dm^{-3}. Curve 2: acetic acid was added in each experiment to maintain the constant concentration (1.53 mol dm^{-3}) of acetic acid; initial concentration of dec-1-ene was 0.125 mol dm^{-3}

0.05–0.5 mol dm^{-3}. This means that an epoxidizing species is generated in the course of the interaction of the catalyst with PAA. The olefin does not take part in this step; its role is to accept all epoxidizing species generated in the process. The cyclohexane oxidation rate under identical conditions is a few times lower than the dec-1-ene epoxidation rate. The former—unlike the epoxidation rate—is proportional to the initial concentration of cyclohexane.

The data presented in Tables 1 and 2 demonstrate that up to 75% conversion of limonene and carvone the epoxides are the main products of their oxidation. The total yield of the epoxides based on the consumed olefin are 97 and 95%, respectively. The decrease of the epoxide yields after relatively long period of the reaction is apparently due to over-oxidation of the epoxides. This 'deep' oxidation can be occurred by species that are

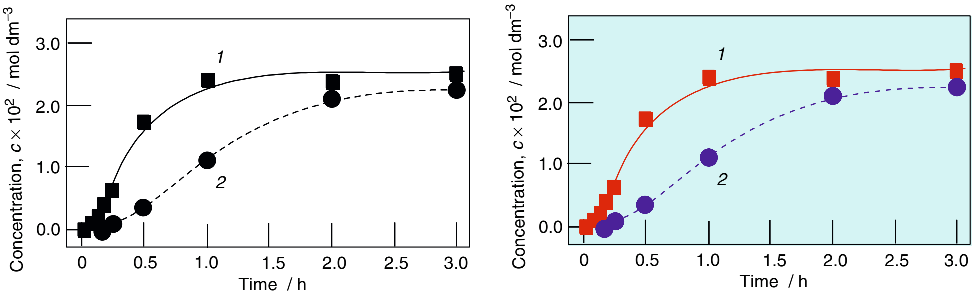


Fig. 4 Cyclohexane (0.23 mol dm^{-3}) oxidation in MeCN at 25 °C with PAA (0.72 mol dm^{-3}) catalyzed complex **1** (5 × 10^{-5} mol dm^{-3}). Concentrations of cyclohexanol (curve 1) and cyclohexanone (curve 2) were measured (as in all other experiments) after reduction of the reaction mixture with PPh_3

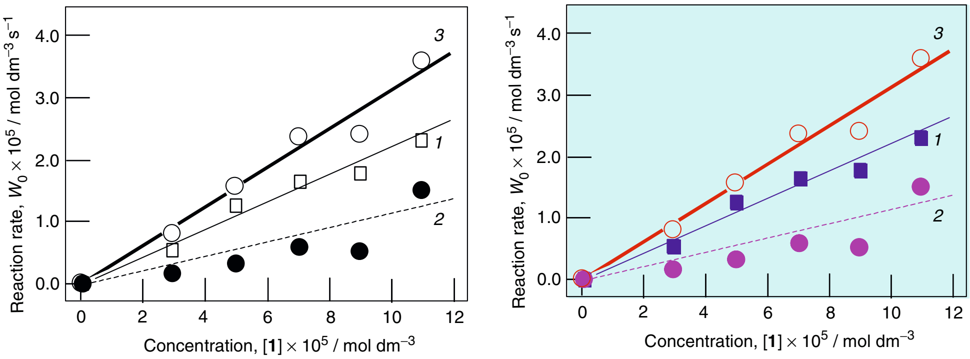


Fig. 5 Initial rates of the formation of cyclohexanol (curve 1), cyclohexanone (curve 2) and their sum (curve 3) versus concentration of **1** in the cyclohexane (0.23 mol dm^{-3}) oxidation in MeCN at 25 °C with PAA (0.72 mol dm^{-3})

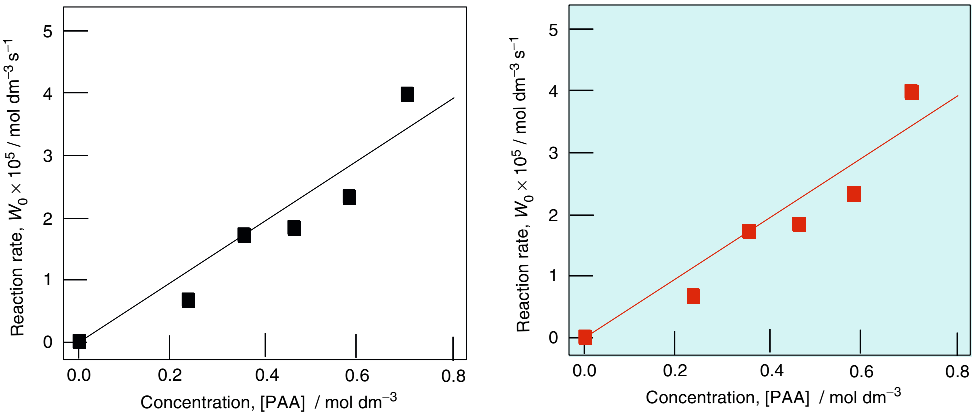


Fig. 6 Initial rates of the formation of cyclohexanone and cyclohexanol (sum) versus initial concentration of PAA in the cyclohexane (0.23 mol dm^{-3}) oxidation in MeCN at 25 °C catalyzed with **1** (5 × 10^{-5} mol dm^{-3}). Acetic acid was added in each experiment to maintain the constant concentration (1.53 mol dm^{-3}) of acetic acid

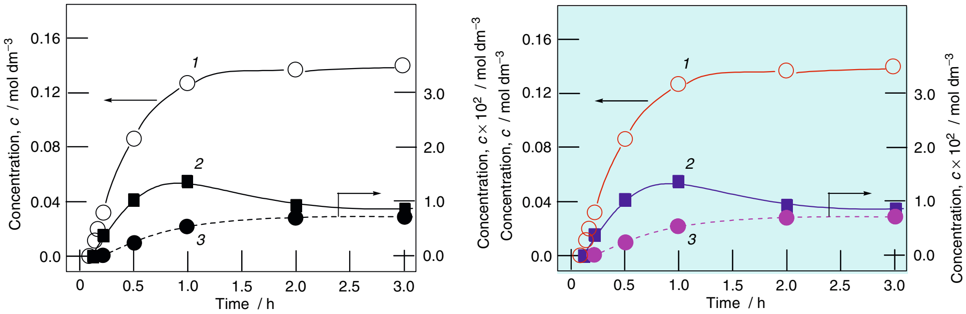


Fig. 7 Accumulation of dec-1-ene epoxide (curve 1), cyclohexanol (curve 2) and cyclohexanone (curve 3) in the competitive oxidation of dec-1-ene (0.25 mol dm^{-3}) and cyclohexane (0.23 mol dm^{-3}) in MeCN at 25 °C with PAA (0.36 mol dm^{-3}) catalyzed by complex **1** (5 × 10^{-5} mol dm^{-3})

capable of oxidizing alkanes. The long-chain dec-1-ene bears more C–H bonds that limonene and carvone, and the oxidation of methylene groups in this linear olefin gives rise in this case to the lower yield of the corresponding epoxide. This assumption is supported by the fact that at the lower PAA concentration in the presence of cyclohexane the oxidation of dec-1-ene gives the same yield of the epoxide (Fig. 7) as in the case when two times higher concentration of PAA is used but in the absence of cyclohexane (Fig. 1).

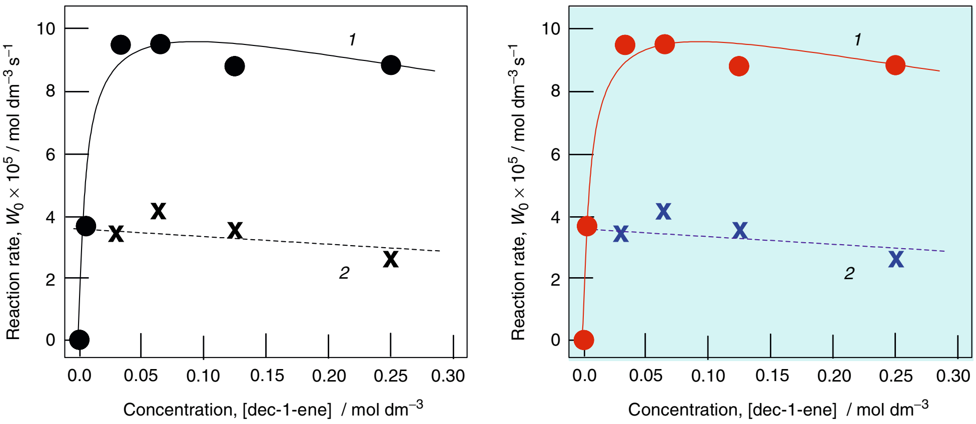


Fig. 8 Competitive oxidation of dec-1-ene and cyclohexane (0.23 mol dm^{-3}). Initial rates of the formation of dec-1-ene epoxide (curve 1) and a sum of cyclohexanone and cyclohexanol (curve 2) versus concentration of dec-1-ene in the oxidation by PAA (0.72 mol dm^{-3}) in MeCN at 25 °C catalyzed with **1** (5 × 10^{-5} mol dm^{-3})

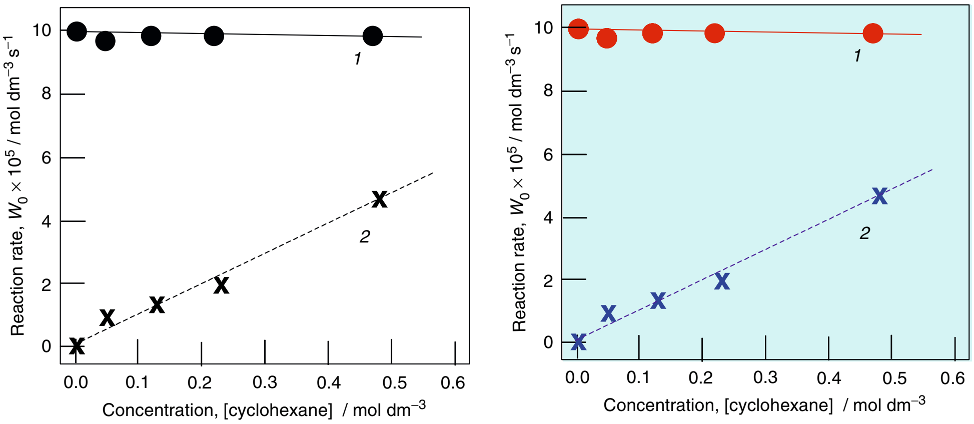


Fig. 9 Competitive oxidation of dec-1-ene (0.25 mol dm^{-3}) and cyclohexane. Initial rates of the formation of dec-1-ene epoxide (curve 1) and a sum of cyclohexanone and cyclohexanol (curve 2) versus concentration of cyclohexane in the oxidation by PAA (0.72 mol dm^{-3}) in MeCN at 25 °C catalyzed with **1** (5 × 10^{-5} mol dm^{-3})

As both dec-1-ene and cyclohexane can be oxidized by the system under discussion and the rates of oxidations are proportional to the concentrations of PAA (Figs. 3, 6) and catalyst **1** (Figs. 2, 5) a question arises if both these reactions could occur via the formation of the same oxidizing species. To get insight into this problem we studied the effect of (i) different concentrations of cyclohexane on the dec-1-ene epoxidation rate (at [dec-1-ene]$_0$ = 0.25 mol dm^{-3}) and (ii) different concentration of dec-1-ene on the cyclohexane oxidation rate (at [cyclohexane]$_0$ = 0.23 mol dm^{-3}) in competitive transformations of both hydrocarbons (Figs. 8, 9). We have found that addition of cyclohexane does not affect the rate of the dec-1-ene epoxide accumulation and addition of dec-1-ene only negligibly decreases the rate of oxygenates formation from cyclohexane. Thus we can conclude that the olefin epoxidation and the alkane oxidation are induced by different oxidizing species X_1 and X_2, respectively. The formation process of X_1 and X_2 *do not* include the steps of their interconversion, $X_1 \rightleftharpoons X_2$. This conclusion is a bit different from the assumption of Banfi et al. [11] who studied olefin epoxidation and arene hydroxylation with PAA catalyzed by manganese phthalocyanine complexes. If species X_1 and X_2 were generated in the consecutive interconversions (for example, as it has been assumed in [11] where the hydroxylating species was derived from the epoxidizing one), the additive of dec-1-ene which accepts all formed species X_1 would substantially suppress the cyclohexane oxidation due to the decrease of the stationary concentration of species X_2. Since this is in contradiction with our experimental data (Fig. 8) we have to assume that X_1 and X_2 are generated in two independent parallel routes.

A simple mechanism which satisfactorily describes our experimental data is the following one:

$$cat + \mathrm{PAA} \rightleftharpoons X_1 \quad K_1 = k_{+1}/k_{-1} \tag{1}$$

$$cat + \mathrm{PAA} \rightleftharpoons X_2 \quad K_2 = k_{+2}/k_{-2} \tag{2}$$

$$X_1 + \text{dec-1-ene} \rightarrow \text{dec-1-ene epoxide} + cat \quad k_3 \tag{3}$$

$$X_2 + \mathrm{MeCN} \rightarrow \text{products of MeCN oxidation} + cat \quad k_4 \tag{4}$$

$$X_2 + \mathrm{CyH} \rightarrow \mathrm{CyOOH} + cat \quad k_5 \tag{5}$$

$$X_2 + \text{dec-1-ene} \rightarrow \text{products of } \mathrm{CH_2}\text{oxidation in dec-1-ene} + cat \quad k_6 \tag{6}$$

Here *cat* is complex **1** or its derivative.

For reactions 3–6, in the left parts of the equations, the reactants that take part in rate-limiting transformations are written. In the right parts of these equations, the main reaction products are given. These products, generally speaking, can be obtained as a result of the consequence of transformations with the rates limited by transformations shown in the left parts of the equations.

Assuming that concentrations of species X_1 and X_2 are quasi-stationary, that is the rates of reverse reactions (–1) and (–2) are much lower than the rates of reaction (3) and a sum of the rates of reactions (4), (5), (6), respectively, we can easily obtain the kinetic equations for the rate dependences on reagent concentrations. In our analysis, we took into account that the rate of reaction (3) is much higher than the rate of reaction (5), $W_3 \gg W_5$, because the epoxidation rate does not depend on dec-1-ene concentration and the dec-1-ene concentration does not affect the rate of cyclohexane oxidation. We considered also the fact that the cyclohexane oxidation rate is proportional to the alkane concentration. The analysis gave rise to the following equations:

$$\frac{\mathrm{d}[\text{Dec-l-ene epoxide}]}{\mathrm{d}t} = k_{+1}[cat][\text{PAA}] \qquad (7)$$

$$\frac{\mathrm{d}[\text{CyOOH}]}{\mathrm{d}t} = \frac{k_5k_{+2}}{k_4[\text{MeCN}]} \times [cat][\text{PAA}][\text{CyH}] \qquad (8)$$

These equations are in good agreement with our experimental data and allow us to determine the following parameters:

$$k_{+1} = 3.5\pm1\text{mol}^{-1}\text{dm}^3\text{s}^{-1} \quad \text{and} \quad \frac{k_5k_{+2}}{k_4[\text{MeCN}]} = 3\pm1\text{mol}^{-1}\text{dm}^6\text{s}^{-1}$$

In accordance with the proposed scheme we can assume that species X_1 is an effectively epoxidizing manganese peroxo derivative (with fragments Mn–OOH or Mn–OO–Mn) whereas species X_2 is an alkane hydroxylating manganese oxo complex (with Mn=O fragment). It should be noted that earlier we proposed that in the "**1**–H_2O_2–carboxylic acid" system, the processes of alkane oxidation and dioxygen evolution on the one hand and of the olefin epoxidation on the other hand are induced by different intermediate species [33].

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