



# Oxidations by the system 'hydrogen peroxide–[Mn<sub>2</sub>L<sub>2</sub>O<sub>3</sub>]<sup>2+</sup> (L = 1,4,7-trimethyl-1,4,7-triazacyclononane)–oxalic acid'. Part 11. Degradation of dye Rhodamine 6G and oxygenation of cyclohexene

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## ABSTRACT

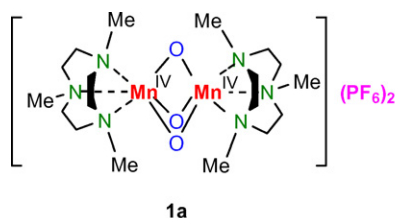
Two dinuclear manganese(IV) compounds, soluble [LMn(O)<sub>3</sub>MnL](PF<sub>6</sub>)<sub>2</sub> (**1a**) and insoluble [LMn(O)<sub>3</sub>MnL]<sub>2</sub>[SiW<sub>12</sub>O<sub>40</sub>] (**1b**) (L is 1,4,7-trimethyl-1,4,7-triazacyclononane, TMTACN) are efficient catalysts in oxidative decoloration of dye Rhodamine 6G and oxygenation of cyclohexene with hydrogen peroxide in acetonitrile or water in the presence of oxalic acid which is an obligatory co-catalyst. It has been concluded on the basis of the detailed kinetic study that both oxidation processes occur with the formation of transient species **D** (which exhibits the properties of a relatively weak radical and is able to abstract the hydrogen atom from C–H bonds of hydrocarbons) and **E** (which is responsible for the cyclohexene epoxidation). Species **D** is probably an oxygen-centered radical containing also manganese ions. Species **E** is apparently an oxoderivative of high-valent manganese. Catalyst **1a** generates predominantly species **E**. When heterogenized catalyst **1b** is used species **D** prevail. As a very intensive dye degradation occurs also in aqueous solution the studied systems can be used for decoloration of pollutants in waste streams.

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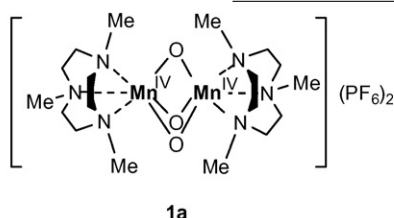
## 1. Introduction

Complexes of transition metals are widely used in catalytic oxidations of hydrocarbons with molecular oxygen and peroxides (see reviews [2] and selected recent original papers [3]). Manganese derivatives are among the most active catalysts in such oxidations [4]. The dinuclear manganese(IV) complex [LMn(O)<sub>3</sub>MnL](PF<sub>6</sub>)<sub>2</sub> (catalyst **1a**; L is 1,4,7-trimethyl-1,4,7-triazacyclononane, TMTACN) [5] and relevant derivatives [6] are efficient catalysts for oxidations of certain organic compounds, such as olefins and phenols as well as for bleaching (see reviews [7] and recent original publications [8]).

Earlier [1] we have found [9a,10a] that compound **1a** catalyzes the oxidation by hydrogen peroxide much more efficiently if a small amount of a carboxylic acid is added to the reaction solution. Further, we demonstrated [9a–g,i,10a,c,f–h,11] that the '1a/carboxylic acid/H<sub>2</sub>O<sub>2</sub>' combination in acetonitrile solution very efficiently oxidizes inert alkanes to afford primarily the corresponding alkyl hydroperoxides which are transformed further into the more stable ketones (aldehydes) and alcohols. It turned out that the system oxidizes not only alkanes but also epoxidizes olefins [9c,e–g,10e,h], transforms alcohols into ketones (aldehydes) [9c,h,10d] and sulfides into sulfoxides [9c]. The reaction with olefins gave rise to the



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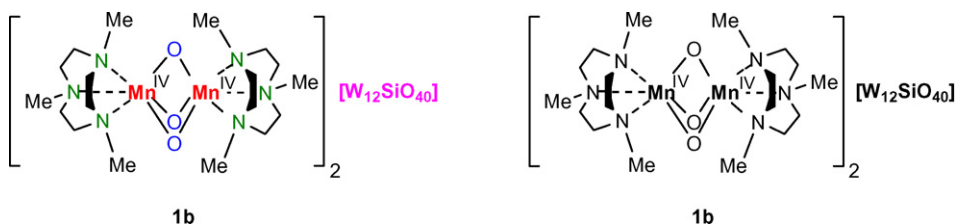
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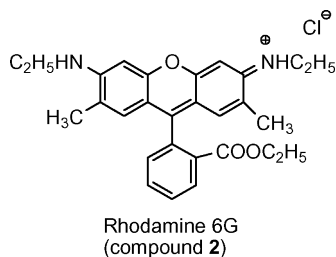
products of dihydroxylation [9e] in addition to the corresponding epoxides. Alkanes [9f], olefins [9f], and alcohols [9h] were oxidized also in the absence of acetonitrile. A relevant soluble polymer-bound Mn(IV) complex with *N*-alkylated 1,4,7-

triazacyclononane was used as a catalyst in the  $\text{H}_2\text{O}_2$  oxygenation of alkanes [10c].

Bosch and Veghini [12] prepared insoluble salt of formula  $[\text{LMn}(\mu\text{-O})_3\text{MnL}]_2[\text{SiW}_{12}\text{O}_{40}]$  (catalyst **1b**) which is an active catalyst in the oxidation of alcohols [9h,12] and olefins [12]. It is important that almost no oxidation reaction can be observed in the absence of a carboxylic acid as a co-catalyst in all cases mentioned above. Recently our '1a/carboxylic acid/ $\text{H}_2\text{O}_2$ ' system has been used by other authors [13] for the *cis*-hydroxylation and epoxidation of olefins. We have also demonstrated that alkanes and olefins can be oxidized by *tert*-butyl hydroperoxide [9c,10b] or peroxyacetic acid [9a,10a,i] using complex **1a** as a catalyst. The reaction with *tert*-butyl hydroperoxide is significantly accelerated in the presence of a small amount of a carboxylic acid [9c,10b]. Mechanisms of oxidation reactions with participation of manganese complexes were discussed in many publications [14].



Continuing the studies of oxidations by our system '1/carboxylic acid/ $\text{H}_2\text{O}_2$ ' we decided to explore a possibility of dye decoloration by this system. We have chosen Rhodamine 6G (**2**) as a substrate for the investigation. Catalytic processes are used for oxidative degradation of toxic and colored pollutants in industrial waste streams [15] and for laundry bleach [16]. Dyes including Rhodamine can be model systems in studies of degradation processes [17]. Rhodamine degradation occurs *via* the formation of free radicals (e.g. peroxy radicals) and two competitive pathways are possible: *N*-dealkylation and the destruction of the conjugated structure [18].



It is also interesting to compare the oxidative degradation of Rhodamine 6G with the cyclohexene oxygenation by the same system. Cyclohexene has two fragments accessible for the attack by catalytically active species (the double bond and relatively weak C–H bonds) and comparison of rates of the epoxidation and C–H bond oxygenation could give valuable information on the nature of the oxidizing species.

## 2. Results and discussion

In the present work, we have studied oxidative degradation of xanthene dye Rhodamine 6G (compound **2**) under the action of the systems based on soluble manganese complex containing  $\text{PF}_6^-$  anions (catalyst **1a**) and heterogenized insoluble catalyst **1b** containing heteropoly anions. Rhodamine 6G (**2**) is a substrate convenient for kinetic measurements because its destruction is followed by the decrease of the characteristic absorption band intensity. This band is a relatively narrow peak with maximum at 520 nm ( $\epsilon = 88,000 \text{ M}^{-1} \text{ cm}^{-1}$ ). The intensity of the band at vari-

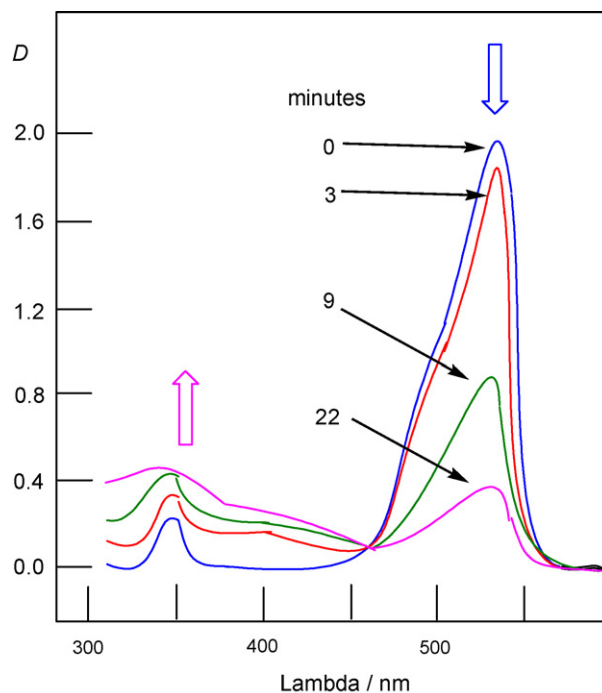
ous time intervals corresponds to the **2** concentration which is still present in the reaction solution (Fig. 1).

### 2.1. Catalysis by soluble compound 1a

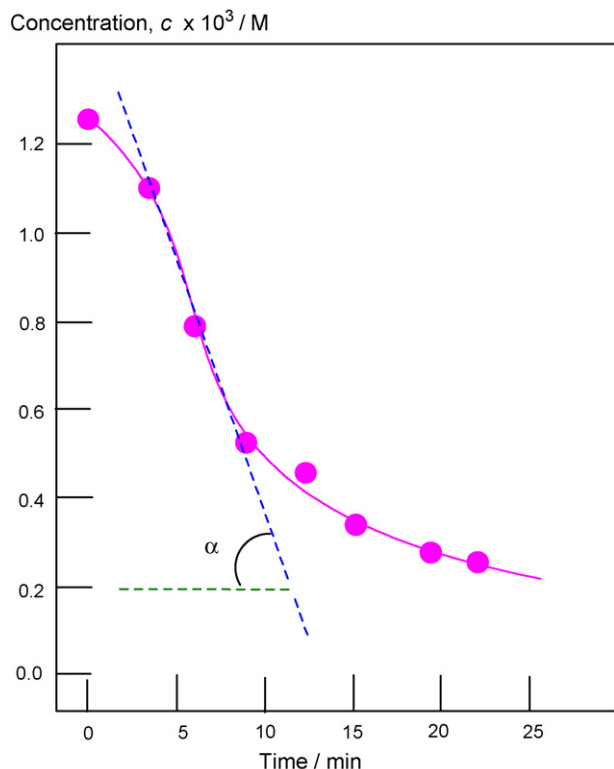
The degradation of **2** under the action of the ' $\text{H}_2\text{O}_2$ –**1a**–oxalic acid' system in acetonitrile occurs with auto-acceleration. In our further discussion we will operate with the maximum Rhodamine 6G consumption rate,  $W_0$ . To measure value  $W_0$  we drew a tangent to the kinetic curve in the region of the most fast **2** consumption (which is simply the gradient of the linear portion of the kinetic curve) as shown in Fig. 2. Tangent of angle  $\alpha$  which is equal to the slope of the linear portion of the kinetic curve gave us value  $W_0$ .

The value of lag phase depends on the conditions used and varied from one to a few minutes. The time period during which

maximum rate is attained (the lag time) does not practically depend on concentrations of the dye and the catalyst but it depends on concentration of oxalic acid. The lag period decreases upon the increase of oxalic acid concentration. We studied also the kinetics of the **2** degradation in the presence of some other carboxylic acids and found that duration of the lag period depends on the nature of the carboxylic acid: it becomes shorter when oxalic acid is used instead of more weak acetic or propionic acids. However the initial decol-



**Fig. 1.** Changes in the absorption spectrum of **2** in the course of its destruction by the ' $\text{H}_2\text{O}_2$ –**1a**–oxalic acid' system in acetonitrile. Conditions:  $[\mathbf{2}]_0 = 1.25 \times 10^{-3} \text{ M}$ ,  $[\text{catalyst } \mathbf{1a}] = 5 \times 10^{-5} \text{ M}$ ,  $[\text{oxalic acid}] = 5 \times 10^{-2} \text{ M}$ ,  $[\text{H}_2\text{O}_2]_0 = 0.1 \text{ M}$ ,  $23^\circ \text{C}$ . The reaction solution was diluted by 50 times with water before the spectrophotometrical analysis ( $l = 1 \text{ cm}$ ).

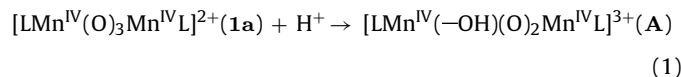


**Fig. 2.** A kinetic curve for the destruction of **2** by the 'H<sub>2</sub>O<sub>2</sub>-**1a**-oxalic acid' system in acetonitrile. Conditions: [**2**]<sub>0</sub> = 1.25 × 10<sup>-3</sup> M, [catalyst **1a**] = 5 × 10<sup>-5</sup> M, [oxalic acid] = 5 × 10<sup>-2</sup> M, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 0.1 M, 23 °C.

oration rates have been measured approximately equal for the three acids. These facts allow us to assume, as we proposed in our previous work [10j], that the lag period is due to the process of the formation of a catalytically active species. It should be noted that despite generally oxalic acid is a reducing agent the role of this compound in our system under conditions described above is the role of acid only. In accordance with this statement we have demonstrated previously [10j] that the formation of the catalytically active species is very slow under the action of only oxalic acid.

We studied dependences of rates  $W_0$  on initial concentrations of the reactants, viz. oxalic acid, catalyst **1a**, hydrogen peroxide, and substrate **2** (Figs. 3–6). In addition, the effects of various additives (hydrocarbons, ionol) were investigated (Figs. 7–9). All these primary experimental data allowed us to propose the mechanistic scheme of the dye decoloration which is in agreement with all measures of kinetic parameters.

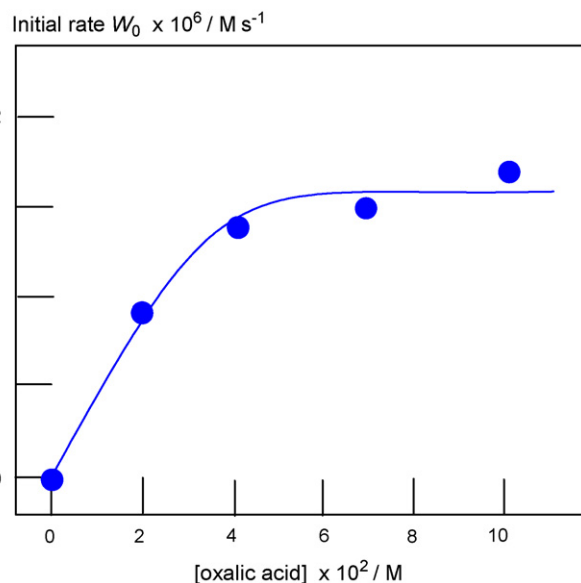
We assume that the initial molecule **1a** under the action of the proton from the oxalic acid is transformed into a new complex in which at least one of three oxobridges is protonated and the valent states of the two manganese ions as previously:



Further, in a non-rate-limiting stage the protonated species **A** is reduced with the hydrogen peroxide molecule to afford species **B** which is a mixed-valent dimeric complex:

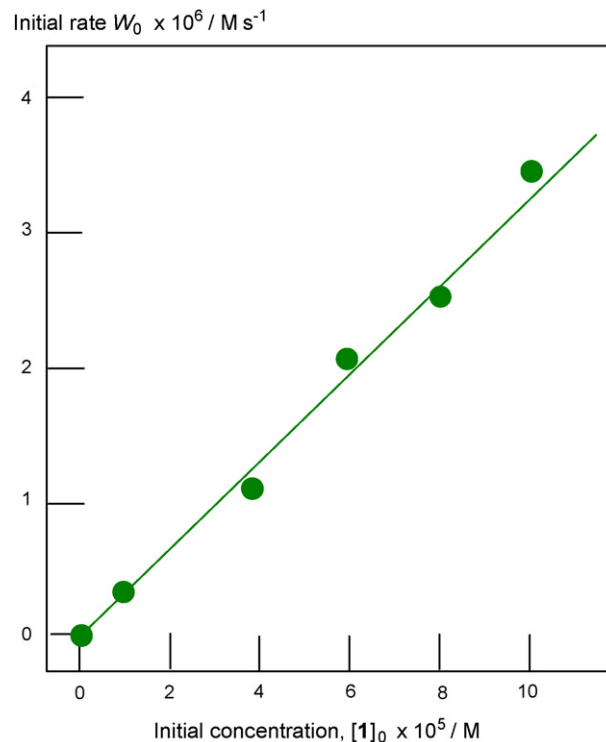
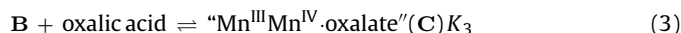


We conventionally depict species **B** as “Mn<sup>III</sup>Mn<sup>IV</sup>” because its structure is unknown. It can be, for example ion [LMn<sup>III</sup>(-OH)(O)<sub>2</sub>Mn<sup>IV</sup>L]<sup>2+</sup>. Species **B** is generated in stages (1) and (2) during the lag period (see Fig. 2).

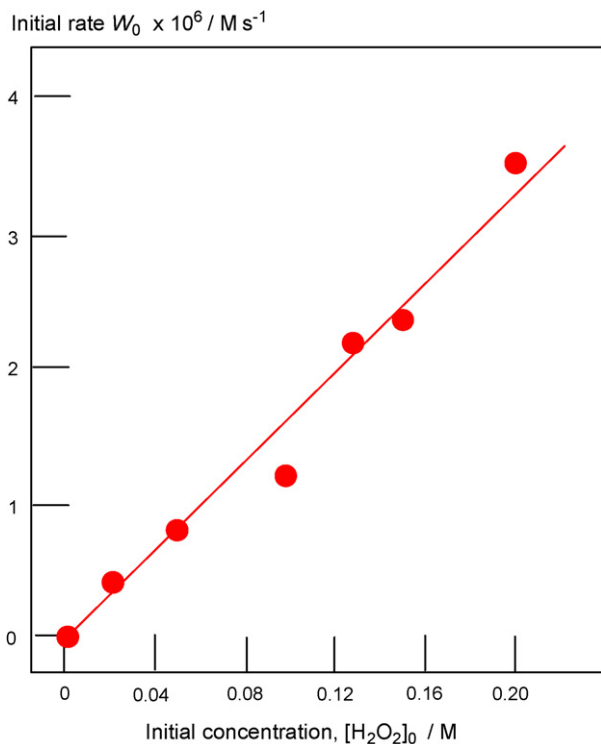


**Fig. 3.** Dependence of reaction rate of the **2** destruction by the 'H<sub>2</sub>O<sub>2</sub>-**1a**-oxalic acid' system on concentration of oxalic acid. Conditions: [**2**]<sub>0</sub> = 2.5 × 10<sup>-3</sup> M, [catalyst **1a**] = 5 × 10<sup>-5</sup> M, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 0.1 M, 23 °C, solvent was acetonitrile.

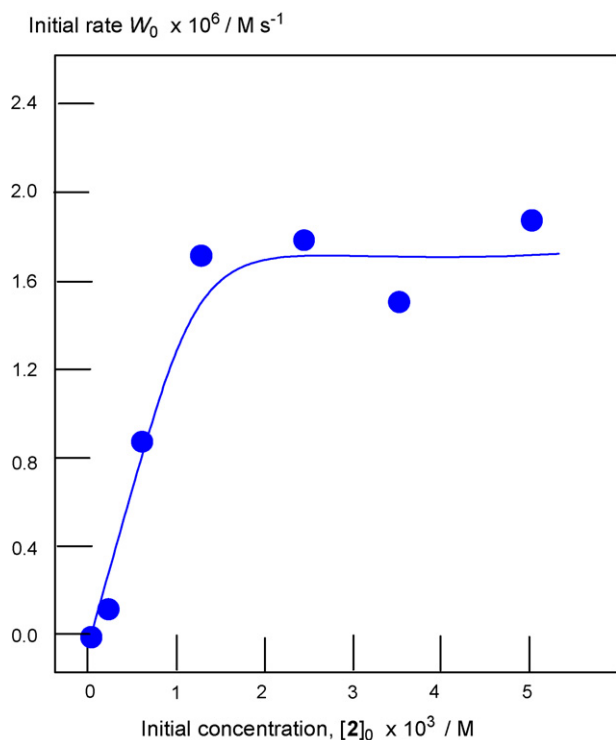
It can be seen in Fig. 3 that at [oxalic acid] > 0.04 M the rate  $W_0$  does not more depend on the oxalic acid concentration. This is the situation typical for the formation (at the stationary phase of the decoloration process) of a complex between species **B** and the oxalic acid. This complex **C** contains apparently the oxalate anion and we will depict it conventionally as “Mn<sup>III</sup>Mn<sup>IV</sup> oxalate”:



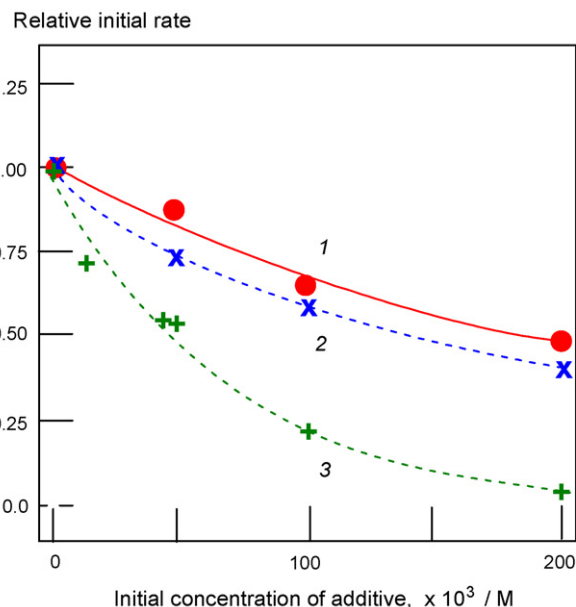
**Fig. 4.** Dependence of the **2** degradation rate on concentration of **1a** in the oxidation by the 'H<sub>2</sub>O<sub>2</sub>-**1a**-oxalic acid' system. Conditions: [**2**]<sub>0</sub> = 2.5 × 10<sup>-3</sup> M, [oxalic acid] = 5 × 10<sup>-2</sup> M, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 0.125 M, 23 °C, solvent was acetonitrile.



**Fig. 5.** Dependence of the **2** destruction rate on concentration of hydrogen peroxide in the oxidation by the 'H<sub>2</sub>O<sub>2</sub>-**1a**-oxalic acid' system. Conditions: [2]<sub>0</sub> = 2.5 × 10<sup>-3</sup> M, [oxalic acid] = 5 × 10<sup>-2</sup> M, [1a]<sub>0</sub> = 5 × 10<sup>-5</sup> M, 23 °C, solvent was acetonitrile.



**Fig. 6.** Dependence of the **2** consumption rate on concentration of **2** in the oxidation by the 'H<sub>2</sub>O<sub>2</sub>-**1a**-oxalic acid' system. Conditions: [1a]<sub>0</sub> = 5 × 10<sup>-5</sup> M, [oxalic acid] = 5 × 10<sup>-2</sup> M, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 0.1 M, 23 °C, solvent was acetonitrile.



**Fig. 7.** Dependence of the relative rate of consumption **2** on concentration of additives, benzene (curve 1), *n*-heptane (curve 2) and cyclohexene (curve 3), in the oxidation by the 'H<sub>2</sub>O<sub>2</sub>-**1a**-oxalic acid' system. Conditions: [1a]<sub>0</sub> = 5 × 10<sup>-5</sup> M, [oxalic acid]<sub>0</sub> = 5 × 10<sup>-2</sup> M, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 0.125 M, 23 °C, solvent was acetonitrile.

Complex **C** is the species which was called above as "a catalytically active species". This complex is involved into the catalytic cycle which affords dye-oxidizing species.

The curve with a plateau in Fig. 3 corresponds to the extent of the transformation of initial complex **1a** (via **A** and **B**) into species **C**. In accordance with Eq. (3) and taking into account that [B]<sub>0</sub> = [1a]<sub>0</sub> we will obtain at [oxalic acid]<sub>0</sub> » [1a]<sub>0</sub> the following ratio:

$$[C] = \frac{K_3[1a]_0[\text{oxalic acid}]_0}{1 + K_3[\text{oxalic acid}]_0} \quad (4)$$

where index "0" means that we consider initial concentrations of the reagents which correspond to the concentrations at the moment of the reaction mixture formation. It follows from Eq. (4) that the reaction rate is proportional to initial catalyst concentration [1a]<sub>0</sub>. Indeed, we have detected this proportionality experimentally (Fig. 4).

The data shown in Fig. 3 allow us to estimate the effective equilibrium constant for the formation of species **C**. This constant  $K_3$  estimated from the value of the half-effect, i.e. from the condition

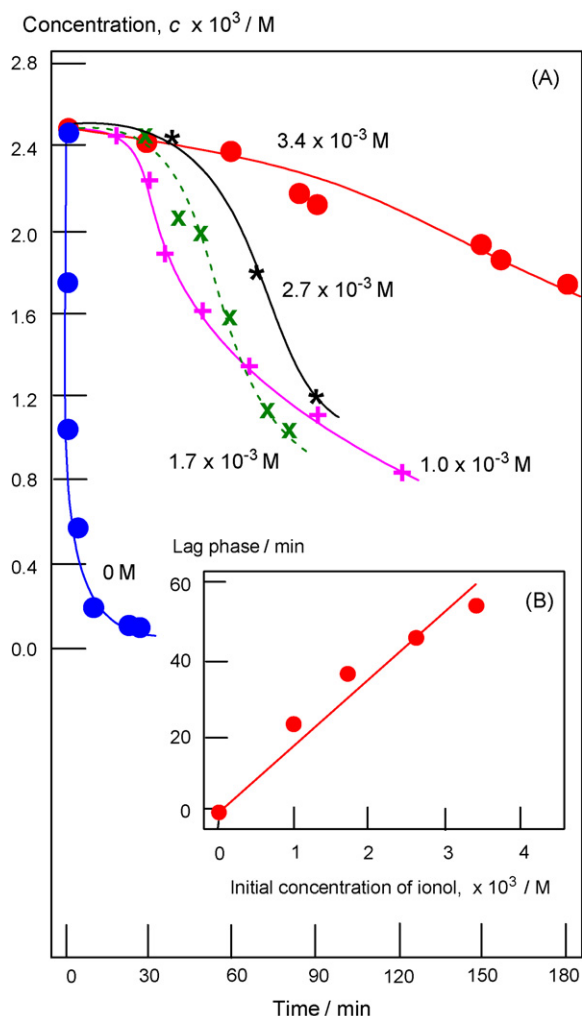
$$1 = K_3[\text{oxalic acid}]_0 \quad (5)$$

is equal to 50 M<sup>-1</sup>. The half-effect value is in this case one half of the maximum attained value of species **C** concentration.

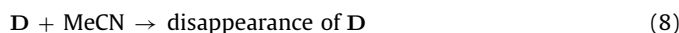
Fig. 5 demonstrates dependence of the dye decoloration rate on initial hydrogen peroxide concentration. The proportionality between  $W_0$  and [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> testifies that the rate-limiting step of the process is bimolecular interaction of the hydrogen peroxide with species **C**.

Dependence of the decoloration rate on the dye **2** initial concentration is shown in Fig. 6. A plateau in the region 10<sup>-3</sup> < [2]<sub>0</sub> < 5 × 10<sup>-3</sup> M can be explained by the following way. This explanation is based on the assumption that the dye oxidation is a result of its interaction in the solution volume with an intermediate species **D** generated in the reaction between **C** and H<sub>2</sub>O<sub>2</sub>. Some additional routes for the disappearance of **D** can exist, for example the interaction of **D** with acetonitrile shown by Eq. (8).



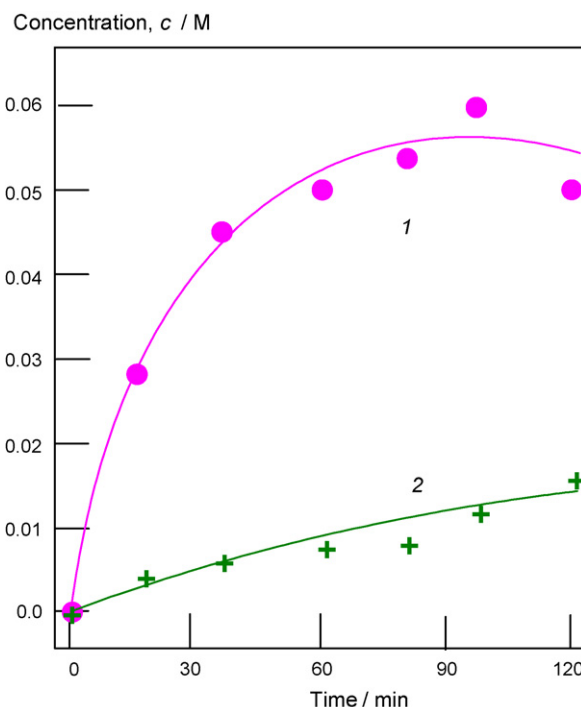


**Fig. 8.** Graph A. Kinetic curves for the destruction of **2** by the ' $\text{H}_2\text{O}_2$ -**1a**-oxalic acid' system in acetonitrile in the presence of ionol in different concentrations (shown in the graph). Conditions:  $[\mathbf{2}]_0 = 2.5 \times 10^{-3}$  M,  $[\text{catalyst } \mathbf{1a}]_0 = 5 \times 10^{-5}$  M,  $[\text{oxalic acid}]_0 = 5 \times 10^{-2}$  M,  $[\text{H}_2\text{O}_2]_0 = 0.125$  M,  $23^\circ\text{C}$ , solvent was acetonitrile. Graph B. Dependence of the lag phase duration in the **2** consumption on concentration of added ionol in the oxidation by the ' $\text{H}_2\text{O}_2$ -**1a**-oxalic acid' system under conditions shown for Graph A.



In this case the fact that the **2** degradation rate does not depend on its concentration (see Fig. 6) is due to the situation when all transient species **D** interact with the dye.

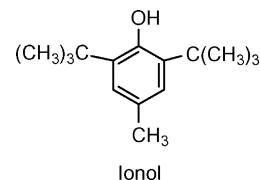
In order to get additional insight into the nature of the oxidizing species and evaluate the mechanism of the process we studied the decoloration process in the presence of certain hydrocarbons: benzene, *n*-heptane and cyclohexene. The former two compounds would not be expected to coordinate with high-valent manganese species. Earlier we have demonstrated that both hydrocarbons are oxidized by the system under discussion. It means that they do interact with a transient oxidizing species generated in the catalytic system. In contrast to the cases of benzene and *n*-heptane, unsaturated cyclohexene can be both epoxidized and  $\alpha$ -hydroperoxidized due to the presence in its molecule both the double bond and activated  $\text{CH}_2$  groups. Therefore, cyclohexene is a convenient substrate to indicate the presence or absence in the catalytic system C–H-oxidizing and epoxidizing species. It should be emphasized that



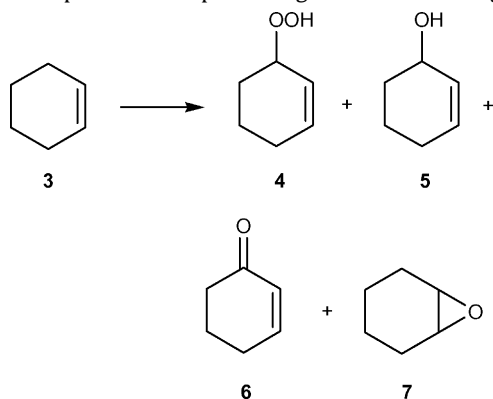
**Fig. 9.** Kinetic curves for the accumulation of cyclohexene epoxide (**7**; curve 1) and a sum of cyclohexenol (**5**) and cyclohexenone (**6**) (curve 2; measured after the reduction with  $\text{PPh}_3$ ) in the cyclohexene (**3**) by the ' $\text{H}_2\text{O}_2$ -**1a**-oxalic acid' system in acetonitrile. Conditions:  $[\mathbf{3}]_0 = 2.0$  M,  $[\text{catalyst } \mathbf{1a}]_0 = 5 \times 10^{-5}$  M,  $[\text{oxalic acid}]_0 = 5 \times 10^{-2}$  M,  $[\text{H}_2\text{O}_2]_0 = 0.125$  M,  $23^\circ\text{C}$ .

all the three hydrocarbon additives were used as potential acceptors of active transient species which compete with our substrate (Rhodamine 6G). We have found a decrease of the decoloration rate in the presence of all additives: benzene, *n*-heptane and cyclohexene (Fig. 7). Note that one of these substances, *n*-heptane, cannot change the distribution of different forms of the catalyst and affect the reaction rate by this way. We can explain the effect of additives on the decoloration rate if we assume that the additives are accepted by dye-oxidizing species **D** [see Eqs. (6)–(8)]. Different efficiency in the effect of the additives on the rate is due to their different reactivity in the reactions with intermediate species **D**. For example, it is well known that the C–H bonds in allylic position of olefins are much more reactive in comparison with the C–H bonds in completely saturated hydrocarbons [19].

The experiments with addition of 2,6-di-*tert*-butyl-4-methylphenol (ionol) also support the mechanisms (6)–(8). When ionol additives were used pronounced lag phases were noticed on the kinetic curves for the dye decoloration (Fig. 8, Graph A). The duration of these lag phases were proportional to concentration of added ionol (see Graph B in Fig. 8). If we assume [20] that inhibiting effect of ionol is due to the reaction between ionol and species **D** and that the inhibiting coefficient is equal to 2 we will be able to estimate from the data of Fig. 8, Graph B the rate of generation of species **D**. This rate is equal to  $1.6 \times 10^{-6} \text{ M s}^{-1}$  under conditions shown in Fig. 8. This value is close to the maximum rate of the dye decoloration ( $1.7 \times 10^{-6} \text{ M s}^{-1}$ ; see Fig. 6).



It has been mentioned above that a study of product distribution in the cyclohexene oxidation can give a valuable information on the nature of the oxidizing species and evaluate the mechanism of the process. We investigated the oxidation of cyclohexene (compound **3**) which can be considered as a more simple model substrate. This oxygenation gives rise to the formation of both the epoxide and the products of the allylic C–H bond oxidation. We used a simple method developed by us earlier [11,21] to demonstrate the formation of cyclohexenyl hydroperoxide (**4**) in cyclohexene (**3**) oxidations and to estimate its concentration in the course of the reaction. If an excess of solid PPh<sub>3</sub> is added to the sample of the reaction solution *ca.* 10 min prior the GC analysis, the alkenyl hydroperoxide present in the solution is completely reduced to the corresponding alcohol. As a result, the chromatogram differs from that of a sample not subjected to the reduction: the alcohol peak rises, while the intensity of the ketone peak decreases. In recent years, our method was applied by other chemists [22] in various oxidations of C–H compounds. Here we have found by this method that oxidation of **3** by the system under discussion affords cyclohexenyl hydroperoxide (**4**), cyclohexenol (**5**), cyclohexenone (**6**) and cyclohexene epoxide (**7**) (for catalytic oxygenation of cyclohexene by hydrogen peroxide, see, for example, [23]). To compare two routes leading to the epoxide on the one hand and the  $\alpha$ -C–H bond oxidation products on the other hand we studied accumulation with time of **7** and a sum **5** + **6** obtained after reduction by PPh<sub>3</sub> (Fig. 9). The initial rate of the formation of the  $\alpha$ -C–H bond oxidation products calculated from curve 2 in Fig. 9 is equal to  $1.8 \times 10^{-6} \text{ M s}^{-1}$  which is close to the rate of the dye decoloration in the absence of cyclohexene ( $1.7 \times 10^{-6} \text{ M s}^{-1}$ , see Fig. 6). This means that the presence of cyclohexene does not affect the concentration of species **C** in the dye-oxidizing system which supports a conclusion that cyclohexene is the acceptor of both epoxidizing and C–H-oxidizing species.



If we take into account all obtained data (that is the decrease in the dye degradation in the presence of hydrocarbon additives and coincidence of the rates of the  $\alpha$ -C–H bond oxidation in cyclohexene and the dye decoloration) we will be able to conclude that both the olefin and dye are oxidized with the same intermediate species. The rate of this species generation does not depend on the presence or absence of the dye. Therefore, the dye oxidation is induced by intermediate species **D** which is generated with the participation of complex **1a**, oxalic acid and hydrogen peroxide. The plateau on the curve shown in Fig. 6 is due to accepting all transient species **D** by the dye **2**.

Schemes (6)–(8) correspond to the interaction of species **D** with dye **2** and acetonitrile. In accordance with this scheme we can easily obtain the following equation for the dependence of the **2** decoloration rate on concentration of **2**:

$$-\frac{d[\mathbf{2}]}{dt} = \frac{W_6}{1 + \frac{k_8[\text{MeCN}]}{k_7[\mathbf{2}]}} \quad (9)$$

where  $W_6$  is the rate of step (6) and  $k_7$  and  $k_8$  are constants of the reactions of species **D** with dye **2** and acetonitrile, respectively.

Using the value of the half-effect which in accord with Fig. 6 is attained at  $[\mathbf{2}] \approx 8 \times 10^{-3} \text{ M}$  we can calculate the ratio  $k_8[\text{MeCN}]/k_7 = 8 \times 10^{-3} \text{ M}$ . Taking into account the acetonitrile concentration ( $\approx 18 \text{ M}$ ) we will obtain  $k_8/k_7 \approx 5 \times 10^{-4}$ . This ratio characterizes the reactivity of the transient species **D**. The effect of *n*-heptane additive on the **2** degradation rate (see Fig. 7, curve 2) allows us to estimate the ratio of constants for the reactions of species **D** with **2** and *n*-heptane. Calculations taking into account the half-effect values showed that this ratio is close to 100. It is known, however, that for the compounds considered in these calculations, namely, the dye and hydrocarbons, the constants for their interactions with hydroxyl radical differ not more than for 10 times. Thus, experimentally measured by us the constant ratio (equal to 100) unambiguously testifies that the hydroxyl radical is not the oxidizing species in our system. The structure of species **D** is not completely clear. We can however assume that this is a species containing a Mn–O• fragment and less probably a Mn–OO• fragment. Hollenberg and coworkers [24a] postulated that a hydroperoxy-iron species (or a protonated analogue of this species) is a viable electrophilic oxidant in some enzymes. Species **D** can be also a coordinated hydroxyl radical. Recently Bach and Dmitrenko [24b] proposed a new mechanism for the P-450 hydroxylation were the “somersault” motion within porphyrin iron(III) hydroperoxide produces the crucial oxidizing species: the isomeric ferryl oxygen hydrogen bonded to an hydroxyl radical, Fe–O••H–O•.

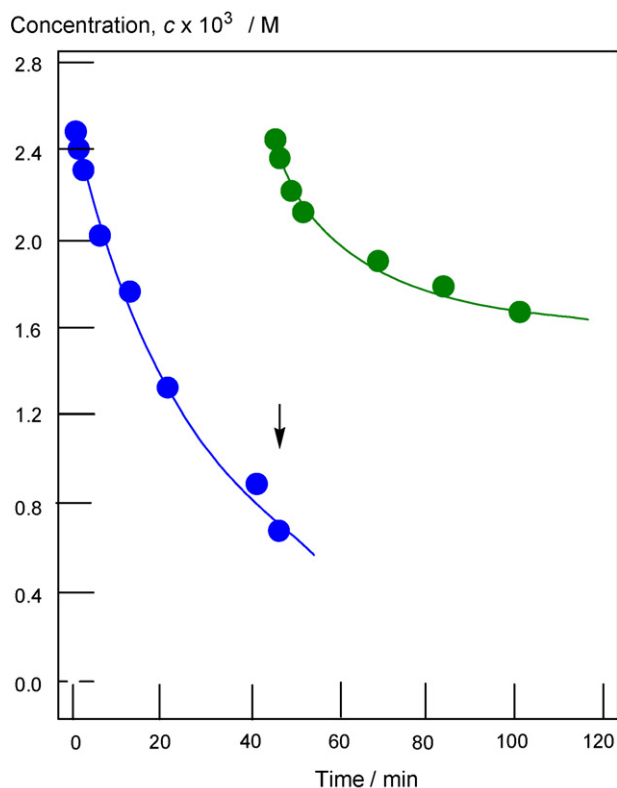
It follows for the data of Fig. 9 that the main pathway of the cyclohexene catalytic transformation catalyzed by **1a** is its epoxidation. This leads us to an assumption that the epoxidation occurs with participation of one more transient active species, **E**, which is apparently an oxoderivative of high-valent manganese and is generated in reaction (10).



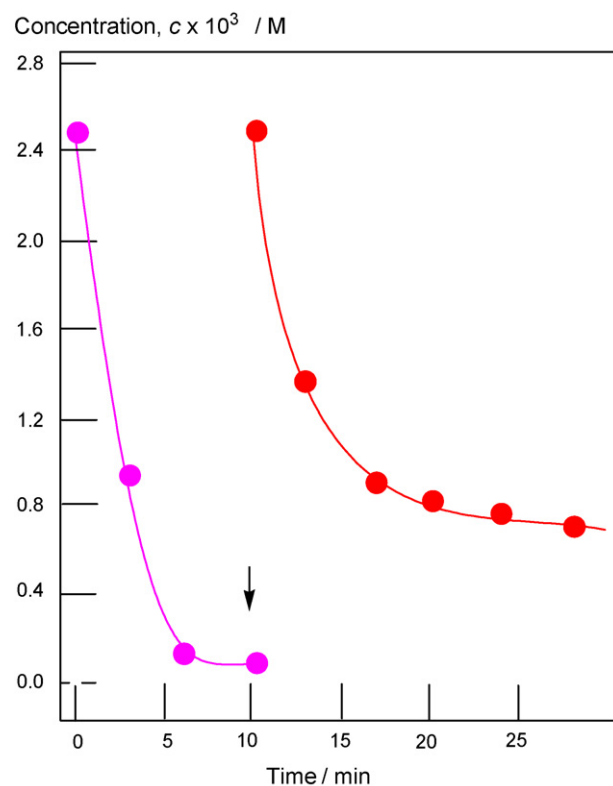
The rate ratio of the generation of the two different intermediates which take part in the **3** epoxidation on the one hand and in the  $\alpha$ -C–H oxygenation of **3** on the other hand is  $k_{10}/k_6 \approx 9$  (see Fig. 9). This ratio is of the same order of magnitude that the value (the ratio was *ca.* 5) obtained in our previous work [9e] where the yields of the epoxide and cyclohexyl hydroperoxide were compared in the competitive oxygenation of dec-1-ene and cyclohexane. It should be noted that, as we used a great excess of cyclohexene over the hydrogen peroxide, the epoxide yield was only 3% based on cyclohexene and *ca.* 50% based on hydrogen peroxide.

Additional experiments were carried out to evaluate the stability of catalyst **1a**. Fig. 10 shows that the catalytic system does not sufficiently lose its activity although some destruction of **1a** occurs in the course of the dye decoloration. Titration by the KI–Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> method of hydrogen peroxide present in the solution under conditions of Fig. 10 demonstrated that the consumption of H<sub>2</sub>O<sub>2</sub> was less than 15% at the moment when in the first run dye **2** was completely decomposed.

We have found that the decoloration of dye **2** by the ‘H<sub>2</sub>O<sub>2</sub>–**1a**–oxalic acid’ system can be efficiently fulfilled also in water solution which is important for the ecological applications of the system (decoloration of sewage containing dyes). It can be seen in Fig. 11 that the decoloration in aqueous solution occurs very rapidly. The catalyst is stable under these conditions and when a new portion of the dye is added the decoloration begins with the same initial rate.



**Fig. 10.** Kinetic curves for the consumption of **2** in its oxidation by the 'H<sub>2</sub>O<sub>2</sub>-**1a**-oxalic acid' system in acetonitrile. Conditions: [2]<sub>0</sub> = 2.5 × 10<sup>-3</sup> M, [1a]<sub>0</sub> = 5 × 10<sup>-5</sup> M, [oxalic acid] = 5 × 10<sup>-2</sup> M, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 0.125 M, 23 °C. At the moment denoted by the arrow a new portion of **2** (up to total concentration [2]<sub>0</sub> = 2.5 × 10<sup>-3</sup> M) was added to the reaction mixture.



**Fig. 11.** Decoloration of **2** by the 'H<sub>2</sub>O<sub>2</sub>-**1a**-oxalic acid' system in water. Conditions: [2]<sub>0</sub> = 2.5 × 10<sup>-3</sup> M, [1a]<sub>0</sub> = 5 × 10<sup>-5</sup> M, [oxalic acid] = 5 × 10<sup>-2</sup> M, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 0.125 M, 23 °C. At the moment denoted by the arrow a new portion of **2** (up to total concentration [2]<sub>0</sub> = 2.5 × 10<sup>-3</sup> M) was added to the reaction mixture.

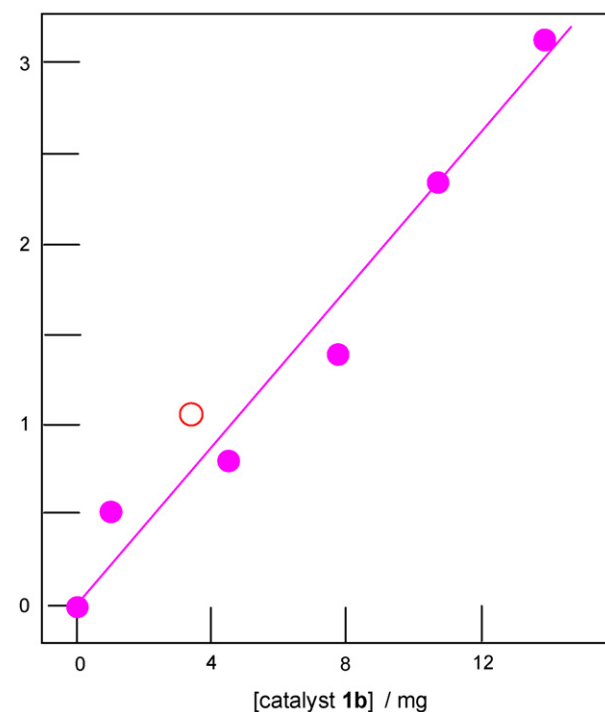
## 2.2. Catalysis by heterogenized compound **1b**

Application of the system under discussion for waste water decoloration would be much more attractive if the catalyst is insoluble in acetonitrile and water because in this case the catalyst can be easily separated from the solution and reused. This idea prompted us to replace in our decoloration studies soluble catalyst **1a** with its heterogenized form **1b** described earlier by Bosch and Veghini [12] and previously used by us in the oxidation of certain alcohols [9h,25].

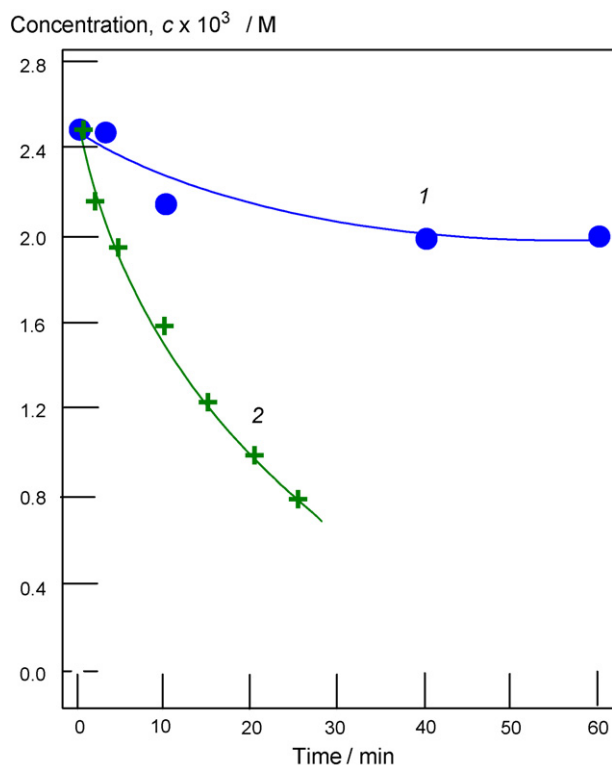
We have found that heterogenized catalyst **1b** is highly efficient in the decoloration of dye **2** in acetonitrile if oxalic acid is present in the solution. The maximum decoloration rate linearly depends on the amount of catalyst **1b** (Fig. 12). The catalyst is relatively stable and can be reused. Indeed, in an additional experiment after the decoloration reaction we filtered off the catalyst **1b**, washed it with water and used again in the next run of the decoloration. The activity of the reused sample (corresponding to an open circle in Fig. 12) was not lower than points for the fresh samples.

Using the data presented in Fig. 12 we can estimate the catalytic activity of heterogenized catalyst **1b**. Since the value of the catalytic active surface is unknown let us assume that all manganese-containing species are situated on the surface and are active in the catalysis. The portion of the dinuclear manganese cation in catalyst **1b** is 35.5% taking into account molecular masses of both cation and anion. Calculated by this way concentration of the cation in the reaction solution for the conditions of Fig. 12 are in the interval from 1.4 × 10<sup>-4</sup> to 1.2 × 10<sup>-3</sup> M. This concentration is approximately 10 times higher than concentration of the soluble catalyst used in the experiment shown in Fig. 4. However the reaction rates in the

Initial rate  $W_0 \times 10^6 / \text{M s}^{-1}$



**Fig. 12.** Dependence of the **2** degradation rate on the amount of **1b** in the oxidation by the 'H<sub>2</sub>O<sub>2</sub>-**1b**-oxalic acid' system. Conditions: [2]<sub>0</sub> = 2.5 × 10<sup>-3</sup> M, [oxalic acid] = 5 × 10<sup>-2</sup> M, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 0.1 M, 23 °C, solvent was acetonitrile, total volume of the reaction solution was 5 mL. An open circle corresponds to the experiment when the sample of **1b** was reused in the decoloration.



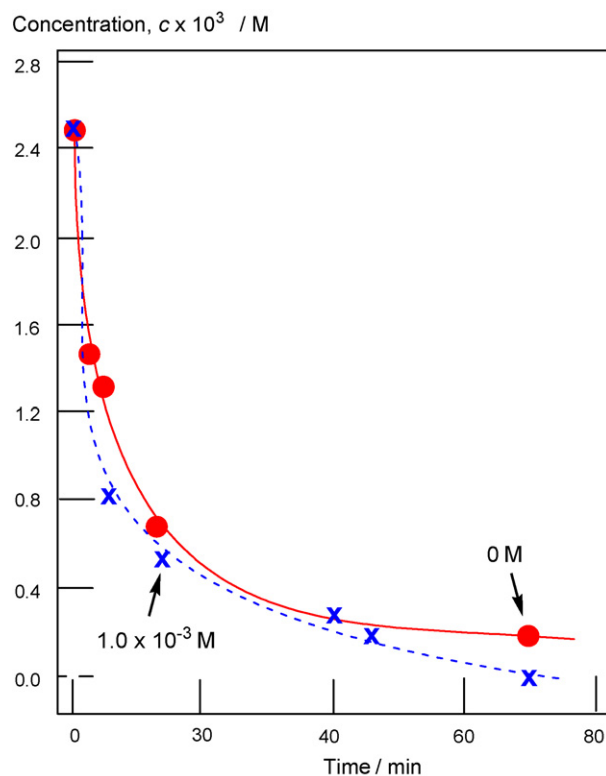
**Fig. 13.** Decoloration of **2** by the 'H<sub>2</sub>O<sub>2</sub>-**1b**-oxalic acid' system in acetonitrile. Conditions: [**2**]<sub>0</sub> = 2.5 × 10<sup>-3</sup> M, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 0.1 M, [oxalic acid] = 0 (curve 1) and 5 × 10<sup>-2</sup> M (curve 2), the amount of **1b** = 7.7 mg, 23 °C, total volume was 5 mL.

experiments shown in Figs. 4 and 12 are similar. The difference found in this estimation can be explained by two ways. We can assume that only a part of catalytically active manganese ions is situated on the surface of the heterogeneous catalyst. Alternatively, some decrease of the catalytic activity can be due to the heterogenization procedure and the incorporation of other anions into the catalyst.

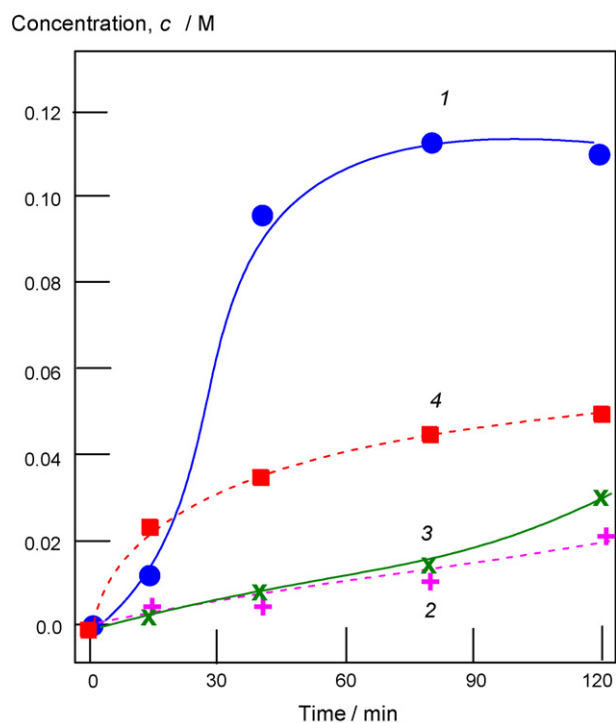
As in the case of the homogeneous system, oxalic acid is an obligatory co-catalyst for the decoloration catalyzed by **1b** (Fig. 13). It is noteworthy that addition of ionol to the **1b**-catalyzed reaction does not inhibit decoloration (Fig. 14), and this discriminates dramatically heterogeneous and homogeneous catalysts (compare Figs. 14 and 8). The difference is evidently due to the fact that in the case of **1b** the dye degradation occurs on the catalyst surface and not in the solution volume.

One can assume that the hydroperoxide formation and the epoxidation proceed *via* different mechanisms with and without participation of free radicals, respectively. If this is really so, addition of ionol to the reaction solution will significantly inhibit the hydroperoxidation and will not affect the epoxide yield. Indeed, this is exactly what we have noticed in our experiment: we added ionol in concentration 2 × 10<sup>-2</sup> M whereas the amount of **1b** was 1.6 mg/mL which is equivalent to manganese concentration 7 × 10<sup>-4</sup> M (see Fig. 16 and compare it with Fig. 15). This observation allows us to propose that the oxygenation catalyzed by heterogeneous compound also proceeds *via* two pathways with participation of species **D** (which is responsible for the α-hydroperoxidation of cyclohexene) and **E** (active in the cyclohexene epoxidation). In contrast to soluble catalyst **1a**, the heterogenized system based on **1b** in the reaction with cyclohexene generates predominantly radical-like species **D**.

It is important to note that addition of Rhodamine 6G in small concentration ([**2**]<sub>0</sub> = 2.5 × 10<sup>-3</sup> M) also dramatically changed the

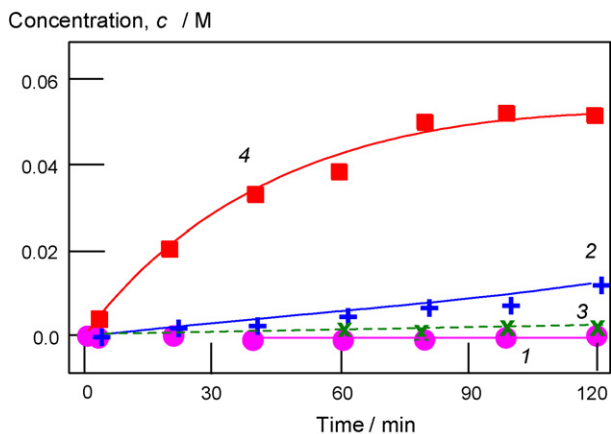


**Fig. 14.** Kinetic curves for the consumption of **2** in its oxidation by the 'H<sub>2</sub>O<sub>2</sub>-**1b**-oxalic acid' system in acetonitrile in the absence (curve 1) and in the presence of ionol (1.0 × 10<sup>-3</sup> M; curve 2). Conditions: [**2**]<sub>0</sub> = 2.5 × 10<sup>-3</sup> M, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 0.1 M, [oxalic acid] = 5 × 10<sup>-2</sup> M, the amount of **1b** = 8.0 mg, 23 °C, total volume was 5 mL.

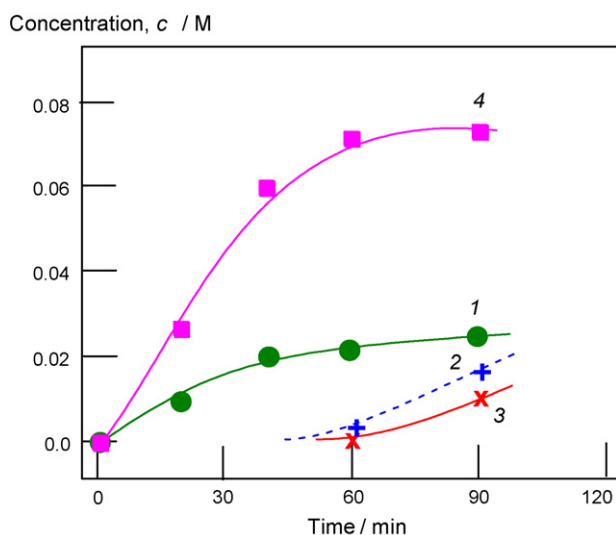


**Fig. 15.** Accumulation of products in oxidation of cyclohexene (**3**) by the 'H<sub>2</sub>O<sub>2</sub>-**1b**-oxalic acid' system in acetonitrile: cyclohexenyl α-hydroperoxide **4** (curve 1), cyclohexen-1-ol **5** (curve 2), cyclohexen-1-one **6** (curve 3), cyclohexene epoxide **7** (curve 4). Conditions: [**3**]<sub>0</sub> = 2.0 M, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 0.125 M, [oxalic acid] = 5 × 10<sup>-2</sup> M, the amount of **1b** = 8.0 mg, 23 °C, total volume was 5 mL.





**Fig. 16.** Accumulation of products in oxidation of cyclohexene (**3**) by the 'H<sub>2</sub>O<sub>2</sub>-**1b**-oxalic acid' system in acetonitrile in the presence of ionol (initial concentration was  $2 \times 10^{-2}$  M). Products: cyclohexenyl  $\alpha$ -hydroperoxide **4** (curve 1), cyclohexen-1-ol **5** (curve 2), cyclohexen-1-one **6** (curve 3), cyclohexene epoxide **7** (curve 4). Conditions:  $[\mathbf{3}]_0 = 2.0$  M,  $[\text{H}_2\text{O}_2]_0 = 0.125$  M,  $[\text{oxalic acid}] = 5 \times 10^{-2}$  M, the amount of **1b** = 8.0 mg, 23 °C, total volume was 5 mL.



**Fig. 17.** Accumulation of products in oxidation of cyclohexene (**3**) by the 'H<sub>2</sub>O<sub>2</sub>-**1b**-oxalic acid' system in acetonitrile in the presence of dye **2** (initial concentration was  $2.5 \times 10^{-3}$  M). Products: cyclohexenyl  $\alpha$ -hydroperoxide **4** (curve 1), cyclohexen-1-ol **5** (curve 2), cyclohexen-1-one **6** (curve 3), cyclohexene epoxide **7** (curve 4). Conditions:  $[\mathbf{3}]_0 = 2.0$  M,  $[\text{H}_2\text{O}_2]_0 = 0.125$  M,  $[\text{oxalic acid}] = 5 \times 10^{-2}$  M, the amount of **1b** = 8.0 mg, 23 °C, total volume was 5 mL.

product distribution: the rate of the hydroperoxide accumulation and its yield became much lower while the epoxidation rate was practically equal to that in the absence of **2** (Fig. 17). Thus, ionol and dye **2** have the same effect on the cyclohexene oxygenation (compare Figs. 16 and 17 and compare these figures with Fig. 15). Based on these results we can propose that both ionol and dye Rhodamine 6G block centers on the catalyst **1b** surface which are active in the generation of radical-like species. These species **D** abstract the hydrogen atom from  $\alpha$ -position of cyclohexene resulting in the formation of  $\alpha$ -oxygenated derivatives. At once, neither ionol nor the dye are able to affect the centers that generate olefin epoxidizing species **E**.

### 3. Conclusion

Oxidative decoloration of Rhodamine 6G (**2**) and oxygenation of cyclohexene (**3**) with hydrogen peroxide in acetonitrile in the pres-

ence of homogeneous (**1a**) and heterogenized (**1b**) catalysts and co-catalyst (oxalic acid) proceed with the formation of transient species **D** and **E**. The first species exhibits the properties of a relatively weak radical and is able to abstract the hydrogen atom from the  $\alpha$ -position of cyclohexene. Species **D** is probably an oxygen-centered radical containing also manganese ions. The pathway with participation of **D** leads to the formation of  $\alpha$ -cyclohexenyl hydroperoxide (**4**). Species **E** is responsible for the transformation of cyclohexene to epoxide **7** and is apparently an oxoderivative of high-valent manganese.

Homogeneous catalyst **1a** generates predominantly species **E** and in this case cyclohexene is transformed mainly to its epoxide. It is noteworthy that when heterogenized catalyst **1b** is used species **D** prevail and  $\alpha$ -cyclohexenyl hydroperoxide is produced with the higher yield in comparison with the yield of epoxide **7**. Both **D** and **E** species are believed to be involved in dye **2** degradation process. Species **D** gives more substantial contribution to the total decoloration rate.

### 4. Experimental

Catalysts **1a** and **1b** were prepared as described in Refs. [5] and [12], respectively. The oxidations of dye **2** and cyclohexene **3** were carried out in acetonitrile in air in thermostated (23 °C) Pyrex cylindrical vessels with vigorous stirring. Typically the total volume of the reaction solution was 5 mL. Initially, a portion of H<sub>2</sub>O<sub>2</sub> (35% aqueous) was added to the solution of the catalyst **1a** or **1b**, co-catalyst (typically oxalic acid) and **2** or **3**. After certain time intervals samples of the reaction solution were taken. In the experiments on the **2** oxidative degradation samples were diluted with water by 50 times and concentration of **2** was determined by UV-vis spectroscopy (instrument "Specord UV-vis";  $l = 1$  cm) (see Figs. 1 and 2). No further decoloration of the dye was noticed after the dilution with water.

In the experiments on cyclohexene oxidation samples of the reaction solutions were analysed by GC (instrument "LKhM-8-LD; Inerton AW-DMCS with XE-60; carrier gas was argon) twice, before and after addition of an excess of solid triphenylphosphine (for this method, see Refs. [11] and [21]).

### Acknowledgement

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