



Oxidations by the system 'hydrogen peroxide–[Mn₂L₂O₃]²⁺ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane)–oxalic acid'. Part 11. Degradation of dye Rhodamine 6G and oxygenation of cyclohexene

Georgiy B. Shul'pin*, Yuriy N. Kozlov, Svetlana N. Kholuiskaya, Maryam I. Plieva

Semenov Institute of Chemical Physics, Russian Academy of Sciences, Ulitsa Kosygina, dom 4, Moscow 119991, Russia

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ABSTRACT

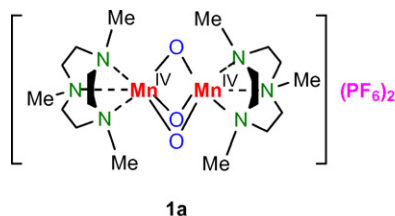
Two dinuclear manganese(IV) compounds, soluble [LMn(O)₃MnL](PF₆)₂ (**1a**) and insoluble [LMn(O)₃MnL]₂[SiW₁₂O₄₀] (**1b**) (L is 1,4,7-trimethyl-1,4,7-triazacyclononane, TMTACN) are efficient catalysts in oxidative decoloration of dye Rhodamine 6G and oxygenation of cyclohexene with hydrogen peroxide 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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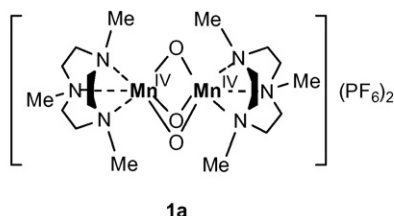
1. Introduction

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)₃MnL](PF₆)₂ (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/H₂O₂' 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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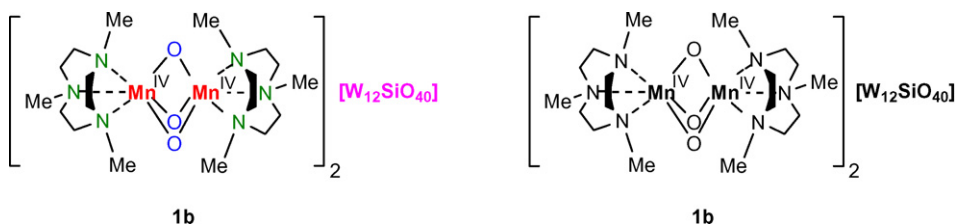
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* Corresponding author. Tel.: +7495 939 7317; fax: +7495 137 6130.
E-mail addresses: shulpin@chph.ras.ru, gbsh@mail.ru (G.B. Shul'pin).

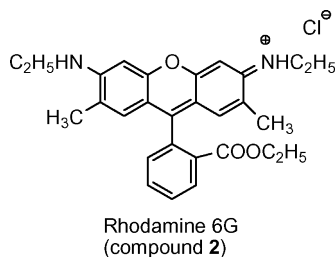
products of dihydroxylation [9e] in addition to the corresponding epoxides. Alkanes [9f], olefins [9f], and alcohols [9h] were oxidized also in the absence of acetonitrile. A relevant soluble polymer-bound Mn(IV) complex with *N*-alkylated 1,4,7-

triazacyclononane was used as a catalyst in the H_2O_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/ H_2O_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/ H_2O_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 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 ' H_2O_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 α 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-

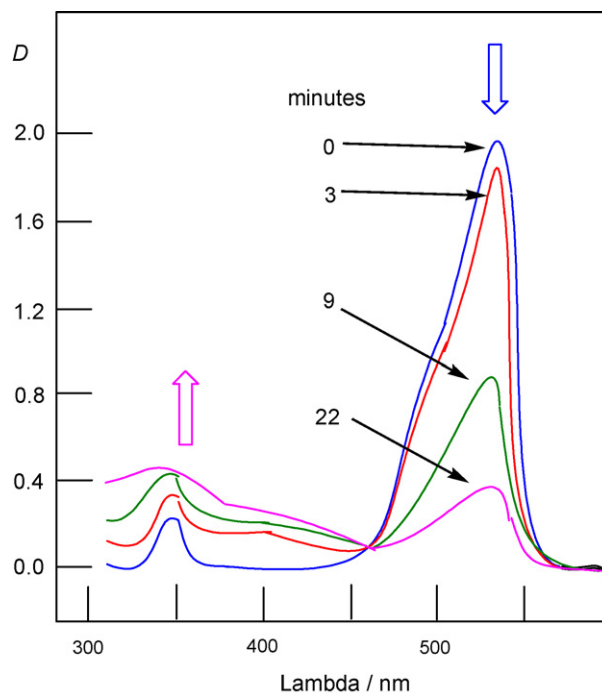


Fig. 1. Changes in the absorption spectrum of **2** in the course of its destruction by the ' H_2O_2 –**1a**–oxalic acid' system in acetonitrile. Conditions: $[\mathbf{2}]_0 = 1.25 \times 10^{-3} \text{ M}$, $[\text{catalyst } \mathbf{1a}] = 5 \times 10^{-5} \text{ M}$, $[\text{oxalic acid}] = 5 \times 10^{-2} \text{ M}$, $[\text{H}_2\text{O}_2]_0 = 0.1 \text{ M}$, 23°C . The reaction solution was diluted by 50 times with water before the spectrophotometrical analysis ($l = 1 \text{ cm}$).

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