

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

Part 3. Oxygenation of ethane, higher alkanes, alcohols, olefins and sulfides[☆]

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Abstract

The manganese(IV) complex salt $[L_2Mn_2O_3](PF_6)_2$ ($L = 1,4,7$ -trimethyl-1,4,7-triazacyclononane) (compound **1**, see Scheme 1) very efficiently catalyzes the hydroperoxidation of saturated hydrocarbons, including ethane by H_2O_2 in acetonitrile or nitromethane solution at low (room or lower) temperature, provided a carboxylic (typically acetic) acid is present. The hydroperoxidation of tertiary positions in disubstituted cyclohexanes proceeds with partial retention of configuration in nitromethane or acetonitrile solution, while the stereoselectivity of the reaction is only negligible in acetone solution. The system “ H_2O_2 –compound **1**– $MeCO_2H$ ” also transforms secondary alcohols into the corresponding ketones with quantitative yields at room temperature within a few minutes; the yields of aldehydes and carboxylic acids in the oxidation of primary alcohols are lower. Terminal aliphatic olefins such as hexene-1 are quantitatively epoxidized by the same system in acetonitrile at room temperature within 20 min, while the epoxide yield in the analogous reaction with styrene attains only 60% under the same conditions. Finally, dimethylsulfide can be quantitatively and selectively converted into dimethylsulfoxide within 3 h at room temperature. The system “*tert*-BuOOH–compound **1**” also oxidizes alkanes, addition of acetic acids has less pronounced effect on the direction and efficiency of the reaction. Two other checked derivative of Mn(IV) (compounds **2** and **3**) as well a porphyrin complex of Mn(III) (compound **4**) exhibited lower activity in catalysis of alkane oxidation with *tert*-BuOOH. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Alcohols; Alkanes; Alkyl hydroperoxides; *tert*-Butyl hydroperoxide; Carboxylic acids; Homogeneous catalysis; Hydrogen peroxide; Ketones; Manganese complexes; Metal-complexes; Oxygenation; Oxidation

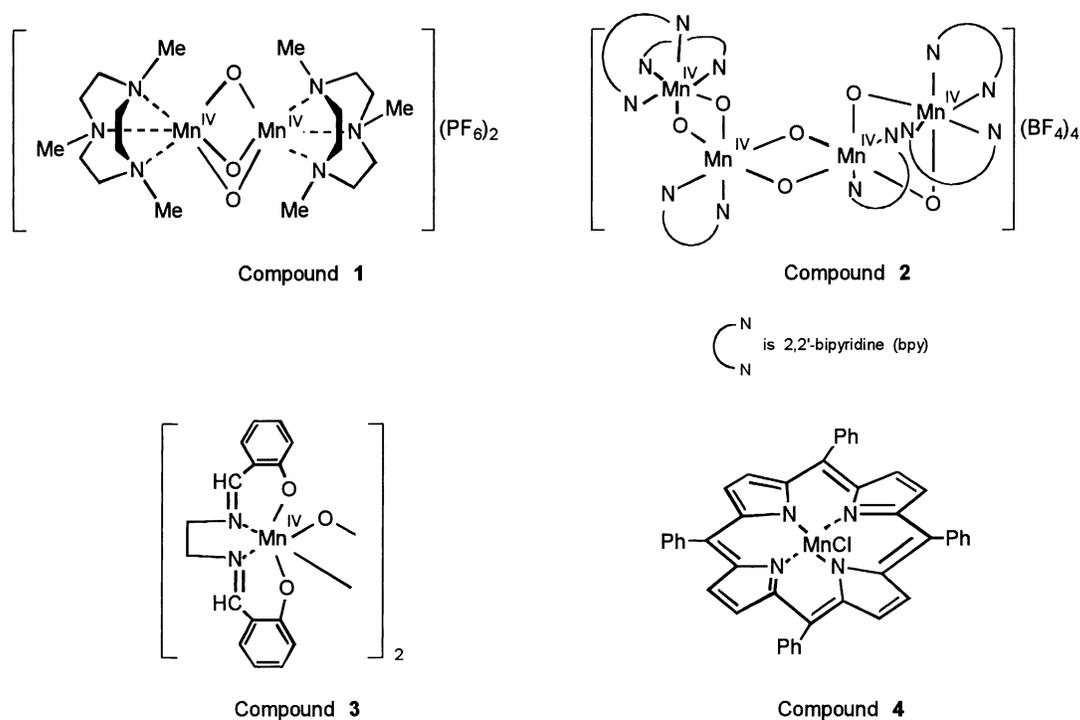
1. Introduction

Manganese complexes are known to catalyze various oxidation reactions, epoxidation of olefins [1–23], oxygenation of saturated [24–29] and aromatic [30–32] hydrocarbons, oxidation of alcohols [33–35], sulfur-containing compounds [36], as well

[☆] For communications 1 and 2, see [105,106], respectively. A preliminary communication of previous parts has been also published [107].

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Scheme 1. Manganese derivatives used in this work as catalysts of oxidation reactions.

as some other derivatives [37–41] by peroxides and other reagents (see also for stoichiometric oxidations [42–44]. Manganese-containing enzymes are very efficient in the hydroperoxide decomposition (catalase activity) [45–48]. The photosynthetic water oxidation enzyme has a tetranuclear manganese core [49–51]. Many complexes of this metal have been used as models of enzymatic processes [52–68]. Oxidations with participation of di- and polynuclear complexes of transition metals [69–81], particularly manganese [82–98], are especially interesting because many enzymes have been found to contain polynuclear metal active centers [99–104].

Recently we discovered [105–107] that the catalytic activity of the manganese(IV) salt $[L_2Mn_2O_3](PF_6)_2$ ($L=1, 4, 7$ -trimethyl-1,4,7-triazacyclononane) (compound **1**, see Scheme 1) for the oxidation of saturated hydrocarbons with hydrogen peroxide increases dramatically, if small amounts of a carboxylic acid are added to the reaction solution. Without a carboxylic acid, compound **1** catalyzes the decomposition of hydrogen peroxide to molecular oxygen in acetonitrile

solution at room temperature. If an alkane is added to the reaction solution, only very small amounts of oxygenated products are formed and compound **1** exhibits only catalase activity [105]. Surprisingly, in the presence of a carboxylic acid (in low concentration, 0.05 – 0.5 mol dm⁻³), very efficient oxidation of the alkane occurs at the expense of the dioxygen production. Acetic acid is the most convenient co-catalyst in this reaction, although other carboxylic acids such as propionic or trifluoroacetic acids can be used [105]. The hydroxylation of some alkanes containing tertiary C–H bonds proceeds stereoselectively, thus the oxidation of the two decalin isomers gives (after treatment with triphenylphosphine) alcohols hydroxylated in the tertiary positions, the *cis/trans* ratio being ~ 2 in the case of the oxidation of *cis*-decalin, and the *trans/cis* ratio being ~ 30 in the case of the oxidation of *trans*-decalin, i.e. in the latter case the reaction is stereospecific [106]. The initial products of the alkane oxidation are alkyl hydroperoxides which, in the course of the reaction, are transformed gradually into the corresponding carbonyl compounds and alcohols.

Selective transformations of very inert saturated hydrocarbons under mild conditions constitute a challenging goal of homogeneous metal-complex catalysis [108,109]. Thus, it was important to investigate the oxidation of various saturated hydrocarbons by the system described in [105–107], to use other assay compounds with tertiary C–H bonds, in order to get an additional insight into the selectivity features of the process. It was also of interest to try to extend the catalytic system to related compounds.

2. Results and discussion

In the present work, we report the oxidation of ethane and some other alkanes by the system “hydrogen peroxide–compound **1**–carboxylic acid” in various solvents, as well as the applicability of the system in the oxidative transformations of other organic compounds. We also investigated the catalytic activity of the compounds **2–4** with respect to that of **1** for the oxidation of alkanes with hydrogen peroxide and with *tert*-butyl hydroperoxide. It should be noted that generally speaking the solvent is not inert towards hydrogen peroxide, especially in the presence of a metal-complex catalyst [110,111]. For example, trichloroacetonitrile, acetone (in the presence of a base) [112,113] and acetone [114] give, respectively, a peroxyimidic acid and tetrameric acetone peroxide. Thus, we cannot exclude that in some cases the substrate oxidations occur via hydrogen peroxide derivatives.

2.1. Oxidation of ethane and propane with H₂O₂

Usually, the reactivity of ethane is very low as compared to the reactivity of higher alkanes. This is

not surprising, since ethane does not contain methylene groups. The oxidation of ethane by the system “hydrogen peroxide–compound **1**–propionic acid” in acetonitrile gives, according to the GC analysis, acetaldehyde and ethyl alcohol. If, prior to GC analysis, an excess of solid triphenylphosphine is added to the sample of the reaction solution (for this method, see [108,109,115–125]), the amount of acetaldehyde decreases, while that of ethyl alcohol increases. This difference is due to the complete decomposition of the primary product ethyl hydroperoxide in the GC injector to give MeCHO and EtOH. It should be noted that in some cases, in this and previous works (see [121,122]), we were able to detect in chromatograms peaks which were due to alkyl hydroperoxides. Triphenylphosphine reduces ethyl hydroperoxide easily and quantitatively to ethyl alcohol. By comparing the concentrations of acetaldehyde and of ethyl alcohol measured before and after the treatment of the sample with PPh₃, it is possible to estimate [108,109,115–125] the real concentrations not only of acetaldehyde and of ethyl alcohol but also that of ethyl hydroperoxide. The concentrations of the products calculated by this method are given in Table 1.

It follows from the data summarized in Table 1 that ethyl hydroperoxide is the major product of the oxidation. This compound slowly decomposes in the course of the reaction to produce acetaldehyde as well as ethyl alcohol. At low temperature (+5°C), the relative content of EtOOH is significantly higher than at 25°C. The yield of the oxygenated products depends on the initial ethane pressure, and the total turnover number, TON, is two times higher at 20 bar than at 10 bar.

Propane is significantly more reactive than ethane. The oxidation of this alkane gives after 3 h at 27°C predominantly (concentration, mol dm⁻³, is given in parenthesis) 2-hydroperoxypropane (0.059),

Table 1
Oxidation of ethane with H₂O₂^a

Pressure (bar)	Temperature (°C)	Time (h)	Products (mol dm ⁻³)			TON ^b
			EtOOH	MeCHO	EtOH	
20	25	2	0.007	0.006	0.005	360
10	25	2	0.004	0.003	0.002	180
20	5	75	0.013	0.001	0.006	400

^a Conditions: H₂O₂, 1.0 mol dm⁻³; compound **1**, 0.5 × 10⁻⁴ mol dm⁻³; propionic acid, 0.25 mol dm⁻³.

^b Moles of all detected products per one mole of compound **1**.

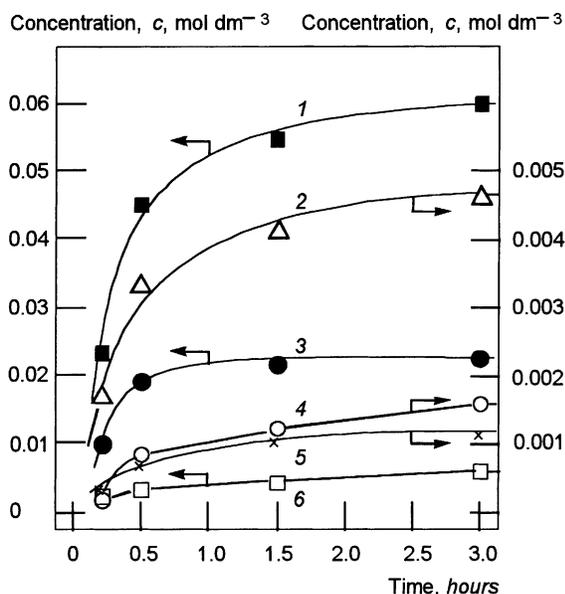


Fig. 1. Reaction profile of the oxidation of propane (initial pressure 7 bar) with H_2O_2 (0.5 mol dm^{-3}) catalyzed by compound **1** ($0.4 \times 10^{-4} \text{ mol dm}^{-3}$) in the presence of MeCOOH (0.25 mol dm^{-3}) in MeCN at 27°C . Products: 2-hydroperoxypropane (curve 1); 2-propanol (2); acetone (3); 1-hydroperoxypropane (4); 1-propanol (5); propionic aldehyde (6).

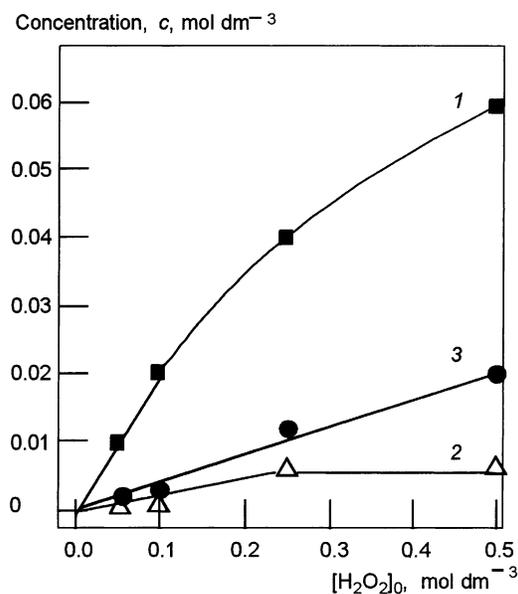


Fig. 2. Concentration of 2-hydroperoxypropane (1), 2-propanol (2), and acetone (3) versus initial concentration of hydrogen peroxide in the propane (initial pressure 7 bar) oxidation in MeCN (compound **1**, $0.4 \times 10^{-4} \text{ mol dm}^{-3}$; 27°C ; 3 h).

acetone (0.022), 2-propanol (0.0045), as well as smaller amounts of propionic aldehyde (0.0070), 1-hydroperoxypropane (0.0017), and 1-propanol (0.0012), the total TON being equal 1900. The kinetics of the formation of these products are shown in Fig. 1. A short induction period (a few minutes) can be noticed. The rate of the reaction (measured as the yield of oxygenates) increases with growth of the initial hydrogen peroxide concentration, this dependence being linear when hydrogen peroxide concentration is less than 0.2 mol dm^{-3} (Fig. 2).

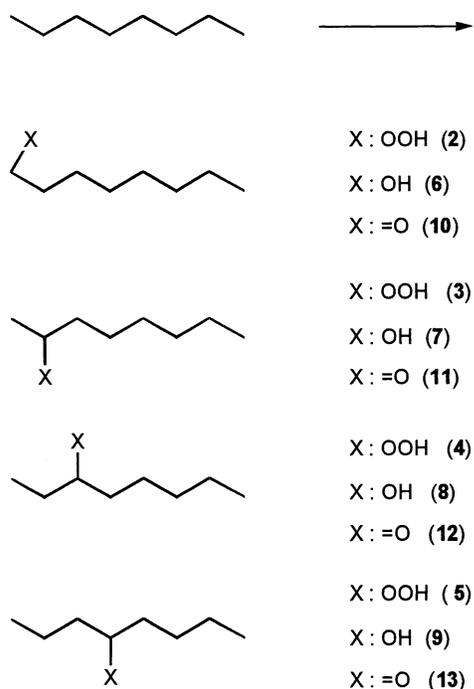
2.2. Oxidation of higher alkanes with H_2O_2 and *tert*-BuOOH

In the oxidations of higher alkanes we employed a method which uses the reduction with triphenylphosphine and allows to determine the real concentrations not only of the ketone (aldehyde) and the alcohol but also that of the alkyl hydroperoxide [108,109,115–125] (*vide supra*). For the kinetics we

used only the concentrations of the ketone and alcohol found experimentally, because a sum of their concentrations (measured after reduction with triphenylphosphine) corresponds precisely to the reaction rate. Using experimental data obtained only after reduction with triphenylphosphine simplifies the figures and enhances the accuracy in determination of the reaction rates. In some cases, however, we will demonstrate estimated real concentrations of the three products (measured by comparison of the chromatograms of the reaction samples prepared before and after their reduction with triphenylphosphine).

2.2.1. Oxidation with H_2O_2

Normal octane is oxidized by the system under consideration to produce the corresponding isomeric octyl hydroperoxides as main products. The concentrations of the oxygenates (Scheme 2) as a function of time are summarized in Table 2. These concentrations were calculated using the data obtained before and after reduction of the reaction samples with triphenylphosphine; in some runs we were able to detect by the

Scheme 2. Products of *n*-octane oxidation.

GC peaks corresponding to isomeric alkyl hydroperoxides. The site selectivity of this oxidation after 60 min is C(1):C(2):C(3):C(4) = 1.0:29.2:25.5:24.4, the ratio C(1):C(2):C(3):C(4) being normalized (i.e. calculated taking into account the number of hydrogen atoms at each position) relative reactivities of hydrogens at 1, 2, 3, and 4 carbon atoms of the alkane chain, respectively. The calculations are based on the

concentrations of only corresponding alcohols after reduction of the reaction samples with triphenylphosphine. The selectivity of the *n*-octane oxidation with this catalytic system is significantly higher than that we found for the oxidation of this hydrocarbon by H₂O₂ in MeCN in air under UV light irradiation, (C(1):C(2):C(3):C(4) = 1.0:6.8:5.9:5.1). Since the photodecomposition of H₂O₂ is known to generate hydroxyl radicals [126], the selectivity difference proves the Mn-catalyzed oxidation not to involve hydroxyl radicals as active species.

The branched saturated hydrocarbon isooctane (2,2,4-trimethylpentane) turned out to be much less reactive in comparison with normal octane (Scheme 3 and Table 3). This is due to relatively low concentration of reactive tertiary hydrogen atoms (because isooctane molecule contains only one *tert*-C–H bond in comparison with six CH₂ groups in *n*-octane) and also to spatial shielding of the sole methylene group which hinders the attack of a voluminous active species on the secondary hydrogen atoms. A relatively high (in comparison with normal octane) concentration of primary hydroperoxides is detected. However, the normalized ratio 1°:2°:3° of hydrogen atom reactivities at primary, secondary and tertiary carbons within the isooctane molecule is noticeably higher in the case of the Mn-catalyzed oxidation (1.0:2.6:31.6), as compared with isooctane oxidations by hydroxyl-radical-generating systems “H₂O₂–*hν*” (1.0:1.75:6.2) and “H₂O₂–FeSO₄” (1.0:2.75:6.0) in aqueous acetonitrile (the calculations were based on the concentrations of alcohols after reduction of the reaction samples with triphenylphosphine).

Table 2
Oxidation of *n*-octane with H₂O₂ (products, mmol dm⁻³)^a

Time (min)	Hydroperoxides				Alcohols				Ketones		
	1- (2)	2- (3)	3- (4)	4- (5)	1- (6)	2- (7)	3- (8)	4- (9)	2- (11)	3- (12)	4- (13)
10	0.07	2.7	2.2	2.0	0.02	0.7	0.55	0.5	0.30	0.25	0.24
20	0.14	5.8	5.0	4.4	0.06	2.3	2.0	1.8	1.35	1.3	1.1
30	0.19	7.5	6.9	6.2	0.08	3.2	3.0	2.8	2.0	1.9	1.8
40	0.20	9.0	8.5	8.0	0.08	4.2	4.0	3.8	2.6	2.2	2.0
60	0.4	12.5	11.5	11.0	0.08	4.2	3.8	3.4	3.2	3.1	2.8
120	0.5	18.1	16.2	15.3	0.08	4.1	3.9	3.7	5.5	5.1	4.4
7200	0.6	20.5	19.0	17.2	0.10	4.1	4.0	3.8	6.9	6.5	5.8

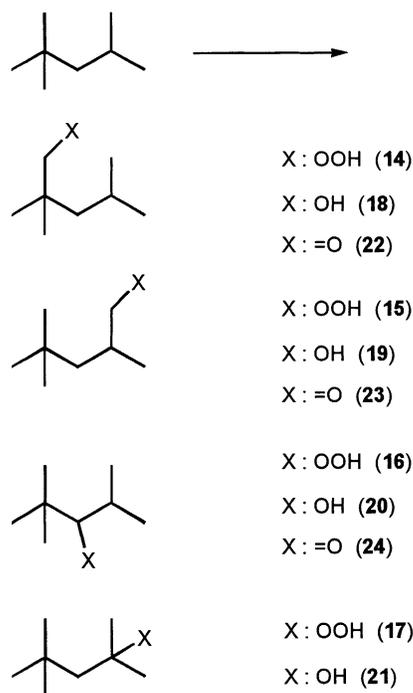
^a Conditions: solvent, MeCN; *n*-octane, 0.62 mol dm⁻³; H₂O₂, 0.5 mol dm⁻³; compound **1**, 0.5 × 10⁻⁴ mol dm⁻³; MeCOOH, 0.25 mol dm⁻³; 23°C. Numbers 1-, 2-, 3-, and 4- denote position in the hydrocarbon chain, bold numbers in parentheses correspond the isomer numbers in Scheme 2.

Table 3
Oxidation of 2,2,4-trimethylpentane with H₂O₂ (products, mmol dm⁻³)^a

Time (min)	Hydroperoxides			Alcohols			Ketone and aldehydes 1° + 2° (22 + 23 + 24)
	1° (14 + 15)	2° (16)	3° (17)	1° (18 + 19)	2° (20)	3° (21)	
5	0.5	0.2	3.0	0	0.05	0.1	0.2
15	1.7	0.8	6.0	0.25	0.10	1.0	3.6
30	2.5	1.2	8.1	0.3	0.18	1.5	4.3
45	3.4	1.7	9.5	0.4	0.20	2.0	4.8
60	4.3	1.9	10.1	0.4	0.2	2.2	5.0
120	6.0	2.8	12.5	0.4	0.22	2.4	5.0

^a Conditions: solvent, MeCN; 2,2,4-trimethylpentane, 0.62 mol dm⁻³; H₂O₂, 0.5 mol dm⁻³; compound **1**, 0.5 × 10⁻⁴ mol dm⁻³; MeCOOH, 0.25 mol dm⁻³; 20°C. Numbers 1°, 2°, and 3° denote isomers bearing the substituent at primary, secondary and tertiary carbon atoms, respectively; bold numbers in parentheses correspond the isomer numbers in Scheme 3.

Other manganese derivatives used in this work, compounds **2–4**, turned out to exhibit only a very low catalytic activity in the alkane oxidation with hydrogen peroxide. Compound **2** catalyzes hydrogen peroxide decomposition with evolution of molecular oxygen both in the presence and absence of small amounts of acetic acid and products of



Scheme 3. Products of 2,2,4-trimethylpentane oxidation.

alkane oxidation were detected only in negligible concentrations.

The oxidation of methyl-*n*-propylketone (0.2 mol dm⁻³) with H₂O₂ (0.5 mol dm⁻³) catalyzed by compound **1** (10⁻⁴ mol dm⁻³) in the presence of acetic acid (0.25 mol dm⁻³) in acetonitrile is not efficient and gave at 23°C after 1 h only 0.01 mol dm⁻³ of acetylacetone. The formation of MeC(OH)(OOH)^{*n*}Pr could be suspected in this reaction. The low yield of acetylacetone in this case can be due to the deactivation of the two methylene groups in methyl-*n*-propylketone by the electron-withdrawing carbonyl group. The low efficiency could be explained also by a further reaction of acetylacetone with the catalyst. It is interesting that no corresponding hydroperoxide has been detected. The neighboring ketone group apparently transforms C–OOH into C=O.

2.2.2. Oxidation with *tert*-BuOOH

Compound **1** catalyzes also the alkane oxidation with *tert*-butyl hydroperoxide. In comparison with the corresponding H₂O₂ oxidation, the reaction of cyclooctane proceeds much slower and gives lower yields of the products (see Fig. 3). Another feature of the oxidation with *tert*-BuOOH is the weaker effect of the acetic acid addition on the efficiency of the catalytic reaction. Indeed, the oxidation with *tert*-BuOOH in MeCN proceeds also in the absence of MeCOOH (Fig. 3a). Fig. 4 demonstrates that acetic acid accelerates the oxidation of cyclohexane, the maximum being observed at [MeCOOH] = ca. 0.1–0.2 mol dm⁻³. The kinetic curve shapes and

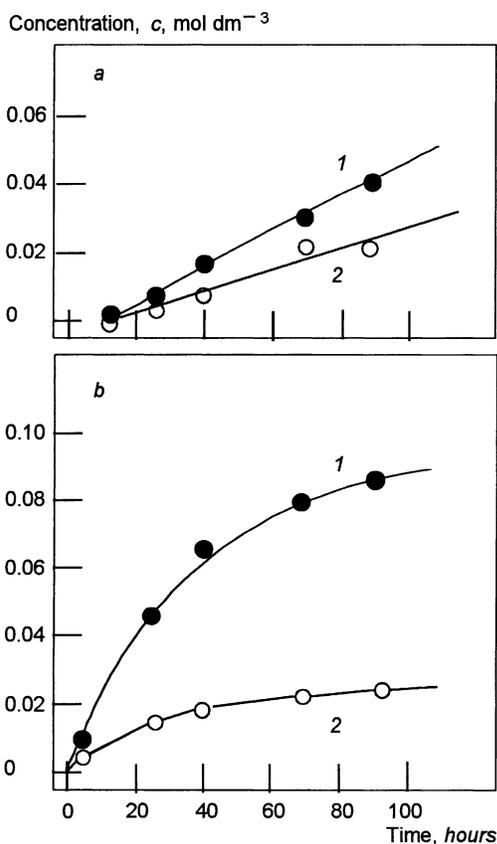


Fig. 3. Accumulation of cyclooctanone (curve 1) and cyclooctanol (curve 2) in the oxidation of cyclooctane (initial concentration 0.62 mol dm^{-3}) with 70% aqueous *tert*-BuOOH (0.14 mol dm^{-3}) in the absence (graph a) and in the presence of MeCOOH (0.25 mol dm^{-3} ; graph b) in MeCN at 30°C catalyzed by compound **1** ($0.5 \times 10^{-4} \text{ mol dm}^{-3}$). All product concentrations were measured without prior reduction with PPh_3 .

the cyclohexanone/cyclohexanol ratio depend on the acetic acid concentration. The reaction is of a first order with respect to the catalyst (compound **1**) concentration since the initial rate of the reaction (measured as the product yields after 5 h) is proportional to $[\text{compound } \mathbf{1}]$ (Fig. 5). The profiles of the *n*-octane oxygenation by this system is shown in Fig. 6. The total turnover number (TON) attains in this case 470.

The influence of some additives on the reaction has been investigated. If CBrCl_3 (0.05 mol dm^{-3}) is added to the reaction solution ($[\text{cyclohexane}]_0 = 0.46 \text{ mol dm}^{-3}$; $[\text{tert-BuOOH}]_0 = 0.14 \text{ mol dm}^{-3}$;

$[\text{compound } \mathbf{1}] = 0.5 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{MeCOOH}] = 0.045 \text{ mol dm}^{-3}$; 20 h at 20°C) bromocyclohexane is detected as the main product ($0.0036 \text{ mol dm}^{-3}$) with much smaller concentrations of cyclohexanone and cyclohexanol (0.0002 and $0.0004 \text{ mol dm}^{-3}$, respectively; all concentration were determined after the reduction with PPh_3). Under the same conditions, the addition of 2,5-di(*tert*-butyl)-4-methylphenol ($0.003 \text{ mol dm}^{-3}$) gave rise to the formation of only cyclohexanol ($0.00035 \text{ mol dm}^{-3}$). These data testify that the reaction proceeds via the formation of free radicals. It is noteworthy that the addition of isopropanol (0.13 mol dm^{-3}) does not affect the rate of the reaction (yield 0.007 and $0.014 \text{ mol dm}^{-3}$ of cyclohexanone and cyclohexanol, respectively, after; that is: 20 h at 20°C ; concentrations of the components as in reaction in the presence of CBrCl_3 , see above). Assuming free radicals to be involved in the reaction is also in agreement with the predominant formation of cyclohex-2-enone ($0.074 \text{ mol dm}^{-3}$) and cyclohex-2-enol ($0.034 \text{ mol dm}^{-3}$) while cyclohexene epoxide is formed only in negligible concentration ($0.0015 \text{ mol dm}^{-3}$) (conditions: cyclohexene, 0.45 mol dm^{-3} ; *tert*-BuOOH, 0.14 mol dm^{-3} ; MeCOOH, 0.25 mol dm^{-3} ; compound **1** $0.5 \times 10^{-4} \text{ mol dm}^{-3}$; 20°C ; 1 h; without prior reduction with PPh_3).

The oxidation of cyclooctane with *tert*-BuOOH catalyzed by the tetranuclear Mn(IV) derivative $[\text{Mn}_4\text{O}_6(\text{bpy})_6](\text{BF}_4)_4$ (compound **2**, see Scheme 1) proceeds more efficiently than that with H_2O_2 , however in this case the product yields are not high. It is important to note that in this oxidation, acetic acid added in small concentration does not accelerate the reaction, the accumulation of products is even slower in the presence of the acid (compare graphs a and b in Fig. 7). Under analogous conditions, cyclohexene is converted predominantly into cyclohex-2-enone ($0.032 \text{ mol dm}^{-3}$) and cyclohex-2-enol ($0.036 \text{ mol dm}^{-3}$) and only traces of cyclohexene epoxide were found.

The salen manganese(IV) derivative $[\text{Mn}(\text{salen})-(\mu\text{-O})_2]$ (compound **3**, Scheme 1) and the tetraphenylporphyrin complex of Mn(III) (compound **4**, Scheme 1) catalyze the oxidation of cyclooctane with *tert*-BuOOH in the absence of acetic acid to produce corresponding alkyl hydroperoxide, ketone and alcohol, however the efficiency of both reactions is not high (Fig. 8).

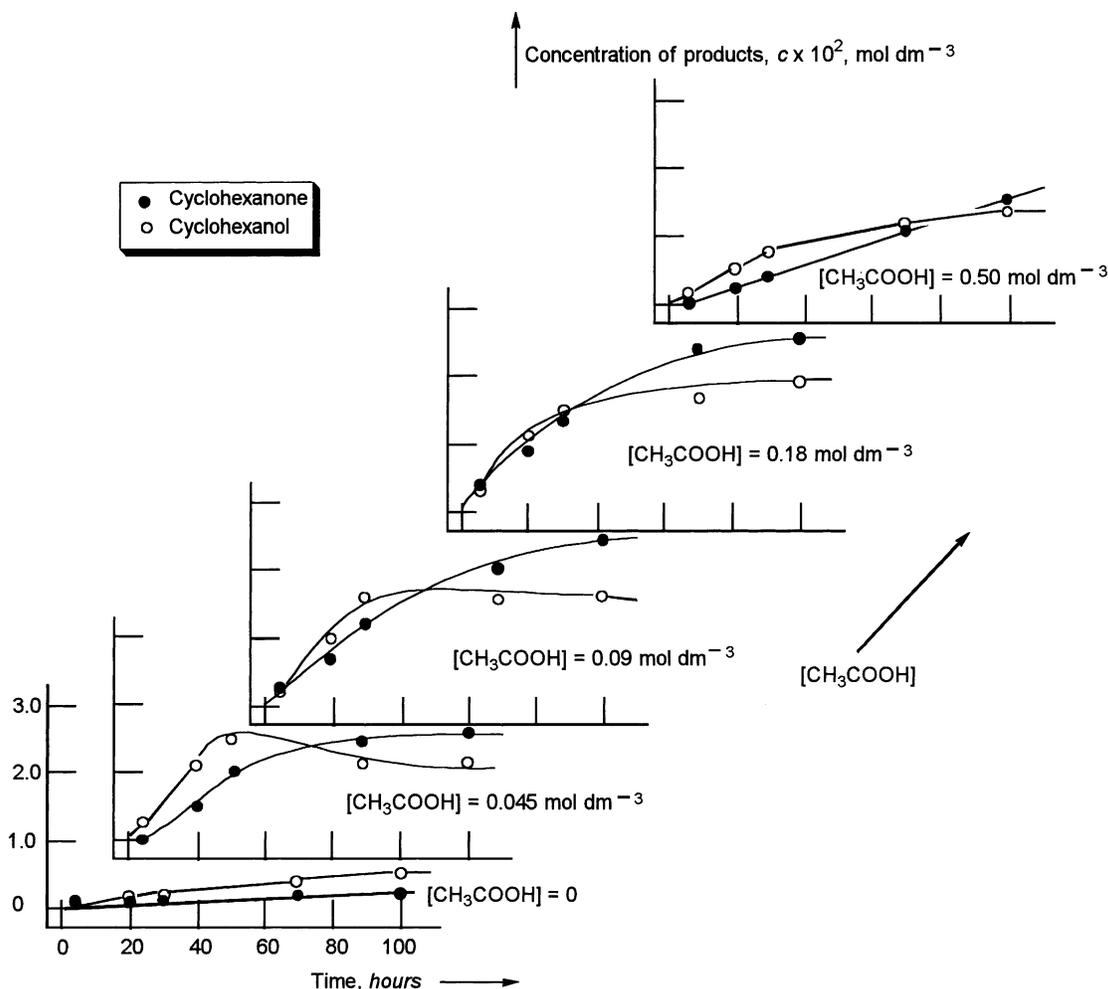


Fig. 4. Accumulation of cyclohexanone (closed circles) and cyclohexanol (open circles) in the oxidation of cyclohexane (initial concentration 0.46 mol dm^{-3}) with 70% aqueous *tert*-BuOOH (0.14 mol dm^{-3}) in MeCN at 20°C catalyzed by compound **1** ($0.5 \times 10^{-4} \text{ mol dm}^{-3}$) at various concentrations of added MeCOOH. All product concentrations were measured after the reduction with PPh_3 .

2.3. Stereoselectivity of the reaction with alkanes

We investigated the stereoselectivity of the oxidation of six cyclohexane derivatives bearing two substituents at various positions, *cis*- and *trans*-isomers of decalin, 1,2-dimethylcyclohexane and 1,4-dimethylcyclohexane. The oxidation of one of the two tertiary C–H bonds in these compounds gives hydroperoxidated or hydroxylated products and can proceed with either retention or inversion of the configuration (Scheme 4). In many cases only

partial retention of configuration (partial epimerization) is observed [127]. The oxidation data of disubstituted cyclohexanes obtained in this work are summarized in Table 4. It is convenient to use a simple *trans/cis* parameter which is the ratio $(\text{trans-tert-ol})/(\text{cis-tert-ol})$, where (trans-tert-ol) and (cis-tert-ol) are the concentrations of *cis*- and *trans*-isomers, of the monohydroxylated product formed in the oxidation. For the oxidation of decalins this ratio will be $(\text{trans-decal-9-ol})/(\text{cis-decal-9-ol})$. The lower the value of this *trans/cis* parameter in the

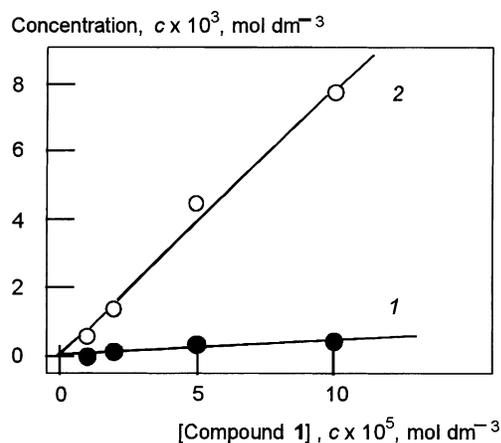


Fig. 5. Concentration of cyclohexanone (curve 1) and cyclohexanol (2) versus concentration of compound 1 in the cyclohexane (initial concentration 0.46 mol dm^{-3}) oxidation with 70% aqueous *tert*-BuOOH (0.14 mol dm^{-3}) in the presence of MeCOOH (0.18 mol dm^{-3}) in MeCN (22°C ; 5 h). All product concentrations were measured after the reduction with PPh_3 .

oxidation of *cis*-isomers of disubstituted cyclohexanes, the higher the stereoselectivity of the reaction. On the other hand, if the oxidation of *trans*-isomers exhibits a high value of this *trans/cis* parameter, this testifies that the reaction is stereoselective. The oxidation of disubstituted cyclohexanes (especially decalin isomers) by non-stereoselective reagents gives approximately equal *trans/cis* values for both

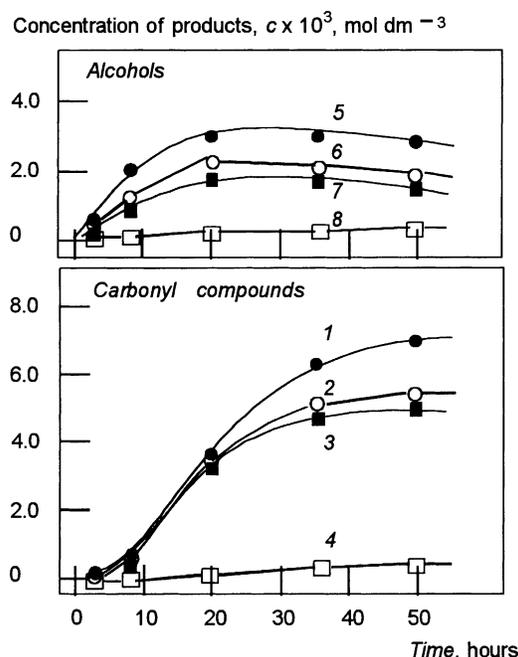


Fig. 6. Reaction profile of the oxidation of *n*-octane (initial concentration 0.62 mol dm^{-3}) with 70% aqueous *tert*-BuOOH (0.28 mol dm^{-3}) in MeCN at 21°C catalyzed by compound 1 ($0.5 \times 10^{-4} \text{ mol dm}^{-3}$) in the presence of MeCOOH (0.18 mol dm^{-3}). All product concentrations were measured after the reduction with PPh_3 . Products: octane-2-one (1); octane-3-one (2); octane-4-one (3); octanal (4); octane-2-ol (5); octane-3-ol (6); octane-4-ol (7); octane-1-ol (8).

Table 4
Oxidation of disubstituted cyclohexanes (*trans/cis* ratio)^a

Entry	Oxidizing system	Oxidation of					
		<i>cis</i> -Decalin	<i>trans</i> -Decalin	<i>cis</i> -1,2-DMCH	<i>trans</i> -1,2-DMCH	<i>cis</i> -1,4-DMCH	<i>trans</i> -1,4-DMCH
1	H_2O_2 -compound 1-MeCO ₂ H in MeCN	0.12	33.4	0.34	4.09	0.50	2.15
2	H_2O_2 -compound 1-MeCO ₂ H in MeNO ₂	0.13	25.8	0.32	6.6	0.40	8.6
3	H_2O_2 -compound 1-MeCO ₂ H in Me ₂ CO	0.97	3.7	0.54	2.5	0.95	2.1
4	<i>tert</i> -BuOOH-compound 1-MeCO ₂ H in MeCN	1.70	3.0	0.71	0.92		
5	<i>tert</i> -BuOOH-compound 2 in MeCN	2.80	2.3	1.50			
6	<i>tert</i> -BuOOH-compound 3 in MeCN	5.3	10.1				
7	<i>tert</i> -BuOOH-compound 4 in MeCN	5.3	5.0				
8	H_2O_2 - <i>h\nu</i> in MeCN	1.28	2.7	0.92	1.0	1.5	1.4
9	H_2O_2 -FeSO ₄ in MeCN	3.4	8.8	1.3	1.2	1.5	1.5
10	H_2O_2 -VO ₃ ⁻ -PCA ^b in MeCN	2.09	2.40	0.75	0.78	1.45	1.6

^a The *trans/cis* ratio of isomers of *tert*-alcohols formed in the oxidation of disubstituted cyclohexanes (Scheme 3) was measured after treatment of the reaction sample with triphenylphosphine. DMCH, dimethylcyclohexane.

^b PCA, pyrazine-2-carboxylic acid. For this system, see [108,109,115,118,121–125].

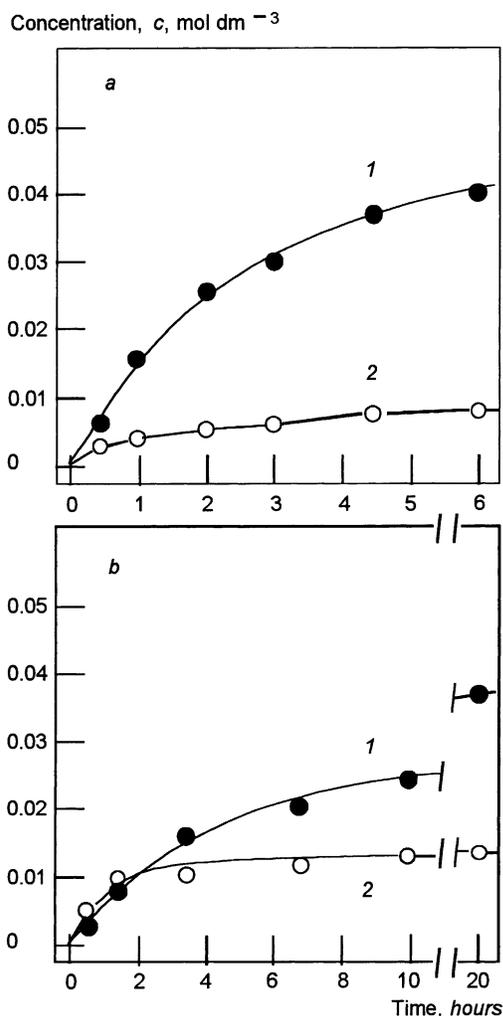


Fig. 7. Accumulation of cyclooctanone (curve 1) and cyclooctanol (curve 2) in the oxidation of cyclooctane (initial concentration 0.62 mol dm^{-3}) with 70% aqueous *tert*-BuOOH (0.14 mol dm^{-3}) in MeCN at 20°C catalyzed by compound **2** ($0.5 \times 10^{-4} \text{ mol dm}^{-3}$) in the absence (graph a) and in the presence of MeCOOH (0.25 mol dm^{-3}) (graph b). All product concentrations were measured after the reduction with PPh_3 .

cis- and *trans*-hydrocarbons, these parameters being usually different from unity (see [121,125]). Indeed, non-stereoselective reactions lead to the predominant formation of the most thermodynamically stable or less strained isomer (usually *trans*-isomer of *tert*-alcohol). The relative concentrations of tertiary alcohols were measured after reduction of

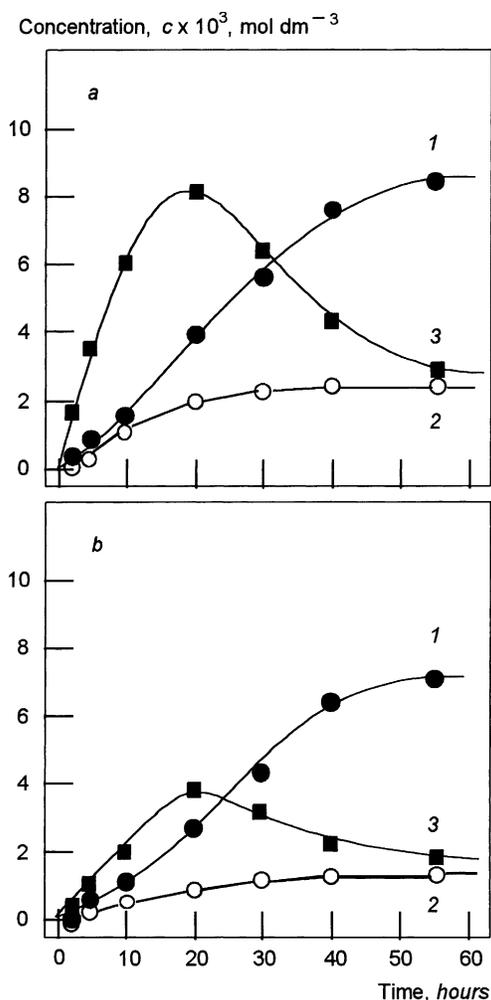
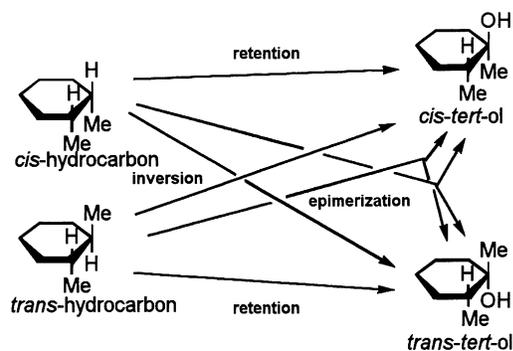


Fig. 8. Accumulation of cyclooctanone (curve 1), cyclooctanol (2) and cyclooctyl hydroperoxide (3) in the oxidation of cyclooctane (initial concentration 0.62 mol dm^{-3}) with 70% aqueous *tert*-BuOOH (0.14 mol dm^{-3}) in MeCN at 30°C catalyzed by (concentration $0.5 \times 10^{-4} \text{ mol dm}^{-3}$) compound **4** (graph a) and compound **3** (graph b). Product concentrations were estimated by the comparison of cyclohexanone and cyclohexanol concentrations measured before and after the reduction with PPh_3 .

reaction samples with triphenylphosphine which converted tertiary hydroperoxides into the corresponding alcohols.

Table 4 demonstrates that the oxidation by the system " H_2O_2 -compound **1**- MeCO_2H " in MeCN proceeds stereoselectively in the case of all disubstituted cyclohexanes studied. Indeed, the value of the *trans/cis*



Scheme 4. Hydroxylation of 1,2-dimethylcyclohexane isomers with retention and inversion of configuration and with epimerization.

parameter is noticeably less than unity for the reaction with *cis*-hydrocarbons and exceeds unity in the case of *trans*-hydrocarbons (most pronounced in the oxidation of *trans*-decalin). The oxidation of disubstituted cyclohexanes in nitromethane (entry 2), the polarity and coordination ability of which are similar to those of acetonitrile, gives approximately the same *trans/cis* values. Going from MeCN and MeNO₂ to the less polar acetone, leads to a significant decrease of the stereoselectivity. In this case the corresponding parameters are comparable with those obtained by us for the systems “H₂O₂-*hν*” (entry 8) and “H₂O₂-FeSO₄” (entry 9) [108,109,128–132] and “H₂O₂-VO₃⁻-PCA” [108,109,115,118,121–125] (entry 10) in MeCN which are known to oxidize via the formation of

Table 5
Oxidation of adamantane in MeCN at room temperature

Entry	System	Ratio of isomers	
		OL-2/ONE/OL-1 ^a	3°:2° ^b
1	H ₂ O ₂ -1-MeCO ₂ H	1.0:1.0:6.1	2.00
2	<i>tert</i> -BuOOH-1-MeCO ₂ H	1.0:4.3:6.1	2.15
3	<i>tert</i> -BuOOH-1	1.0:3.4:6.1	2.33
4	<i>tert</i> -BuOOH-2	1.0:3.5:13.9	2.05
5	<i>tert</i> -BuOOH-3	1.0:11.3:11.6	8.6
6	<i>tert</i> -BuOOH-4	1.0:1.8:12.7	7.2
7	H ₂ O ₂ - <i>hν</i>	1.0:0.43:1.16	0.90
8	<i>tert</i> -BuOOH- <i>hν</i>	1.0:1.75:2.1	1.15
9	H ₂ O ₂ -VO ₃ ⁻ -PCA ^c	1.0:0:1.11	0.74

^a Non-normalized ratio of concentrations adamantanol-2:adamantanone:adamantanol-1.

^b Parameter 3°:2° is normalized (i.e. calculated taking into account the number of hydrogen atoms at each position) relative reactivities of hydrogen atoms at tertiary and secondary carbons, respectively. All product concentrations were measured without prior reduction with PPh₃.

^c PCA, pyrazine-2-carboxylic acid. For this system, see [108,109,115,118,121–125].

free hydroxyl radicals. Thus, the stereoselectivity of the oxidation by the system “H₂O₂-compound 1-MeCOOH” strongly depends on the nature of the solvent. Oxidation reactions with *tert*-butyl hydroperoxide catalyzed by compounds 1–4 proceed without retention of stereo-configuration (entries 4–7).

Table 5 summarizes the findings for the oxidation of adamantane. If the reaction proceeds via attack of

Table 6
Oxidation of alcohols^a

Run	Alcohol	Conversion (%) ^b	Products	Yield (%) ^c
1	CH ₃ CH(OH)CH ₃	100	CH ₃ COCH ₃	98
2	CH ₃ CH(OH)CH ₂ CH ₃	100	CH ₃ COCH ₂ CH ₃	98
3	CH ₃ (CH ₂) ₂ CH(OH)CH ₃	99	CH ₃ (CH ₂) ₂ COCH ₃	97
4	CH ₃ CH ₂ CH(OH)CH ₂ CH ₃	98	CH ₃ CH ₂ COCH ₂ CH ₃	97
5	(CH ₃) ₂ CHCH(OH)CH ₃	100	(CH ₃) ₂ CHCOCH ₃	100
6	CH ₃ (CH ₂) ₂ CH(OH)CH ₂ CH ₃	97	CH ₃ (CH ₂) ₂ COCH ₂ CH ₃	96
7	Cyclo-C ₆ H ₁₁ OH	95	cyclo-C ₆ H ₁₀ O	91
8	CH ₃ CH ₂ CH ₂ OH	40	CH ₃ CH ₂ CHO CH ₃ CH ₂ COOH	19 17
9	CH ₃ (CH ₂) ₃ CH ₂ OH	59	CH ₃ (CH ₂) ₃ CHO CH ₃ (CH ₂) ₃ COOH	42 11

^a Conditions: alcohol, 0.23 mol dm⁻³; H₂O₂, 1.0 mol dm⁻³; compound 1, 0.4 × 10⁻⁴ mol dm⁻³; acetic acid, 0.5 mol dm⁻³; solvent, MeCN, 20°C; 3 h. Yields of the products were measured by GC after treatment of the samples with triphenylphosphine.

^b The ratio of the reacted alcohol amount to its initial amount.

^c Yields are based on the initial alcohol amounts.

hydroxyl radicals on the C–H bonds, the $3^\circ:2^\circ$ ratio should be less than unity (entries 7 and 9). For the catalytic systems studied here (entries 1–6), this parameter is noticeably higher than unity. So it may be concluded that in these cases the reaction does not involve free hydroxyl radicals. In the case of catalyzed oxidations with *tert*-butyl hydroperoxide, possibly *tert*-BuO• radicals attack the C–H bonds of the alkane.

2.4. Oxidation of alcohols

The system “H₂O₂–compound 1–MeCO₂H” oxidizes very efficiently secondary alcohols to the corresponding ketones in acetonitrile solution. It should be noted that hydrogen peroxide in the presence of an organic acid could be transformed into the corresponding peroxy acid active in alcohol oxidation [110,133]. Some data are summarized in Table 6. The reaction proceeds almost quantitatively in all cases (runs 1–7). Primary alcohols are oxidized less easily, and in this case the conversion and the yields of the products (corresponding aldehyde and carboxylic acid) is lower than 100% (runs 8 and 9).

The kinetics of the isopropanol oxidation are shown in Fig. 9. The rate of the reaction (but not its yield) strongly depends on the catalyst concentration (compare Fig. 9a and b). In the absence of acetic acid, isopropanol was not oxidized under the conditions of the experiment shown in Fig. 9a. Fig. 10 (graphs a and b) demonstrates that acetonitrile is much better as a solvent as acetone for the oxidation of alcohols. Other secondary alcohols (cyclohexanol and 1-phenylethanol) are transformed quantitatively into the corresponding ketones at room temperature within 2–3 h (Figs. 11 and 12).

Compound 1 catalyzes also the oxidation of butanol-2 by H₂O₂ in the presence of acetic acid in aqueous solution. However, the rate and yield of the reaction in this solvent are very low.

2.5. Epoxidation of olefins

Hexene-1, a terminal aliphatic olefin, is quantitatively epoxidized by the system “H₂O₂–compound 1–MeCO₂H” in acetonitrile solution at room temperature (Fig. 13a). If in the presence of 0.25 mol dm⁻³ of acetic acid the concentration of the epoxide at-

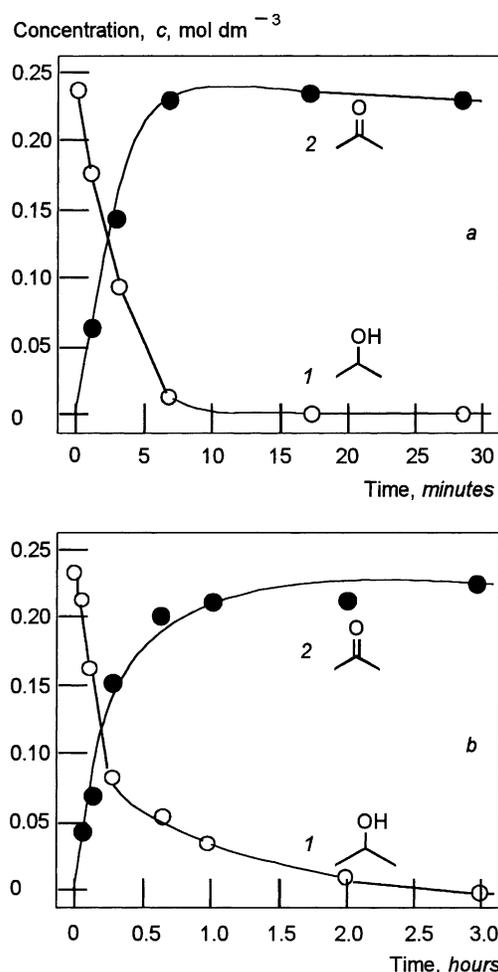


Fig. 9. Accumulation of acetone (curve 2) in the oxidation of isopropanol (initial concentration 0.23 mol dm⁻³, curve 1) with H₂O₂ (0.5 mol dm⁻³) in the presence of MeCOOH (0.25 mol dm⁻³) in MeCN at 22°C catalyzed by compound 1 at its different concentrations: 0.5 × 10⁻⁴ mol dm⁻³ (graph a) and 0.2 × 10⁻⁴ mol dm⁻³ (graph b).

tains 0.22 mol dm⁻³ after 10 min, in the absence of MeCO₂H the concentration of the epoxide is only 0.002 mol dm⁻³ after 1 h. The corresponding reaction in acetone, even in the presence of acetic acid, is much less efficient (Fig. 13b). It is interesting that the epoxidation of styrene (as well as of cyclohexene) occurs with non-productive hydrogen peroxide decomposition to molecular oxygen as a side-reaction; the

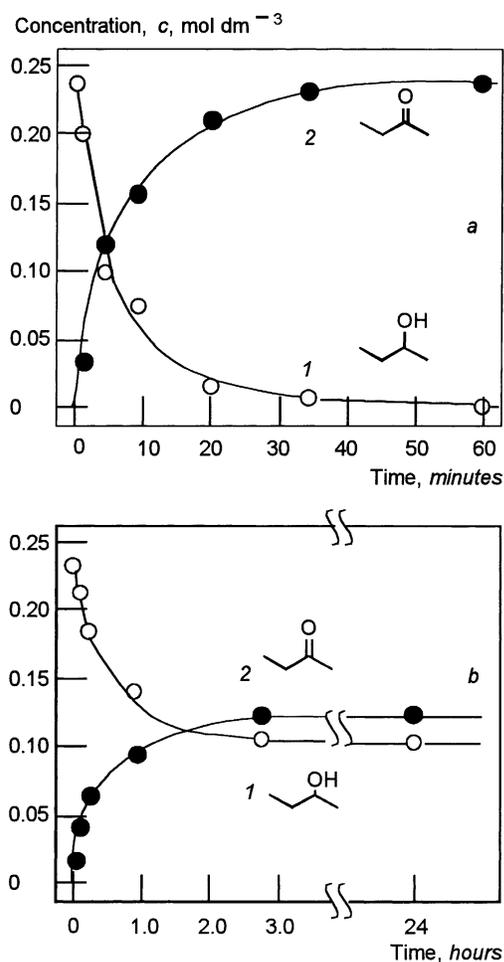


Fig. 10. Accumulation of methylethylketone (curve 2) in the oxidation of 2-butanol (initial concentration 0.23 mol dm^{-3} , curve 1) with H_2O_2 (0.5 mol dm^{-3}) catalyzed by compound **1** ($0.5 \times 10^{-4} \text{ mol dm}^{-3}$) in the presence of MeCOOH (0.25 mol dm^{-3}) at 22°C in MeCN (graph a) and acetone (graph b).

oxidation slows down after 30 min, the yield of the epoxide being less than quantitative (Fig. 14).

2.6. Oxygenation of sulfides

Dimethylsulfide under the action of the system " H_2O_2 -compound **1**- MeCO_2H " is transformed into dimethylsulfoxide. Under the conditions of the experiment shown in Fig. 15, the reaction is complete after 3 h at room temperature without formation of dimethylsulfone.

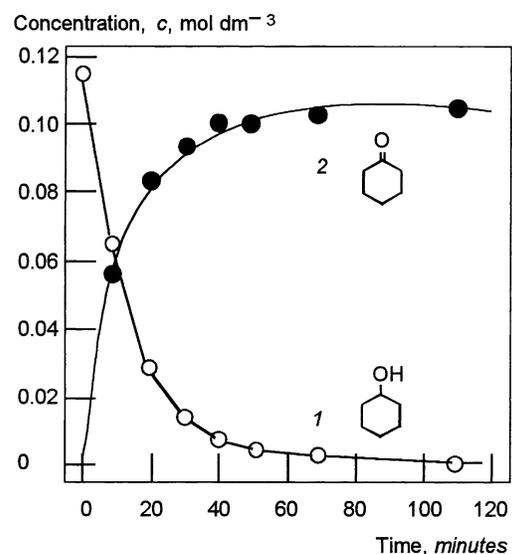


Fig. 11. Reaction profile of the oxidation of cyclohexanol (initial concentration $0.115 \text{ mol dm}^{-3}$, curve 1) into cyclohexanone (curve 2) with H_2O_2 (0.5 mol dm^{-3}) catalyzed by compound **1** ($1.0 \times 10^{-4} \text{ mol dm}^{-3}$) in the presence of MeCOOH (0.25 mol dm^{-3}) in MeCN at 22°C .

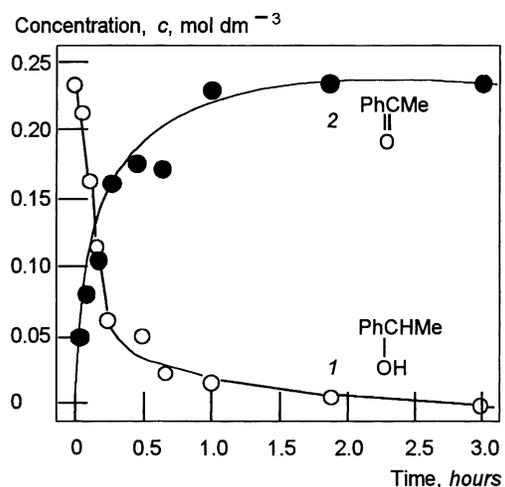


Fig. 12. Reaction profile of the oxidation of 1-phenylethanol (initial concentration 0.23 mol dm^{-3} , curve 1) into acetophenone (curve 2) with H_2O_2 (0.5 mol dm^{-3}) catalyzed by compound **1** ($0.5 \times 10^{-4} \text{ mol dm}^{-3}$) in the presence of MeCOOH (0.25 mol dm^{-3}) in MeCN at 22°C .

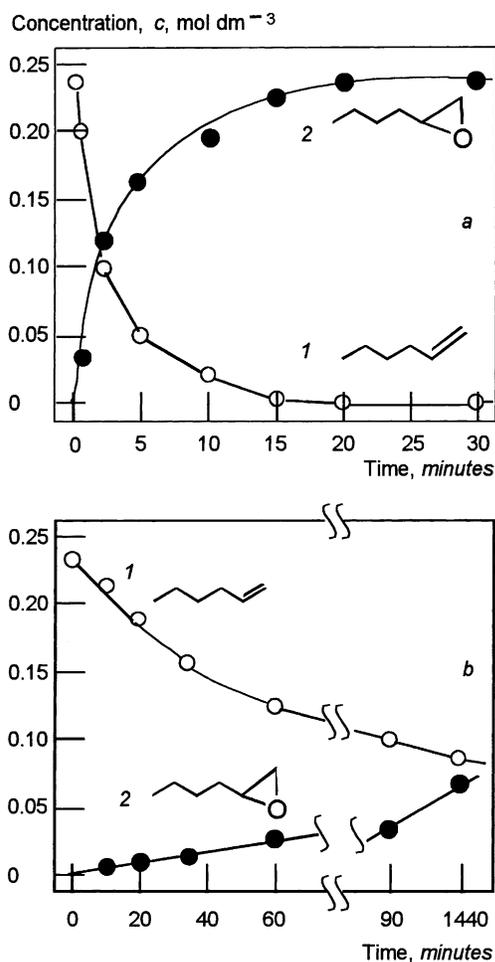


Fig. 13. Consumption of hexene-1 (initial concentration 0.23 mol dm^{-3} , curve 1) and accumulation of hexene-1 epoxide (curve 2) in the epoxidation with H_2O_2 (0.5 mol dm^{-3}) catalyzed by compound **1** ($0.5 \times 10^{-4} \text{ mol dm}^{-3}$) in the presence of MeCOOH (0.25 mol dm^{-3}) at 22°C in MeCN (graph a) and acetone (graph b).

2.7. On the nature of oxidizing species

We have not carried out a special study devoted to the evaluation of the reaction mechanism. Nevertheless, based on our data and on the literature, we can assume tentatively that the oxidation of the organic substrate (e.g. an alkane) implies the interaction of the organic molecule with an oxo derivative of high-valent manganese. Oxo derivatives of Mn(V) have been proposed previously to take part in oxida-

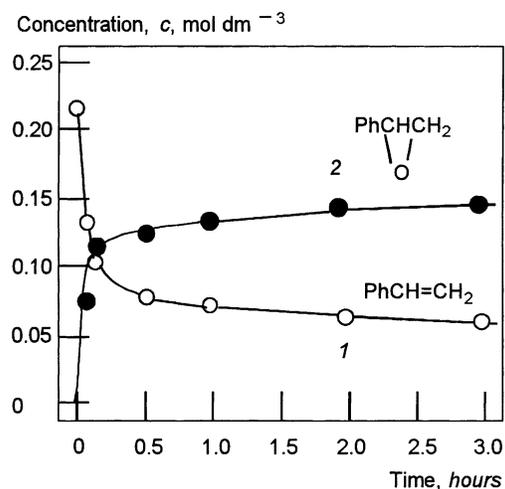


Fig. 14. Consumption of styrene (initial concentration 0.21 mol dm^{-3} , curve 1) and accumulation of styrene epoxide (curve 2) in the epoxidation with H_2O_2 (1.0 mol dm^{-3}) catalyzed by compound **1** ($0.5 \times 10^{-4} \text{ mol dm}^{-3}$) in the presence of MeCOOH (0.25 mol dm^{-3}) at 22°C in MeCN.

tion processes and have been characterized in some cases by spectroscopy and even isolated [134–147]. The Mn(V)=O species in a solvent cage abstracts a hydrogen atom from the alkane, RH , to give a hydroxy

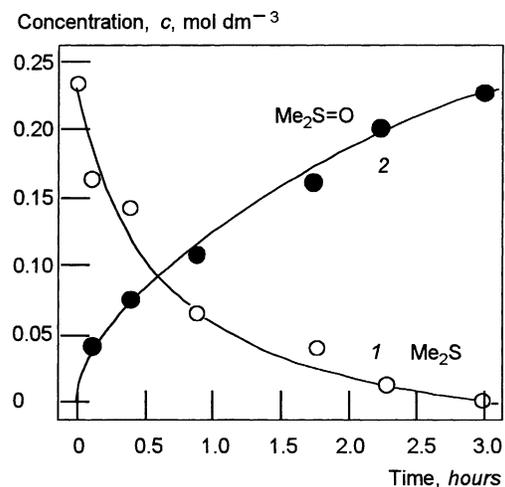


Fig. 15. Reaction profile of the oxidation of dimethylsulfide (initial concentration 0.23 mol dm^{-3} , curve 1) to dimethylsulfoxide (curve 2) with H_2O_2 (1.0 mol dm^{-3}) catalyzed by compound **1** ($0.5 \times 10^{-4} \text{ mol dm}^{-3}$) in the presence of MeCOOH (0.25 mol dm^{-3}) in MeCN at 22°C .

manganese species Mn(IV)–OH and a radical R•. In the case of 1,2-dimethylcyclohexane oxidation, equilibrium with inversion at the carbon bound with three different groups is possible (it is known, for example, that such inversion proceeds in the case of *tert*-butyl radical with the energy 2.1–2.8 kJ mol⁻¹ [148,149]). The rate of this inversion may depend on the nature of the solvent, being lower in the case of more polar and solvating acetonitrile or nitromethane. When radical R• reacts with dioxygen a hydroperoxyl radical, ROO•, can be formed with retention of configuration at one of two tertiary carbons and giving a peroxy radical with *cis*-configuration of the methyl groups. Further, this peroxy radical will be transformed into *cis-tert*-hydroperoxide and then into *cis-tert*-alcohol.

3. Conclusions

Compound **1** exhibits a very high catalytic activity in hydrogen peroxide oxidation of alkanes, alcohols, olefins, and sulfides, provided a carboxylic (usually acetic) acid is used as an additive. In the absence of the acid, only non-productive decomposition of H₂O₂ occurs to give molecular oxygen. Polar coordinating solvents such as acetonitrile and nitromethane are the solvents of choice for this reaction, while the oxidation in acetone proceeds much less efficiently, and without retention of configuration at the tertiary carbon atoms in the case of disubstituted cyclohexanes. These features found for compound **1** in acetonitrile in the presence of acetic acid, distinguish the discussed catalytic oxidation reaction from known from the literature analogous oxygenations catalyzed by manganese complexes including complexes containing 1,4,7-trimethyl-1,4,7-triazacyclononane as a ligand. For example, in the olefin epoxidation catalyzed by the system “MnSO₄–1,4,7-trimethyl-1,4,7-triazacyclononane”, acetone or methanol have been found to be suitable solvents, while the reaction efficiency in acetonitrile is very low [9]. It is noteworthy that we have been unable to obtain even small amounts of the oxygenated products from alkanes using the combination “MnSO₄–1,4,7-trimethyl-1,4,7-triazacyclononane–MeCO₂H” in acetonitrile instead of the system “compound **1**–MeCO₂H” as the catalyst. Thus, we can conclude that systems “MnSO₄–1,4,7-trimethyl-1,4,7-triazacyclononane” in acetone (efficient in olefin epox-

idation) on the one hand and “compound **1**–MeCO₂H” in acetonitrile (efficient in alkane hydroperoxidation, as well as in oxidations of secondary alcohols, sulfides and epoxidation of olefins) on the another hand are not similar and act via different mechanisms.

Compound **1** exhibits moderate catalytic activity in the alkane oxidation with *tert*-butyl hydroperoxide, the reaction being accelerated by acetic acid added in small concentration. The efficiency of other manganese derivatives checked in this work (compounds **2–4**) in the alkane oxidation with *tert*-butyl hydroperoxide is low, while only negligible amounts of oxygenates were detected when hydrogen peroxide was used as an oxidant.

4. Experimental

The synthesis of compounds **1** [150,151], **2** [152] and **3** [153] has been described in the literature. Commercially available sample of compound **4** has been used. The oxidations of higher hydrocarbons, alcohols, olefins and dimethylsulfide were carried out in air in thermostated Pyrex cylindrical vessels with vigorous stirring. The total volume of the reaction solution was 10 ml. In a typical experiment, initially, a portion of 35% aqueous solution of hydrogen peroxide (“Fluka”) was added to the solution of the catalyst, substrate and acetic acid in acetonitrile (“Fluka”). The oxidations of ethane and propane were carried out in a glass inlet tubes placed into a stainless steel autoclave with intensive stirring (volume of the reaction solution was 5 ml and total volume of autoclave was 100 ml).

The samples of the reaction solutions were analysed by GC (chromatographs DANI-86.10; fused silica capillary column 25 m × 0.32 mm × 0.25 μm, CP-WAX52CB, helium integrator SP-4400 and LKhM-80-6, 2-m column packed with 5% Carbowax 1500 on 0.25–0.315 mm Inerton AW-HMDS, argon) twice: before and after addition of an excess of solid triphenylphosphine. In the case of the alkane oxidation, triphenylphosphine reduces hydrogen peroxide to water and the alkyl hydroperoxide to the corresponding alcohol which allowed the determination of the real concentrations of the alkyl hydroperoxide, alcohol, and ketone (or aldehyde). In the case of the oxidation of alcohols, olefins, and sulfides, this

procedure allows to avoid reactions between substrates and hydrogen peroxide in the GC injector.

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