

Oxidation with the "H₂O₂—manganese(IV) complex—carboxylic acid" reagent

1. Oxidation of saturated hydrocarbons with peroxy acids and hydrogen peroxide

G. B. Shul'pin^{a*} and J. R. Lindsay-Smith^b

^a*N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
4 ul. Kosygina, 117977 Moscow, Russian Federation.*

Fax: +7 (095) 938 2156. E-mail: gb@shulpin.msk.ru

^b*The University of York, Department of Chemistry,
York, Heslington YO1 5DD, UK.*

Fax: + (44) 1904 43 25 16. E-mail: JRLS1@york.ac.uk

The complex [LMn^{IV}(O)₃Mn^{IV}L](PF₆)₂ (**1**), where L is 1,4,7-trimethyl-1,4,7-triazacyclononane, catalyzes a highly efficient stereoselective oxygenation of saturated hydrocarbons in the presence of H₂O₂. A carboxylic acid is an obligatory component of the reaction mixture, while acetonitrile or acetone can be used as solvent. The reaction occurs, forming alkyl hydroperoxide, ketone, and alcohol. Substitution at the tertiary carbon atom proceeds more easily than that at the secondary carbon atom, whereas primary C—H bonds are rather inactive. Oxidation of alkanes and alcohols with peroxy acids catalyzed by complex **1** occurs with lower efficiency.

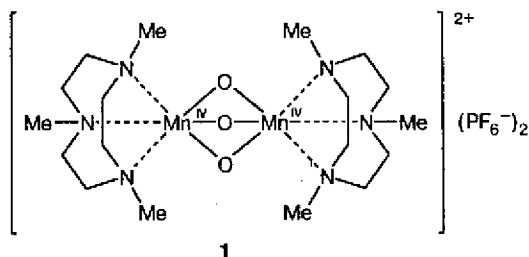
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Oxidation with molecular oxygen or with donors of the oxygen atom (in particular, hydrogen peroxide and peroxy acids) is one of the most important methods of conversion of saturated and alkylaromatic hydrocarbons into valuable chemicals. The use of metal complexes efficiently catalyzing such reactions makes it possible to perform conversion of hydrocarbons at high rates under mild conditions.^{1,2} Various organic compounds (*e.g.*, olefins) are efficiently oxygenated with peroxy acids;^{3–7} however, oxidation of C—H bonds in saturated hydrocarbons with these reagents usually occurs in low yields and requires strongly acid media. The most interesting feature of the reactions of oxidation with peroxy acids is their stereoselectivity, *e.g.*, partial retention of the configuration at the tertiary carbon atom in disubstituted cycloalkanes: oxygenation of *cis*-1,2-dimethylcyclohexane results in the preferable formation of *cis*-1,2-dimethylcyclohexan-1-ol as the main product, whereas the concentration of *trans*-1,2-dimethylcyclohexan-1-ol obtained is much lower. The reactions of oxidation with peroxy acids are catalyzed with transition metal complexes, which makes it possible to increase the synthetic value of these methods.^{8–12}

Manganese complexes are efficient catalysts used in various oxidation processes.^{13–27} Recently,^{28–37} high catalytic activity of manganese(IV) complexes with macrocyclic nitrogen-containing ligand, 1,4,7-trimethyl-1,4,7-triazacyclononane (TMTACN), in the reactions of

oxidation of several organic substrates (olefins, alcohols, phenols) with hydrogen peroxide in both aqueous and organic media was demonstrated.

In this series of reports we describe the reactions of oxidation of hydrocarbons and other organic compounds with hydrogen peroxide and several other donors of the oxygen atom catalyzed by manganese complexes with nitrogen-containing ligands. In this work, which is the first communication in the series, we describe stereoselective oxidation of hydrocarbons with peroxy acids or with hydrogen peroxide catalyzed by dinuclear cationic manganese(IV) complex with TMTACN (**1**) described previously.^{38,39}



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Oxidation occurs most efficiently when hydrogen peroxide is used in combination with a carboxylic acid. Investigations of this reagent will be continued.

Experimental

Oxidation of hydrocarbons and other organic substrates was carried out in air in thermostatted cylindrical glass vessels with intense stirring. In most cases, the volumes of the reaction solutions were 5 mL. Usually, a 35% aqueous solution of hydrogen peroxide (Fischer) or a solution of peroxyacetic acid in acetic acid (Fluka), or solid *m*-chloroperoxybenzoic acid (Fluka) was added to a solution of catalyst (usually, 0.2 mmol L⁻¹) and substrate oxidized in MeCN. The conditions of particular reactions are given in the legends to the tables and figures.

The reaction mixtures were analyzed by GLC using a PYE UNICAM PU 4500 ("Phillips") chromatograph (an Alltech ECONO-CAP Carbowax column, 30 m × 0.25 mm; 0.25 μm; with helium as carrier gas). Each specimen was analyzed twice, before and after addition of an excess of solid triphenylphosphine. Quantitative analysis was performed after calibrating the chromatograms using solutions of the products with known concentrations.

Results and Discussion

Previously,^{28–37} it was found that TMTACN manganese complexes, which were synthesized preliminarily or obtained immediately in the reaction solution by mixing a manganese(II) salt and TMTACN, catalyze epoxidation of olefins and oxidation of several other compounds with hydrogen peroxide. Acetone and water were most often used as solvents. In this work, we showed that epoxidation of substituted styrenes (0.1 mol L⁻¹) in acetone with excess hydrogen peroxide (1.0 mol L⁻¹) in the presence of catalytic amounts of complex **1** (0.5 mmol L⁻¹) at 0 °C had a short (a few minutes) induction period and was over after about 3 h to give epoxides in nearly quantitative yields. Performing of competing reactions of unsubstituted and *p*-methoxy-, *p*-methyl-, and *p*-chlorosubstituted styrenes indicates that the epoxidizing reagent possesses weak electrophilic properties: the value of the parameter ρ was estimated at -0.78 from correlation with σ constants.

It was of interest to study the possibility of applying this oxidizing system to inert hydrocarbons containing hydrogen atoms at the sp³-hybridized carbon atoms. However, it turned out that in this case the formation of molecular oxygen from hydrogen peroxide is observed instead of oxidation that occurs inefficiently. It is possible to increase the yields of the products of alkane or arylalkane oxygenation to a certain extent if hydrogen peroxide is added gradually over a period of several hours rather than in one portion in the initial stage of the reaction. Acetonitrile was found to be the most convenient solvent in these reactions. Thus, a solution of H₂O₂ (0.01 mol L⁻¹) in acetonitrile was added to a solution of toluene (1.0 mol L⁻¹; the total volume of the reaction solution after addition is 10 mL) and complex **1** (a concentration of 0.5 mmol L⁻¹ after addition of the entire volume of hydrogen peroxide solution) over a period of 3 h at 0 °C, then the solution was stirred at

the same temperature for an additional 4 h and allowed to stay at 18 °C for ~10 h. According to GLC analysis, the reaction solution contained benzaldehyde (0.022 mol L⁻¹), benzyl alcohol (0.0056 mol L⁻¹), benzoic acid (0.030 mol L⁻¹), and a mixture of cresol isomers (0.003 mol L⁻¹; the ratio of *ortho*-, *meta*-, and *para*-isomers was 46 : 13 : 41). Comparison of the concentrations of PhCHO and PhCH₂OH determined by GLC before and after treating the specimen of the reaction solution with an excess of solid Ph₃P for 20 min showed^{1,40–43} that the content of benzyl hydroperoxide that decomposes to form PhCHO and PhCH₂OH upon chromatography and is reduced to PhCH₂OH under the action of Ph₃P is ~10% of the total amount of oxygenation products with respect to methyl group.

The efficiency of oxidation of *cis*-1,2-dimethylcyclohexane with hydrogen peroxide catalyzed by complex **1** in acetonitrile under the same conditions as those described for toluene except for temperature (at 20 °C) is low: the turnover number of the catalyst defined as the total number of moles of the products per mole of catalyst amounts merely to 7. In this case it seemed to be more interesting to determine the degree of retention of the configuration (*RC*) at the tertiary carbon atom. However, the value of this parameter (*RC*_{*cis*}) defined as

$$RC_{cis} (\%) = 100(c_{cis} - c_{trans}) / (c_{cis} + c_{trans}), \quad (1)$$

where *c*_{*cis*} and *c*_{*trans*} are the concentrations of isomers of the hydroxylation products of tertiary C—H bonds containing methyl groups in the *cis*- and *trans*-positions, respectively, appeared to be small, *RC*_{*cis*} = 11% (*i.e.*, nearly complete racemization is achieved in the course of oxidation). Analogously, the efficiency of hydroxylation of *cis*-1,2-dimethylcyclohexane with *tert*-butyl hydroperoxide in acetonitrile at 20 °C is low: the turnover number of the catalyst is less than 10, while *RC*_{*cis*} = 14%.

A quite different situation was observed when performing oxidation of hydrocarbons with peroxy acids catalyzed by complex **1**. It turned out that use of *m*-chloroperoxybenzoic acid (*m*-PBA) and peroxyacetic acid (PAA) makes it possible to oxidize alkanes and arylalkanes attaining large turnover numbers of the catalysts (Table 1). The efficiency of oxidation with PAA in acetonitrile is particularly high. As follows from the data in Table 1, a rather high bond selectivity of the reaction is observed, *i.e.*, the reaction rate changes for different types of bonds in the following order: primary ≪ secondary < tertiary.

Characteristics of the kinetics of this reaction are shown in Figs. 1 and 2 taking the accumulation of the products of cyclohexane and cycloheptane oxygenation with *m*-PBA and PAA, respectively, as examples. The concentrations of alcohols and ketones formed in the oxidation were determined after reduction of the specimens of the reaction solutions with an excess Ph₃P. A comparison of the chromatograms of the specimens of the reaction solutions obtained before and after treat-

Table 1. Oxidation of hydrocarbons with peroxy acids catalyzed by complex 1^a

Run	Substrate	Product	<i>m</i> -PBA			PAA		
			<i>c</i> · 10 ³ /mol	L ⁻¹ ^b	TNC ^c	<i>c</i> · 10 ³ /mol	L ⁻¹ ^b	TNC ^c
1	Cyclohexane	Cyclohexanone	4.8	(<0.05)	28	76.6	(<0.05)	485
		Cyclohexanol	9.4	(0.08)		20.6	(<0.05)	
2 ^d	<i>n</i> -Hexane	Hexan-2-one	1.0		5	8.2		86
		Hexan-3-one	0.8			3.4		
		Hexan-1-ol	<0.02			<0.02		
		Hexan-2-ol	0.9			3.1		
		Hexan-3-ol	1.1			2.5		
3 ^e	Methylcyclohexane	Cyclohexanecarboxyaldehyde	0.15		17	3.9		595
		2-, 3- and 4-Methylcyclohexanones ^f	2.8 ^g			59 ^h		
		1-Methylcyclohexanol	4.3			44		
		Cyclohexylmethanol	0.07			2.3		
		2-, 3- and 4-Methylcyclohexanols ^f	1.3			14		
4 ⁱ	<i>cis</i> -1,2-Dimethylcyclohexane	<i>cis</i> -2,3- and 3,4-Dimethylcyclohexanones ^f	<0.05	(<0.05)	53	15		470
		<i>cis</i> -1,2-Dimethylcyclohexan-1-ol	18.9	(2.2)		66.9	(<0.1)	
		<i>trans</i> -1,2-Dimethylcyclohexan-1-ol	3.1	(0.34)		3.3		
		<i>cis</i> -1-Hydroxymethyl-2-methylcyclohexane	0.2	(<0.02)		0.3		
		<i>cis</i> -2,3- and 3,4-Dimethylcyclohexanols ^f	4.3	(0.87)		8.6		
5 ^j	<i>trans</i> -1,2-Dimethylcyclohexane	<i>trans</i> -2,3- and 3,4-Dimethylcyclohexanones ^f	<0.05	(<0.05)	19	15.9	(<0.05)	168
		<i>trans</i> -1,2-Dimethylcyclohexan-1-ol	5.2	(0.16)		10.0	(<0.05)	
		<i>cis</i> -1,2-Dimethylcyclohexan-1-ol	0.52	(<0.05)		0.9		
		<i>trans</i> -2,3- and 3,4-Dimethylcyclohexanols ^f	3.9	(<0.05)		6.7		
6 ^k	Adamantane ^l	Adamantanone	6.9		120	0.07		306
		Adamantan-1-ol	48.5			58.4	(<0.02)	
		Adamantan-2-ol	4.6			2.8		
7	Toluene	Benzaldehyde	0.3		7	5.4		32
		Benzyl alcohol	3.0			1.1		
8	Ethylbenzene	Acetophenone	8.9		41	43.5		278
		1-Phenylethanol	6.2			12		
		Styrene epoxide	5.3			<0.05		
9	Cumene	1-Methyl-1-phenylethanol	12.0		29	24		200
		Acetophenone	2.4			16		
10	Benzene	Phenol	0.3		0.6	2.7		14
11	Styrene	Acetophenone	37		74	81		405
12	Cyclohexanol	Cyclohexanone	110		220	210	(12.2)	1050

^a Reaction conditions: substrate (0.4 mol L⁻¹), peroxy acid (0.5 mol L⁻¹), complex 1 (0.5 mmol L⁻¹ for *m*-PBA and 0.2 mmol L⁻¹ for PAA); acetonitrile as solvent; the reaction solution of volume 5 mL; 30 °C, 1 h.

^b Data given in parentheses correspond to the absence of complex 1.

^c The turnover number of the catalyst.

^d C(2) : C(3) = 1.0 : 1.0 (*m*-PBA) and 1.9 : 1.0 (PAA).

^e 1° : 2° : 3° = 1.0 : 9.7 : 77 (*m*-PBA) and 1.0 : 9.5 : 57 (PAA).

^f The sum of all isomers.

^g In a 36 : 50 : 14 ratio.

^h In a 25 : 55 : 20 ratio.

ⁱ RC_{*cis*} = 72% (73% in the absence of complex 1) (*m*-PBA) and 91% (PAA).

^j RC_{*trans*} = 82% (*m*-PBA) and 83% (PAA).

^k 3° : 2° = 6.3 (*m*-PBA) and 30.2 (PAA).

^l The suspension of the substrate (0.002 mol) in the reaction solution (5 mL).

ment with Ph₃P indicates that a small amount of cycloheptyl hydroperoxide is present in solution in the initial period of reaction. From Figs. 1 and 2, it follows that (1) accumulation of the oxygenation products begins only after a short (~15 min) induction period, and (2) the corresponding alcohol and ketone are first formed at equal rates in the oxidation with PAA; however, already after 40 min the concentration of ketone is much higher than that of alcohol.

In the course of the induction period, the color of the solution changes from bright pink, which is due to the presence of complex 1, to yellow. The solution turns bright yellow in the course of the most intense oxidation of the substrate, and then the color gradually changes to pale yellow. The curve of the change in the alcohol concentration passes through a maximum. In the presence of a relatively small (0.2 mol L⁻¹) amount of CCl₄, the accumulation of oxygenates in the initial

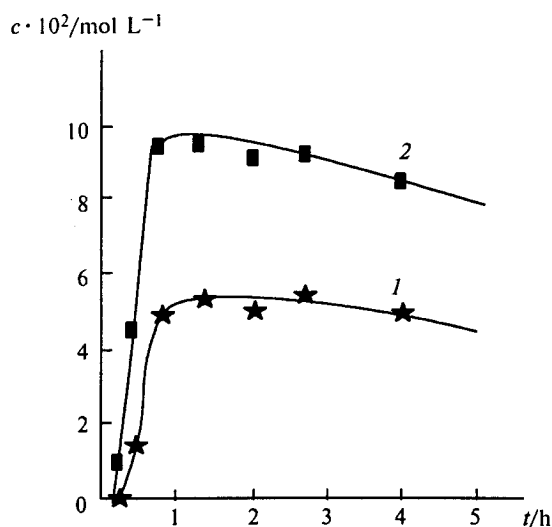


Fig. 1. Accumulation of cyclohexanone (1) and cyclohexanol (2) with *m*-PBA after reduction with Ph_3P . Conditions: cyclohexane (0.43 mol L^{-1}); complex 1 (0.2 mmol L^{-1}); *m*-PBA (0.5 mol L^{-1}); with MeCN as solvent; at 30°C .

period is appreciably accelerated (though the duration of the induction period remains the same) and cycloheptyl chloride is found in the reaction solution (Fig. 2, *b*). It is noteworthy that the introduction of a large amount of CCl_3Br , which is a more efficient trap of alkyl radicals, into the reaction solution results in a rather efficient formation of alkyl bromide. Thus, cyclohexyl bromide as the main product and a small amount of cyclohexanone are obtained from cyclohexane and CCl_3Br (Table 2). In this work, we did not study the bromination of alkanes in detail; however, on the basis of experimental data, one can suggest that alkyl radicals generated in the course of the reaction abstract the bromine atoms not only from CCl_3Br , but also from the molecular bromine formed in the oxidation with peroxy acid.

Partial retention of configuration at the tertiary carbon atom is one of the most characteristic features of

Table 2. Oxidation of cyclohexane with peroxy acids in acetonitrile in the presence of CCl_3Br^a

Products	<i>m</i> -PBA		PAA	
	$c \cdot 10^3/\text{mol L}^{-1}$	TNC ^b	$c \cdot 10^3/\text{mol L}^{-1}$	TNC ^b
Cyclohexyl bromide	100	202	139 (2.0) ^c	700
Cyclohexanone	1.1		1.0 (<0.05) ^c	

^a Reaction conditions: cyclohexane (0.4 mol L^{-1}); peroxy acid (0.5 mol L^{-1}); CCl_3Br (2.0 mol L^{-1}); complex 1 (0.5 mmol L^{-1} for *m*-PBA and 0.2 mmol L^{-1} for PAA); 30°C , 1 h.

^b The turnover number of the catalyst.

^c In the absence of complex 1.

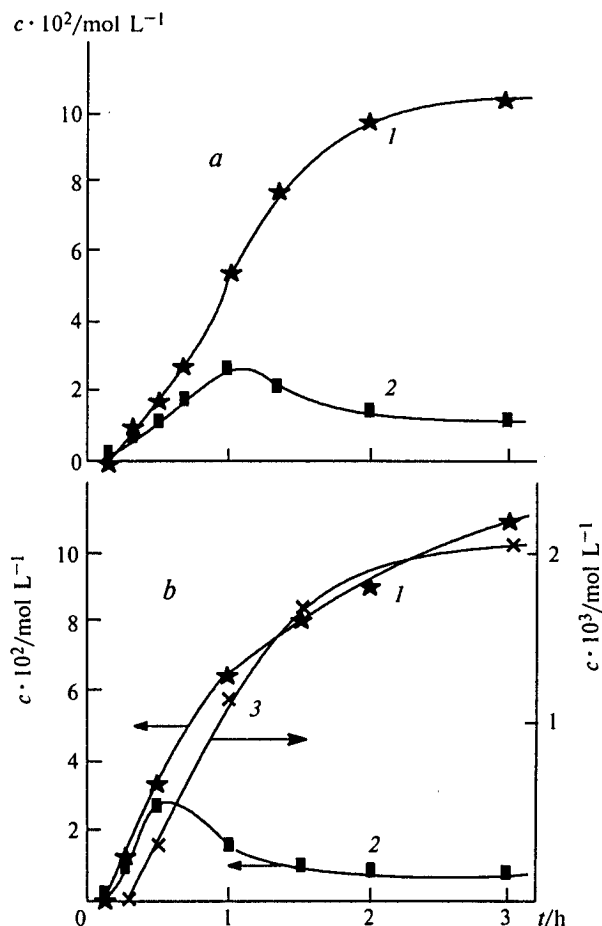


Fig. 2. The kinetics of the formation of cycloheptanone (1), cycloheptanol (2), and cycloheptyl chloride (3) in the oxidation of cycloheptane (0.4 mol L^{-1}) with peroxyacetic acid (0.5 mol L^{-1}) in MeCN at 20°C catalyzed by complex 1 (0.2 mmol L^{-1}) in the absence (*a*) and in the presence (*b*) of CCl_4 (0.2 mol L^{-1}).

the oxidation of alkanes with peroxy acids catalyzed by complex 1. The values of the RC_{cis} and RC_{trans} parameters calculated using formulas (1) and (2) and listed in Table 1 (runs 4 and 5) lie in the range from 70 to 90%. A very close value of the RC_{cis} parameter was also obtained for the non-catalyzed oxidation with *m*-PBA. However, in all cases we failed to obtain pure isomers upon hydroxylation, *i.e.*, the reaction is stereoselective rather than stereospecific (see, *e.g.*, other reactions catalyzed by metal complexes and occurring with retention of configuration^{44,45}):

$$RC_{trans} (\%) = 100(c_{trans} - c_{cis}) / (c_{trans} + c_{cis}) \quad (2)$$

From the data in Table 1 it follows also that arylalkanes are oxidized in somewhat lower yields (runs 7–9) than cycloalkanes, whereas the efficiency of oxidation of benzene into phenol is very low (run 10). Cyclohexanol is readily converted into cyclohexanone (run 12), and styrene is oxidized to give acetophenone.

Table 3. Values of selectivity parameters $n^*/6^*$ for oxidation of cycloalkanes with various reagents in acetonitrile^a

Reagent	5*/6*	8*/6*	12*/6*
<i>m</i> -PBA-1 ^b	~0.2	3.0	0.7
PAA-1 ^b	0.6	3.2	1.8
H ₂ O ₂ -AcOH-1 ^c	0.7	4.3	0.8
O ₂ -H ₂ O ₂ - <i>hν</i> ^d	1.0	1.6	0.9
O ₂ -H ₂ O ₂ -VO ₃ ⁻ -PCA ^e	0.7	1.6	1.0

^a Normalized reactivities of hydrogen atoms in cycloalkanes C_nH_{2n} relative to the reactivity of hydrogen atoms in cyclohexane (6* = 1).

^b Conditions: peroxy acid (0.125 mol L⁻¹), 50 min (*m*-PBA), 30 min (PAA); other conditions are analogous to those described in Table 1.

^c Conditions: H₂O₂ (0.1 mol L⁻¹); AcOH (0.1 mol L⁻¹); 20 °C; 15 min.

^d UV-irradiation at 25 °C; 20 min.

^e PCA is pyrazine-2-carboxylic acid^{1,42,48-50}; 50 °C; 1 h; the value of the 5*/6* parameter was obtained at 30 °C.

To investigate a plausible mechanism of the process, we carried out competing reactions of the oxidation of several cycloalkanes and cyclohexane. Previously,^{46,47} it has been reported that oxidation with participation of free radicals is characterized by specific values of relative reactivities. The data obtained and analogous parameters for oxidation with the "O₂-H₂O₂-VO₃⁻-PCA"^{1,48-50} (PCA is pyrazine-2-carboxylic acid) and "O₂-H₂O₂-*hν*"⁵¹ reagents generating hydroxyl radicals (the latter are given for comparison) are listed in Table 3. As can be seen, for all the reagents studied, the values of relative reactivities are close for each pair of substrates, though the values of these parameters completely coincide only for the "O₂-H₂O₂-VO₃⁻-PCA" and "O₂-H₂O₂-*hν*" reagents. Therefore, one can conclude that the reactions catalyzed by complex 1 occur with participation of radical species that, however, are not hydroxyl radicals.

Since peroxy acids used as oxidants contain considerable amounts of free carboxylic acids (benzoic acid in the commercial *m*-PBA specimen and acetic acid in the PAA specimen), it was of interest to compare the activities of these peroxy acids with the oxidizing power of hydrogen peroxide in the presence of carboxylic acids. We found that the reactions of oxidation of saturated hydrocarbons with hydrogen peroxide used as 35% aqueous solution in acetonitrile are accelerated to a great extent on addition of AcOH. According to the data of GLC analysis of the reaction solution before treating it with Ph₃P, oxidation of *n*-hexane (0.4 mol L⁻¹) with H₂O₂ (1.0 mol L⁻¹) catalyzed by complex 1 (0.2 mmol L⁻¹) in the presence of AcOH (1.0 mol L⁻¹) at 20 °C gave after 1 h a mixture of 2- and 3-hexanones (in a 2.5 : 1.0 ratio; the overall concentration was 0.24 mol L⁻¹) and a mixture of 2- and 3-hexanols (in a 1.2 : 1.0 ratio; the overall concentration was 0.03 mol L⁻¹) and a very

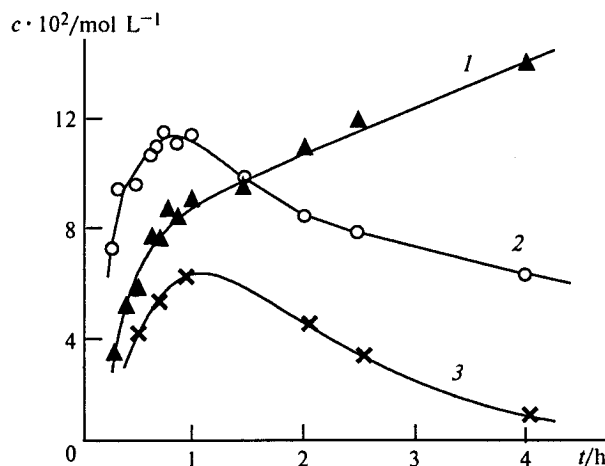


Fig. 3. Accumulation of isomeric 2- + 3-hexanones (1); -hexanols and -hexyl hydroperoxides (2); and -hexyl hydroperoxides (3). Conditions: hexane (0.4 mol L⁻¹); AcOH (1.0 mol L⁻¹); H₂O₂ (0.5 mol L⁻¹); complex 1 (0.2 mmol L⁻¹); with MeCN as solvent; 20 °C.

large turnover number of the catalyst (1350) was attained. Data of GLC analysis of the reaction solution after reducing it with an excess of solid Ph₃P showed that it contains hexanones (0.155 mol L⁻¹; the ratio of isomers was 3.3 : 1.0) and hexanols (0.115 mol L⁻¹; the ratio of isomers was 1.3 : 1.0), which indicates the presence of a considerable amount of isomeric alkyl hydroperoxide results in its complete conversion into ketone in the injector, it is possible to evaluate^{1,40-43} the concentrations of ketone, alcohol, and hydroperoxide in the reaction mixture (0.16, 0.03, and 0.08 mol L⁻¹, respectively).

The kinetics of accumulation of the products of oxygenation of *n*-hexane and cycloheptane with H₂O₂ taken in lower concentration (0.5 mol L⁻¹) is shown in Figs. 3 and 4, respectively. During the first 5 to 10 min after addition of H₂O₂ to the reaction solution it turns from pale pink to yellow and the color intensifies over a period when the oxidation of the substrate occurs at the maximum rate. When the reaction is over, the solution turns pale yellow, its tint and intensity being different for different substrates. The reaction of H₂O₂ with *n*-hexane monitored for a longer time is completed already after 1 h and is followed by a relatively slow conversion of alkyl hydroperoxide into ketone and alcohol (see Fig. 3). The oxidation of cycloheptane (see Fig. 4) results in the formation of cycloheptyl hydroperoxide, cycloheptanone, and cycloheptanol (~0.08, 0.07, and 0.02 mol L⁻¹, respectively; the total turnover number of the catalyst was 850 after 75 min). Under analogous conditions (substrate, 0.4 mol L⁻¹; H₂O₂, 0.5 mol L⁻¹; AcOH, 1.0 mol L⁻¹; 30 °C, 1 h) the oxidation of cyclohexane gave (after reduction of the reaction solution with Ph₃P) cyclohexanone and

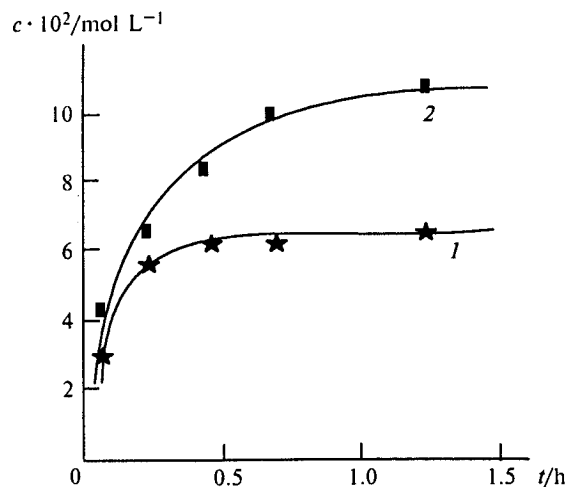


Fig. 4. Accumulation of cycloheptanone (1) and the overall concentration of cycloheptanol and cycloheptyl hydroperoxide (2) in the reaction of oxidation of cycloheptane (0.4 mol L^{-1}) in MeCN in the presence of AcOH (0.1 mol L^{-1}), H_2O_2 (0.5 mol L^{-1}), and complex 1 (0.2 mmol L^{-1}) at 20°C .

cyclohexanol (0.057 and 0.071 mol L^{-1} , respectively; the total turnover number of the catalyst was 640).

The increase in the concentration of AcOH added to the solution results in increasing the initial rate of cyclohexane oxidation (Fig. 5). It should be noted that the reaction between H_2O_2 and cyclohexane in pure AcOH does not result in the formation of considerable amounts of oxygenation products.

Catalyzed oxidation with hydrogen peroxide is stereoselective, though the value of the RC parameter is somewhat smaller than in the case of oxidation with peroxy acids. Thus, *cis*-1,2-dimethylcyclohexane is oxi-

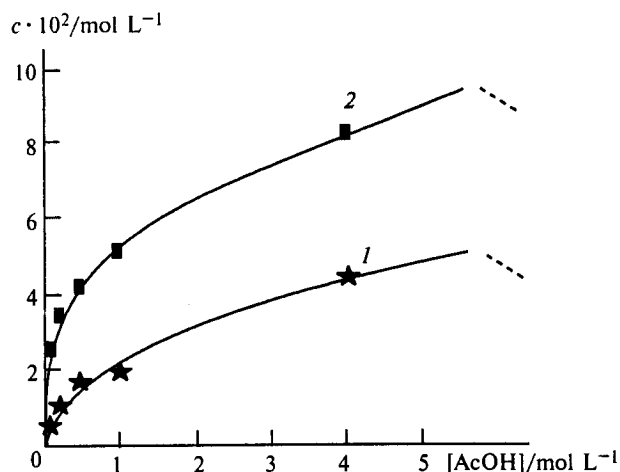


Fig. 5. Dependence of the rate of accumulation of cyclohexanone (1) and cyclohexanol (2) on the AcOH concentration in the reaction of oxidation of cyclohexane (0.4 mol L^{-1}) in the presence of H_2O_2 (0.5 mol L^{-1}) and complex 1 (0.2 mmol L^{-1}) in MeCN after 15 min at 20°C after reduction with Ph_3P .

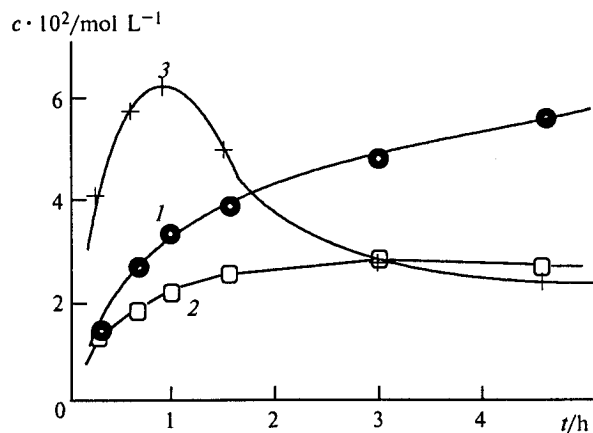


Fig. 6. The kinetics of the accumulation of cyclohexanone (1), cyclohexanol (2), and cyclohexyl hydroperoxide (3) in acetone in the presence of H_2O_2 (0.5 mol L^{-1}), AcOH (1.0 mol L^{-1}), and complex 1 (0.2 mmol L^{-1}) at 20°C .

dized to give *cis*-1,2-dimethylcyclohexan-1-ol (0.11 mol L^{-1} ; $RC_{cis} = 54\%$) as the main product. At the same time, the yield of *trans*-1,2-dimethylcyclohexan-1-ol (0.033 mol L^{-1} ; $RC_{trans} = 66\%$), which is the main product of the oxidation of *trans*-1,2-dimethylcyclohexane, is considerably lower, which is most likely due to the stronger spatial shielding of tertiary hydrogen atoms in the *trans*-isomer as compared to that in the *cis*-derivative. The above parameters were determined by GLC of the reaction solutions reduced with Ph_3P . It is noteworthy that the RC value appears to be much larger when it is measured for a solution before treating it with Ph_3P (e.g., in this case $RC_{trans} = 90\%$).

Among the solvents studied in this work, acetonitrile is the best for performing oxidation of alkanes with the H_2O_2 -AcOH-1 system. When acetone is used as solvent, the reaction occurs less efficiently, though the yields of the products obtained in this case are also rather high (Fig. 6). Oxidation of cyclohexane in methanol does occur despite the high reactivity of this solvent, though the yields of the products are very low: the concentrations of cyclohexanol and cyclohexanone formed after 1 h are 0.06 mol L^{-1} and $0.0023 \text{ mol L}^{-1}$, respectively.

In addition to acetic acid, several other organic acids and their anhydrides appreciably accelerate the oxidation of alkanes with hydrogen peroxide catalyzed by complex 1; however, AcOH is the most efficient promoter of this reaction (Table 4). Propionic and trifluoroacetic acids and acetic anhydride also promote efficient oxidation of hexane. No products of hexane oxygenation were found when HCOOH was added to the reaction solution instead of AcOH, which is likely due to the strong reductive properties of HCOOH .

Addition of CCl_3Br to the reaction solution in the oxidation of cyclohexane (0.4 mol L^{-1}) with hydrogen peroxide (0.5 mol L^{-1}) at 20°C results in the formation of cyclohexyl bromide instead of oxygenation products (Table 5). Thus, even taken in low concentration,

Table 4. Oxidation of *n*-hexane with hydrogen peroxide in acetonitrile catalyzed by complex **1** in the presence of promoters^a

Promoter	Hexanones Hexanols		TNC ^b
	c/mol L ⁻¹		
AcOH	0.240	0.03	1350
EtCOOH	0.134	0.020	770
CF ₃ COOH	0.056	0.013	345
HCOOH	<0.0005	<0.0005	<2
Ac ₂ O	0.065	0.016	405
MeSO ₃ H	0.007	0.001	40

^a Reaction conditions: *n*-hexane (0.4 mol L⁻¹), H₂O₂ (1.0 mol L⁻¹), complex **1** (0.2 mmol L⁻¹), promoter (1.0 mol L⁻¹); 20 °C; 1 h. The concentrations of the products in the reaction solution before reduction with Ph₃P are given.

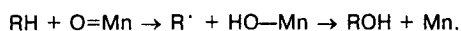
^b The turnover number of the catalyst (the sum of moles of all products per mole of catalyst).

Table 5. Oxidation of cyclohexane with hydrogen peroxide

Solvent	Duration /min	Concentration/mol L ⁻¹		
		AcOH	CCl ₃ Br	cyclo-C ₆ H ₁₁ Br
Acetonitrile	10	0.5	0.1	0.0026
Acetone	30	1.0	0.2	0.0012

CCl₃Br completely suppresses the introduction of oxygen atoms into the C—H bonds of the saturated hydrocarbon.

Taking into account the results of our experiments, one can suggest that abstraction of a hydrogen atom from the saturated C—H bond by an oxygen-containing radical or radical-like species is a starting point of the process of alkane oxidation. Such a species can be a manganese complex, e.g., a manganese oxo derivative, Mn=O. The process can occur in the solvent cage or by the so-called "oxygen-rebound" mechanism:¹



In both cases, the end products with the retention of stereochemical configuration are obtained. However, alkyl radicals R' are capable of leaving the solvent cell before the interaction with molecular oxygen, which results in the formation of ROO' radicals that are then converted into alkyl hydroperoxide ROOH as well as into corresponding ketone and alcohol. Probably, using such a scheme, it is possible to explain why in the case of oxidation of alkanes with the H₂O₂—AcOH—**1** reagent the values of the *RC* parameter for solutions untreated with triphenylphosphine are considerably greater. In fact, in this case thermolysis of alkylhydroperoxides can occur when performing GLC analysis, which results in the formation of products with ring opening, and the relative content of the oxygenation product with racemization decreases, whereas the relative content of tertiary alcohol, the product with reten-

tion of the configuration, increases. An alternative explanation for partial retention of the stereochemical configuration in the oxidation with the H₂O₂—AcOH—**1** reagent involves the abstraction of a hydrogen atom from alkane by a Mn—OO' species to form an alkyl radical R' and a Mn—OOH species, after which an ROOH alkyl hydroperoxide can be formed with retention of the configuration via the "oxygen-rebound" mechanism (see above).

In conclusion, it should be pointed out that the H₂O₂—AcOH—**1** reagent first described in this work is capable of a rather efficient oxidation of saturated hydrocarbons into alkyl hydroperoxides, ketones, and alcohols. Detailed investigation of the characteristics of this reaction, the extension of the range of substrates, and elucidation of the mechanism of the process will be continued.

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