

Cyclohexane Oxidation Catalyzed by Variable-Valence Metal Compounds in the Presence of Propionic Aldehyde

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Abstract—The effect of propionic aldehyde additives on the kinetics and mechanism of cyclohexane oxidation by molecular oxygen catalyzed by variable-valence metal salts is studied. The effect of the catalyst metal (M) on the rate of oxygen consumption, yield, and ratio of reaction products (cyclohexanol, cyclohexanone, cyclohexyl hydroperoxide (CHHP), and propionic acid and peracid) is studied. The catalytic functions of the variable-valence metal salts are determined by their ability to influence the rate of the homolysis of the O–O bonds of peroxide compounds, which correlates with the redox potential of the metal ion for most of the catalysts studied. The fact that other salts of variable-valence metals do not fit this correlation is due to the multifunctional action of catalysts involved in chain initiation, termination, and degenerate branching. The main role of aldehyde in the process under consideration is to promote oxidation. According to the quantum-chemical studies, the catalyst cation largely determines both the structure of the $[M^{n+}-CHHP]$ transition complex and the rates of competitive homolysis and heterolysis of cyclohexyl hydroperoxide.

INTRODUCTION

The liquid-phase oxidation of cyclohexane (CH) by molecular oxygen catalyzed by cobalt naphthenates (stearates) is currently the main industrial method for the production of cyclohexanol (COL) and cyclohexanone (CON), which are intermediate products in the synthesis of polyamide fibers [1–4]. Therefore, the improvement of this process remains topical from the theoretical and practical standpoints. Only few of the available catalytic systems (namely, cobalt naphthenate + CON [3], $Fe(TPPF_{20}Br_8)$ [4], $CoSt_2 + CH_3COOH$, $CoSt_2/CeSt_3 + CH_3COOH$, and $CoSt_2/CrO_3 \cdot 2Py + CH_3COOH$ [7] and chromium and cobalt valerates, naphthenates, or stearates [8]) are highly efficient [1–8].

In the course of the industrial oxidation of cyclohexane (Co(II)-naphthenate; 433–453 K; air pressure, 9–13 torr; reaction duration, 30 min), the maximum overall selectivity to the products COL + CON + CHHP (CHHP is cyclohexyl hydroperoxide) is lower than 75% at a cyclohexane conversion of 9% [9]. This indicates that the process rate and yield of the target products are comparatively low despite severe conditions.

The catalytic oxidation of cyclohexane to cyclohexanol and cyclohexanone in the presence of organic acids [10–12] and aldehydes [13, 14] at rather low temperatures (~373 K) may be substantially accelerated by the additives of aliphatic aldehydes. Earlier studies of the kinetics and mechanism of the liquid-phase oxidation of cyclohexane by molecular oxygen catalyzed by cobalt, manganese, iron, and ruthenium porphyrins [15–17]; cobalt complexes of the Schiff bases [18]; $CuCl_2$ crown ethers [19], $RuCl_3 \cdot nH_2O + CH_3COOH$ and

$RuCl_2(PPh_3)_3$ [20]; and $Fe + CH_3COOH$, $Fe(OOCCH_3)_3$, $FeCl_3 \cdot 6H_2O$ [21], and $Cu(OH)_2$ [22] in the presence of aldehydes suggest that the resulting radicals and metal-containing oxo species are intermediate in the formation of cyclohexanol, cyclohexanone, and cyclohexyl hydroperoxide [13–21].

Several aspects concerning the mechanism of the catalytic oxidation of cyclohexane by molecular oxygen in the presence of aldehydes remain unclear. These include (i) the effect of the catalyst/metal and the process temperature on the rate and selectivity of the formation of the target products (cyclohexanol, cyclohexanone, and cyclohexyl hydroperoxide) and (ii) the influence of a catalyst and aldehyde on the elementary steps of the oxidation. Investigation of the effect of the catalyst and small aldehyde additives on the yield of the target oxidation products at low temperatures (300–350 K) and oxygen pressure (0.1 MPa) is of particular practical interest.

EXPERIMENTAL

The kinetics of molecular oxygen consumption in the course of the liquid-phase oxidation of cyclohexane catalyzed by variable-valence metal salts in the presence of propionic aldehyde was examined on a gas-metric setup [23] in glass reactors at 303.0–341.5 K and an oxygen pressure of 0.1 MPa. The volume of the reaction mixture was 3.0 ml. The reaction vessel was shaken with a frequency that ensured the kinetic control of the process. Cobalt (II) stearate was used as a catalyst. The oxidation lasted 60 min. Peroxide compounds

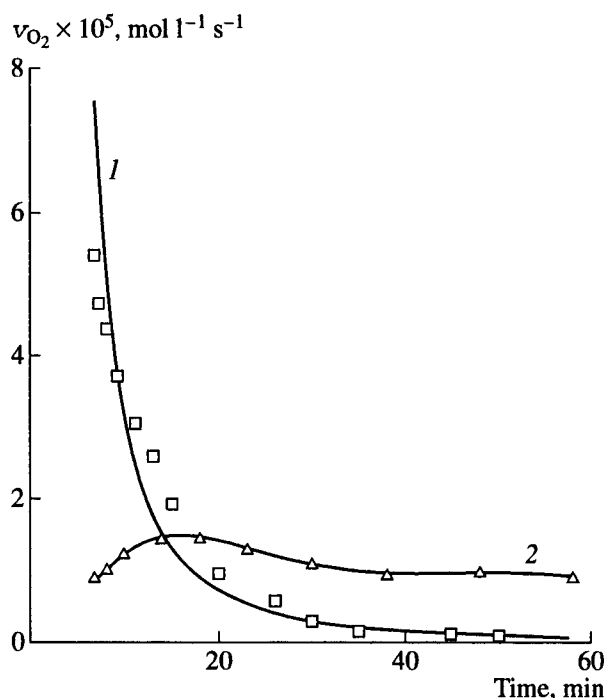


Fig. 1. The rate of oxygen consumption as a function of the duration of cyclohexane oxidation catalyzed by (1) $\text{Mn}(\text{AcAc})_2$ and (2) $\text{Pd}(\text{OAc})_2$ in the presence of propionic aldehyde ($[\text{CH}]_0 = 9.10 \text{ mol/l}$, $[\text{PA}]_0 = 0.15 \text{ mol/l}$, $[\text{Cat}] = 4.2 \times 10^{-4} \text{ mol/l}$, 303.0 K).

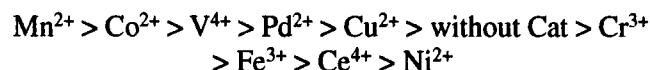
in the oxidation products were qualitatively analyzed by thin-layer chromatography by comparing their retention indices (R_f) with the R_f values for individual peroxides (Silufol plates; eluent, toluene–ethyl acetate mixture (1:1 by volume); developer, saturated acetone solution of NaI). The initial substances and oxidation products were quantitatively identified on an LKhM-80 chromatograph equipped with a flame-ionization detector and a steel column (3 m \times 3 mm) packed with Chromaton N-AW covered with a fixed phase of polyphenylmethylsiloxane (5%). Toluene was used as an internal standard. To determine the true concentrations of cyclohexanol and cyclohexanone in the presence of cyclohexyl hydroperoxide, the mixture was treated with triphenylphosphine. The true concentrations of cyclohexanol, cyclohexanone, and cyclohexyl hydroperoxide were determined as described in [24]. The overall concentration of peroxide compounds was determined by iodometry [25]. The propionic peracid concentration was determined as a difference between the overall concentration of peroxide compounds (obtained by iodometry) and the cyclohexyl hydroperoxide concentration (obtained by thin-layer chromatography). Cyclohexane was purified as described in [26]. Propionic aldehyde was purified by distillation in a fractionating column in nitrogen. Commercial analytically pure substances (Co(II), Ce(IV), Cu(II), and Cr(III) stearates; Mn(II), VO(II), Fe(III), and Ni(II) acetyl acates; and Pd(II) acetate) were used as catalysts.

RESULTS AND DISCUSSION

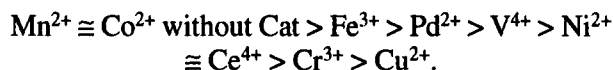
Our main experimental results are presented in Fig. 1 and Table 1.

Table 1 shows that the main products of cyclohexane oxidation in the presence of propionic aldehyde are cyclohexanol, cyclohexanone, cyclohexyl hydroperoxide, propionic acid, and peracid. The efficiency of the catalytic system (as estimated from the yield of the target products and the rate of oxygen consumption (v_{O_2})) depends on the origin of the catalyst/metal. According to their activity, the catalysts may be arranged in the following series:

at 303.0 K



and at 341.5 K



As can be seen, no strict correlation between the redox potential of the central ion of the variable-valence metal salt and its catalytic activity is observed. This suggests that the catalyst is involved not only in the Haber–Weiss cycle, but also in some other elementary steps.

A substantial difference in the activity and selectivity of the catalysts manifests itself in their effect on the overall yield and ratio of the target products (Table 1). The variable-valence metal salts not only catalyze, but also inhibit and control cyclohexane oxidation in the presence of propionic aldehyde. The elementary steps of the process involving variable-valence metal salts, in which the above functions of the catalysts are observed, are discussed in detail below.

In the absence of a catalyst, the curves illustrating how the rate of oxygen consumption varies with the oxidation duration at 303.0 and 341.5 K show the same behavior. Only the numerical v_{O_2} values change from 0.5×10^{-5} and $0.4 \times 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$ at 303.0 K and the oxidation duration of 6 and 10 min, respectively, to 12.0×10^{-5} and $1.2 \times 10^{-5} \text{ mol l}^{-1} \text{ s}^{-1}$ at 341.5 K and the oxidation duration of 6 and 10 min, respectively. At longer reaction times (10–60 min), the rate v_{O_2} decreases more smoothly and attains a virtually constant value close to zero after 20 min from the onset of the process. The curves that illustrate the time variations in the rate of oxygen consumption in the presence of the Mn^{2+} -, Co^{2+} -, and Ni^{2+} -catalysts at 303.0 K are similar to the curve obtained for the noncatalytic process (see, for example, curve 1 in Fig. 1). In contrast to this, the time variations in the rate of oxygen consumption at 303.0 K in the presence of the Pd^{2+} -, V^{4+} -, Fe^{3+} -, and Cu^{2+} -catalysts are described by a different curve (Fig. 1, curve 2). At 341.5 K, the rate of oxygen consumption in the presence of all catalysts studied (except for Co^{2+})

Table 1. Effect of the catalyst on the rate of oxygen consumption and the yield of the products of cyclohexane oxidation in the presence of propionic aldehyde ($[\text{CH}]_0 = 9.10 \text{ mol/l}$; $[\text{PA}]_0 = 0.15 \text{ mol/l}$; $[\text{Cat}]_0 = 4.2 \times 10^{-4} \text{ mol/l}$; reaction duration, 60 min)

Parameter	M^{n+}									
	Without catalyst	Co^{2+}	Ce^{4+}	Mn^{2+}	V^{4+}	Pd^{2+}	Fe^{3+}	Ni^{2+}	Cu^{2+}	Cr^{3+}
E^* , V	–	1.82	1.61	1.51	1.00	0.99	0.77	0.49	0.15	0.15
303.0 K										
$v_{\text{O}_2} \times 10^5, \text{ mol l}^{-1} \text{ s}^{-1}$	0.04	3.21	–	4.55	0.56	0.25	1.09	1.46	0.29	–
$[\text{COL}] \times 10^3, \text{ mol/l}$	0.2	5.14	0.26	4.37	0.43	0.67	0.77	0.06	0.90	0.49
$[\text{CON}] \times 10^3, \text{ mol/l}$	0.2	4.07	0.30	4.86	4.29	1.51	0.56	0.39	3.02	0.43
$[\text{CHHP}] \times 10^3, \text{ mol/l}$	1.6	1.82	0.80	4.70	1.68	3.26	0.27	0.26	3.02	0.92
$[\text{PPAc}] \times 10^2, \text{ mol/l}$	0.16	3.38	0.87	1.84	1.93	1.88	0.61	1.63	1.55	1.07
$[\text{PAc}] \times 10^2, \text{ mol/l}$	–	–	4.1	1.5	1.2	1.2	9.7	9.7	11.1	5.5
$[\text{CON}]/[\text{COL}]$	1.0	0.79	1.15	1.11	9.98	2.25	0.73	6.5	0.95	0.88
$\Sigma\text{P}^{**} \times 10^3, \text{ mol/l}$	2.0	11.03	1.36	13.93	6.40	5.44	1.60	0.71	4.87	1.84
$[\text{CHHP}]/\Sigma\text{P}$	0.8	0.17	0.59	0.34	0.26	0.60	0.17	0.37	0.62	0.50
341.5 K										
$v_{\text{O}_2} \times 10^5, \text{ mol l}^{-1} \text{ s}^{-1}$	12.03	1.80	7.34	3.66	3.12	12.25	6.02	7.75	5.91	4.18
$[\text{COL}] \times 10^3, \text{ mol/l}$	30.2	32.3	18.6	29.7	6.7	18.2	21.9	26.6	4.3	0.02
$[\text{CON}] \times 10^3, \text{ mol/l}$	25.5	25.2	11.3	28.8	32.3	29.4	18.0	12.3	4.3	21.5
$[\text{CHHP}] \times 10^3, \text{ mol/l}$	2.0	0.40	7.40	4.20	0.40	0.40	11.0	0	0	8.6
$[\text{PPAc}] \times 10^2, \text{ mol/l}$	2.05	1.08	1.05	2.72	1.64	2.42	1.74	2.31	2.31	1.83
$[\text{PAc}] \times 10^2, \text{ mol/l}$	–	–	11.7	2.8	2.4	2.3	4.2	4.6	12.6	12.3
$[\text{CON}]/[\text{COL}]$	0.84	0.78	0.61	0.97	4.82	1.62	0.82	0.46	1.00	1075
$\Sigma\text{P}^{**} \times 10^3, \text{ mol/l}$	57.7	57.90	38.35	62.70	39.40	48.00	50.90	38.90	8.60	30.12
$[\text{CHHP}]/\Sigma\text{P}$	0.03	0.07	0.19	0.07	0.01	0.08	0.22	0	0	0.29

* Redox potential of the metal ion.

** $\Sigma\text{P} = [\text{COL}] + [\text{CON}] + [\text{CHHP}]$.

is described by a curve that is similar to curve 1 in Fig. 1. For the cobalt catalyst, the time variations in the rate of oxygen consumption at this temperature is also described by a curve similar to curve 2 in Fig. 1, and the average v_{O_2} value is close to $1.8 \times 10^{-5} \text{ mol l}^{-1} \text{ s}^{-1}$.

In the absence of propionic aldehyde, cyclohexane is not oxidized by molecular oxygen within the temperature range studied (303.0–341.5 K) even in the presence of the catalysts. The propionic aldehyde additives markedly accelerate the catalytic oxidation and increase the yield of the target products. Synergism is observed at 303.0 K, which is especially pronounced for the Mn^{2+} -, Co^{2+} -, V^{4+} -, Pd^{2+} -, and Cu^{2+} -catalysts. The catalytic action of the Cr^{3+} and Ce^{4+} compounds is observed at the same temperature to a much lesser extent, whereas the Ni^{2+} catalyst does not affect the yield of the target products as compared to the noncatalytic process. The maximal yield of the target products and the maximal v_{O_2} value are obtained in the catalytic

systems containing the Mn^{2+} and Co^{2+} compounds (Table 1).

In the presence of the V^{4+} -, Pd^{2+} -, and Ni^{2+} catalysts, cyclohexane oxidation at 303.0 K results in the predominant formation of cyclohexanone. During noncatalytic oxidation and in the presence of the Mn^{2+} and Cu^{2+} compounds, the cyclohexanone and cyclohexanol yields are nearly the same both at 303.0 and 341.5 K (Table 1). Under the same conditions, the Fe^{3+} and Co^{2+} compounds favor a decrease in the $[\text{CON}]/[\text{COL}]$ ratio in the reaction products.

At 341.5 K, only the Mn^{2+} + PA catalytic system exhibits a somewhat positive effect as compared to the noncatalytic process (Table 1). In the presence of all other catalysts, the yield of the target products decreases. Note that, at the same temperature in the presence of the Cr^{3+} catalyst, the $[\text{CON}]/[\text{COL}]$ ratio abruptly increases to 1075, whereas, at 303.0 K, it is only 0.88. This indicates a change in the oxidation

mechanism. This effect is discussed below based on the quantum-chemical calculations.

In our opinion, the peculiarities of the action of the catalysts in the CH + PA system being oxidized is one of the most important problems. Therefore, our main concern in this paper is this particular problem along with the explanation of the effect of the catalyst metal on the elementary steps of the process.

As follows from Table 2, the yield of the target products at 303 K increases with the catalyst activity, which is indirectly related to the redox potential of the metal ion. In this case, the rate of oxygen consumption decreases. This apparently paradoxical effect may be attributed to catalyst deactivation in the course of the oxidation and rapid decarboxylation of acyloxy radicals (VII) accompanied by CO₂ evolution (Table 2). The contributions of these factors to the overall rate of oxygen consumption were estimated as follows.

At 303.0 K, the rate of the thermal decomposition of propionic peracid (reaction (VI)) is

$$v_6 = k_6[\text{PPAc}] = 7.0 \times 10^{-10} \text{ mol l}^{-1} \text{ s}^{-1}.$$

The values of $k_6 = 4.4 \times 10^{-7} \text{ s}^{-1}$ and $[\text{PPAc}] = 0.16 \times 10^{-2} \text{ mol/l}$ are given in Tables 2 and 1, respectively. The rate of the catalytic decomposition of propionic peracid (reaction (X)) is

$$v_{10} = k_{10}[\text{PPAc}][\text{CoSt}_2] = 6.8 \times 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1},$$

where $k_{10} = 4.0 \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$, $[\text{PPAc}] = 3.38 \times 10^{-2} \text{ mol/l}$, and $[\text{CoSt}_2] = 4.2 \times 10^{-4} \text{ mol/l}$.

Therefore, we have at this temperature $v_{10}/v_6 \approx 10^4$.

At 341.5 K, we have

$$v_6 = k_6[\text{PPAc}] = 3.9 \times 10^{-7} \text{ mol l}^{-1} \text{ s}^{-1},$$

where $k_6 = 1.9 \times 10^{-5} \text{ s}^{-1}$ and $[\text{PPAc}] = 2.05 \times 10^{-2} \text{ mol/l}$, and

$$v_{10} = k_{10}[\text{PPAc}][\text{CoSt}_2] = 1.24 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1},$$

where $k_{10} = 27.4 \text{ l mol}^{-1} \text{ s}^{-1}$, $[\text{PPAc}] = 1.8 \times 10^{-2} \text{ mol/l}$, and $[\text{CoSt}_2] = 4.2 \times 10^{-4} \text{ mol/l}$.

In this case, $v_{10}/v_6 = 3.1 \times 10^2$.

The rate of the noncatalytic decomposition of propionic peracid is more sensitive to the temperature than the rate of its catalytic decomposition: the ratio of the v_6 values at 341.5 and 303 K is 5.6×10^2 , whereas the ratio of the v_{10} values at the same temperatures is 18. The v_{10}/v_6 ratio at 303.0 K is by two orders of magnitude higher than that at 341.5 K. This indicates the rapid deactivation of the catalyst by the oxidation products and, hence, the small effect of variable-valence metal salts on the oxidation at high temperatures.

The acyloxy radicals formed by reactions (VI) and (X) undergo rapid decarboxylation (reaction (VII)). Obviously, the evolution of carbon dioxide causes a dramatic decrease in the v_{O_2} value, which is most pro-

nounced for the active catalysts such as Co²⁺ and Mn²⁺. In the presence of these compounds, the rate of RC(O)O· generation from propionic peracid is higher than that in the case of the catalysts with lower redox potentials.

The contribution of reaction (VII) to the overall rate of oxygen consumption was estimated by comparing the v_{O_2} values calculated from the rate of the formation of all oxygen-containing products (v_p) with the experimental rate of oxygen consumption (v_e). The difference between the v_p and v_e values is the true rate of reaction (VII).

The v_p value, calculated from the overall yield of the main oxidation products formed during the first 10 min of the process is $1.9 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1}$ at $[\text{CH}]_0 = 9.1 \text{ mol/l}$, $[\text{PA}]_0 = 0.36 \text{ mol/l}$, $[\text{CoSt}_2]_0 = 5.6 \times 10^{-4} \text{ mol/l}$, and $T = 303.0 \text{ K}$.

The average rate of oxygen consumption during the same period measured on a gasometric setup is $v_e = 4.74 \times 10^{-5} \text{ mol l}^{-1} \text{ s}^{-1}$. Then $v_7 = v_p - v_e = 1.43 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1}$. This indicates that reaction (VII) contributes significantly to the overall rate of oxygen consumption ($(1.43 \times 10^{-4}/1.9 \times 10^{-4})100\% \approx 90\%$).

In contrast to the process occurring at 341.5 K, an increase in the redox potential of the catalyst (especially, in the case of the Co²⁺ and Mn²⁺ compounds) at 303.0 K is accompanied by an increase in the activity of variable-valence metal salts, which in turn results in an increase in both the rate of oxygen consumption and the yield of the target products.

The contribution of the cyclohexyl hydroperoxide yield to the overall yield of the target oxidation products (cyclohexanol, cyclohexanone, and cyclohexyl hydroperoxide) strongly depends on the redox potential of the catalyst, which is most pronounced at low temperatures. The activity of the catalyst cation in cyclohexyl hydroperoxide decomposition, the yield of the target products, and the oxidation rate is almost proportional (except for the Cu²⁺, Pd²⁺, and Ce²⁺ compounds) to the redox potential of the central ion (Table 1). This agrees with a common idea concerning the influence of the catalyst on cyclohexyl hydroperoxide decomposition. This idea implies that the most active Co²⁺ and Mn²⁺ catalysts favor the rapid homolysis of hydroperoxide, a decrease in its concentration, and an increase in the cyclohexanol and cyclohexanone yields due to cyclohexyl hydroperoxide decomposition and the acceleration of the radical initiation of the oxidation.

The above data provide further evidence for the efficiency of the catalyst performance in the low-temperature process and its insignificant effect on the oxidation at high temperatures because of the rapid deactivation of the central ion of a catalyst by the oxidation products (mainly, propionic peracid).

In contrast to the yield of the target products of cyclohexane oxidation, the overall yield (including,

Table 2. Kinetic parameters of the elementary steps of cyclohexane oxidation by molecular oxygen in the presence of propionic aldehyde

Reaction no.	Reaction	A^a	E , kJ/mol	k^a	References
I	$RCHO + O_2 \longrightarrow RC(O) + HOO^\bullet$ ($R = C_2H_5$)	4.5×10^{14}	117	3.0×10^{-6} (303 K) 5.7×10^{-4} (341.5 K)	[27]
II	$RC(O)OO^\bullet + \text{cyclo-C}_6\text{H}_{12} \longrightarrow RC(O)OOH + \text{cyclo-C}_6\text{H}_{11}^\bullet$ ($R = \text{Ph}$)	7.6×10^{13}	70.2	60^b (303 K) 1.4×10^3 (341.5 K)	Our estimates
III	$RC(O)OO^\bullet + RCHO \longrightarrow RC(O)OOH + RC(O)$ ($R = C_2H_5$)	4.2×10^9	32	1.3×10^4 (303 K) 5.4×10^4 (341.5 K)	[31]
IV	$\text{cyclo-C}_6\text{H}_{11}OO^\bullet + \text{cyclo-C}_6\text{H}_{12} \longrightarrow \text{cyclo-C}_6\text{H}_{11}OOH + \text{cyclo-C}_6\text{H}_{11}^\bullet$	1.6×10^8	57.7	1.8×10^{-2} (303 K)	[32]
V	$\text{cyclo-C}_6\text{H}_{11}OO^\bullet + RCHO \longrightarrow \text{cyclo-C}_6\text{H}_{11}OOH + RC(O)$	—	—	0.2 (341.5 K) 3.9^c (303 K) 7.7^b (341.5 K)	Our estimates
VI	$RC(O)OOH \longrightarrow RC(O)O^\bullet + HO^\bullet$ ($R = \text{CH}_3$)	1.4×10^8	84.1	4.4×10^{-7} (303 K) 1.9×10^{-5} (341.5 K)	[33]
VII	$RC(O)O^\bullet \longrightarrow R^\bullet + CO_2$ ($R = C_2H_5$)	—	—	3.3×10^{10} (343 K) $\sim 3.3 \times 10^{10}$ (341.5 K)	[34]
VIII	$RC(O)O^\bullet + \text{cyclo-C}_6\text{H}_{12} \longrightarrow RC(O)OH + \text{cyclo-C}_6\text{H}_{11}^\bullet$ ($R = \text{Ph}$)	4.3×10^8	16.3	6.7×10^5 (303 K) 1.4×10^6 (341.5 K)	[35]
IX	$RC(O)O^\bullet + RCHO \longrightarrow RC(O)OH + RC(O)$	9.8×10^8	15.2	2.3×10^{6d} (303 K) 4.6×10^6 (341.5 K)	Our estimates
X	$RC(O)OOH + M^{n+} \longrightarrow M^{(n+1)+} + RC(O)O^\bullet + HO^-$ $M^{n+} = \text{Ni}^{2+}$, $R = \text{Ph}$ $M^{n+} = \text{Co}^{2+}$, $R = p\text{-CH}_3\text{Ph}$	1.6×10^{15e}	90.0	4.0×10^{-3} (303 K) 0.5 (303 K) 27.4 (341.5 K)	[37] [38]
XI	$RC(O)OOH + M^{(n+1)+} \longrightarrow M^{n+} + RC(O)OO^\bullet + H^+$ ($M^{(n+1)+} = \text{Co}^{3+}$, $R = \text{Ph}$)	—	—	0.8 (298 K)	[39]
XII	$\text{cyclo-C}_6\text{H}_{11}OOH + M^{n+} \longrightarrow M^{(n+1)+} + \text{cyclo-C}_6\text{H}_{11}O^\bullet + HO^-$ $M^{n+} = \text{Co}^{2+}$ $M^{n+} = \text{V}^{4+}$ $M^{n+} = \text{Cr}^{3+}$	8.5×10^7 7.9×10^{10}	42.0 88.0	4.9^f (303 K) 32.0 (341.5 K) 1.4 (303 K) 20.0 (341.5 K) 5.3×10^{-5g} (303 K) 2.7×10^{-3} (341.5 K)	Our estimates [8] [8]
XIII	$\text{cyclo-C}_6\text{H}_{11}OOH + M^{(n+1)+} \longrightarrow M^{n+} + \text{cyclo-C}_6\text{H}_{11}OO^\bullet + H^+$ $M^{(n+1)+} = \text{Co}^{3+}$	—	—	0.01 (298 K)	[40]
XIV	$RC(O)OH + M^{n+} \longrightarrow M^{(n+1)+} + RC(O)O^\bullet + HO^-$ $M^{n+} = \text{Co}^{2+}$, $R = \text{CH}_3$ $M^{n+} = \text{Co}^{3+}$, $R = \text{Ph}$ $M^{n+} = \text{Fe}^{3+}$, $R = \text{C}_2\text{H}_5$ $M^{n+} = \text{Ni}^{3+}$, $R = \text{Ph}$	2.4×10^{12g} 3.0×10^9	79.5 61.9	4.7×10^{-2} (303 K) 1.7 (341.5 K) 6.4×10^{-2} (303 K) 1.0 (341.5 K) 6.8×10^{-2} (293 K) 1.8×10^{-3} (353 K)	Our estimates [42] [43]

Table 2. (Contd.)

Reaction no.	Reaction	A ^a	E, kJ/mol	k ^a	References
XV	cyclo-C ₆ H ₁₁ OO [•] + M ⁿ⁺ → M ⁽ⁿ⁺¹⁾⁺ + cyclo-C ₆ H ₁₁ O + HO ⁻ M ⁽ⁿ⁺¹⁾⁺ = Co ²⁺	1.5 × 10 ^{9f}	27.5 ^f	2.7 × 10 ⁴ (303 K) 9.3 × 10 ⁴ (341.5 K)	Our estimates
	M ⁽ⁿ⁺¹⁾⁺ = Mn ²⁺	9.9 × 10 ^{11f}	53.5 ^f	9.9 × 10 ² (303 K) 6.5 × 10 ³ (341.5 K)	
	M ⁽ⁿ⁺¹⁾⁺ = Cu ²⁺	2.5 × 10 ^{12f}	54.9 ^f	8.6 × 10 ² (303 K)	
XVI	cyclo-C ₆ H ₁₁ OO [•] + M ⁽ⁿ⁺¹⁾⁺ → ... → M ⁿ⁺ + cyclo-C ₆ H ₁₁ OH M ⁽ⁿ⁺¹⁾⁺ = Co ²⁺	5.5 × 10 ^{10f}	37.4 ^f	2.0 × 10 ⁴ (303 K) 1.0 × 10 ⁵ (341.5 K)	Our estimates
	M ⁽ⁿ⁺¹⁾⁺ = Mn ²⁺	8.8 × 10 ^{12f}	56.2 ^f	1.8 × 10 ³ (303 K) 2.2 × 10 ⁴ (341.5 K)	
	M ⁽ⁿ⁺¹⁾⁺ = Cu ²⁺	2.5 × 10 ^{12f}	54.9 ^f	8.6 × 10 ² (303 K) 1.0 × 10 ⁴ (341.5 K)	
XVII	RC(O)OO [•] + M ⁿ⁺ → M ⁽ⁿ⁺¹⁾⁺ + RC(O)OO ⁻ (M ⁿ⁺ = Co ²⁺)	2.9 × 10 ⁹	32.6	7.0 × 10 ^{3h} (303 K) 3.0 × 10 ⁴ (341.5 K)	Our estimates
XVIII	cyclo-C ₆ H ₁₁ OO [•] + M ⁿ⁺ → M ⁽ⁿ⁺¹⁾⁺ + cyclo-C ₆ H ₁₁ OO ⁻ (M ⁽ⁿ⁺¹⁾⁺ = Co ²⁺)	2.9 × 10 ⁹	32.6	7.0 × 10 ^{3h} (303 K) 3.0 × 10 ⁴ (341.5 K)	Our estimates

^a Expressed in s⁻¹, l mol⁻¹ s⁻¹, and l² mol⁻² s⁻¹ for the first-, second-, and third-order reactions, respectively.

^b The C₂Cl₅OO[•] and PhC(O)OO[•] radicals exhibit the same reactivity in the reaction with cyclohexane at 348 K ($k_2 = 2.2 \times 10^3$ l mol⁻¹ s⁻¹) [28]. The activation energy of this reaction was calculated by the equation $E_2 = 0.55D(\text{cyclo-C}_6\text{H}_{11}\text{-H}) - 146.6$ kJ/mol [29], where $D(\text{cyclo-C}_6\text{H}_{11}\text{-H}) = 399.6$ kJ/mol is the C-H bond strength in cyclohexane [30].

^c The rate constant of the reaction of cyclo-C₆H₁₁OO[•] radical with RC(O)H was calculated by the equation $k_5 = k_3k_4/k_2$ using the kinetic parameters of reactions (II), (III), and (IV).

^d The activation energy and the rate constant for this reaction at 399 K were set equal to 15.2 kJ/mol and 1.0×10^7 l mol⁻¹ s⁻¹, respectively, as for the reaction of the (CH₃)₃CO[•] radical with CH₃C(O)H [36].

^e Calculated from the data of [37].

^f Calculated from the data of [8].

^g Calculated from the data of [41].

^h The rate constant for this reaction was set equal to that for the reaction of the CH₂C(OO[•])HPh radical with Co(AcAc)₂ [44].

propionic acid and peracid) is inversely proportional to the catalyst activity, which correlates with the redox potential. This may be explained as follows. The primary product of propionic aldehyde oxidation—propionic acid—decomposes to give acyloxy radicals under the action of the catalyst and in the course of the thermal process. The acyloxy radicals undergo decarboxylation (reaction (VII)) to give CO₂ and the ethyl radical, which finally transforms into ethyl hydroperoxide, which is barely identified under experimental conditions. Because the decarboxylation rate is much higher than the rate of the accumulation of the products of

cyclohexane oxidation, the overall yield of the oxidation products decreases. We can illustrate this using the following calculations. The rate of accumulation (v_{acc}) and consumption (v_{con}) of the products of propionic aldehyde oxidation under the process conditions is determined by reactions (I), (II), (III), (VIII), (IX), (X), and (XIV):

$$v_1 = k_1[\text{PA}][\text{O}_2],$$

$$v_2 = k_2[\text{RC(O)OO}^{\bullet}][\text{CH}],$$

$$v_3 = k_3[\text{RC(O)OO}^{\bullet}][\text{PA}],$$

$$v_8 = k_8[\text{RC}(\text{O})\text{O}^\bullet][\text{CH}],$$

$$v_9 = k_9[\text{RC}(\text{O})\text{O}^\bullet][\text{PA}],$$

$$v_{10} = k_{10}\text{PPAc}[\text{M}^{(n+1)+}],$$

$$v_{14} = k_{14}[\text{PA}][\text{M}^{(n+1)+}].$$

The ratio of the rates of consumption and accumulation is equal to:

$$v_{\text{con}}/v_{\text{acc}} = v_{10}/(v_1 + v_2 + v_3 + v_8 + v_9 + v_{14}).$$

At $[\text{CH}] = 9.1 \text{ mol/l}$, $[\text{PA}] = [\text{PPAc}] = 0.24 \text{ mol/l}$ (when 50% of propionic aldehyde transforms into propionic peracid), $[\text{CoSt}_2] = 2.1 \times 10^{-4} \text{ mol/l}$, $T = 303.0 \text{ K}$, and $v_3/v_2 = k_3[\text{PA}]/k_2[\text{CH}] = 5.7$, that is, $v_3 = 5.7 v_2$ (the rate constants of the corresponding reactions are given in Table 2).

Because reaction (IX), like reaction (VIII), involves $\text{RC}(\text{O})\text{O}^\bullet$ radicals which are rapidly decarboxylated via reaction (VII), the contribution of these reactions to the overall rate of product accumulation may be neglected. Then, after substituting the values obtained into the expression for $v_{\text{con}}/v_{\text{acc}}$, we arrive at:

$$v_{\text{con}}/v_{\text{acc}} = (0.12 \times 10^{-4})/(1.14 \times 10^{-6} + 6.7 \times 60[\text{RC}(\text{O})\text{OO}^\bullet] \times 9.1)$$

$$= (0.12 \times 10^{-4})/(1.14 \times 10^{-6} + 3.6 \times 10^3[\text{RC}(\text{O})\text{OO}^\bullet]).$$

Taking into account that the $\text{RC}(\text{O})\text{OO}^\bullet$ concentration in the reaction mixture is lower than 10^{-10} – 10^{-12} mol/l (as determined by simulating the process kinetics), the second term in the denominator can also be neglected. Then, we have $v_{\text{con}}/v_{\text{acc}} \approx 10$. Thus, the rate of propionic peracid consumption, which is the main intermediate in propionic aldehyde oxidation, is more than ten times higher than the rate of its accumulation, which explains a decrease in the overall yield of the oxidation products in the presence of the active catalysts observed experimentally.

The key elementary steps involving catalysts are (i) the decomposition of peroxide compounds via the Haber–Weiss mechanism (reactions (X)–(XIII)), aldehyde oxidation by the cations of the metals in the highest oxidation state (reaction (XIV)), and chain termination on the catalyst (reactions (XV), (XVI), and (XVII)) (Table 2). As follows from the calculations based on the data of Table 2, most of the products of cyclohexane oxidation are formed via the reactions involving the primary cyclohydroxylperoxy radicals and the catalyst even at the early stages of the process.

$$v_4 = k_4[\text{cyclo-C}_6\text{H}_{11}\text{OO}^\bullet][\text{CH}],$$

$$v_5 = k_5[\text{cyclo-C}_6\text{H}_{11}\text{OO}^\bullet][\text{PA}],$$

$$v_{15} = k_{15}[\text{cyclo-C}_6\text{H}_{11}\text{OO}^\bullet][\text{Co}^{2+}],$$

$$v_{16} = k_{16}[\text{cyclo-C}_6\text{H}_{11}\text{OO}^\bullet][\text{Co}^{3+}].$$

At $[\text{CH}] = 9.1 \text{ mol/l}$, $[\text{PA}] = 0.15 \text{ mol/l}$, $[\text{Co}^{2+}] = 2.1 \times 10^{-4} \text{ mol/l}$, and the rate constants given in Table 2, the ratios of the reaction rates are

$$v_{15}/v_4 = 35.6, \quad v_{15}/v_5 = 9.7,$$

$$v_{16}/v_4 = 26.3, \quad v_{16}/v_5 = 7.1$$

at 303.0 K and

$$v_{15}/v_4 = 10.7, \quad v_{15}/v_5 = 16.8,$$

$$v_{16}/v_4 = 11.5, \quad v_{16}/v_5 = 18.1$$

at 341.5 K.

Thus, the overall yield of the target oxidation products (cyclohexyl hydroperoxide, cyclohexanol, and cyclohexanone), stoichiometrically formed from cyclohexyl hydroperoxy radicals in the presence of the catalyst, ranges from 3 to 10%. In this case, the $[\text{CON}]/[\text{COL}]$ ratio is nearly equal to unity, as in the absence of aldehyde additives. However, note that the catalysts, especially the Co^{2+} and Mn^{2+} compounds, not only control the composition of the oxidation products but also inhibit the process terminating the oxidation chain via reactions (XVII) and (XVIII).

Cr^{3+} , V^{4+} , and Pd^{2+} compounds do not react with peroxy radicals [8], whereas Co^{2+} , Mn^{2+} , and Fe^{2+} compounds do not. This explains a rather high yield of the target oxidation products in their presence despite the low redox potentials of these ions. In our opinion, the low catalytic activity of the Cr^{3+} catalyst in the course of oxidation is due to its minimum redox potential and the heterolysis of peroxide compounds occurring under the action of this catalyst [8] and resulting in the formation of nonradical products. The homolytic component of the decomposition of various peroxides is ~100% on the Co^{2+} catalyst [44], 4–20% on the V^{5+} catalyst [45, 46], 3–13% on the Cr^{3+} catalyst [45], ~4% on the Mn^{2+} catalyst [47], and ~2% on the Ni^{2+} [44] and Cu [48] catalysts.

To explain the experimental data on different effects of cobalt- and chromium-containing catalysts on the composition of cyclohexane oxidation products, we performed the quantum-chemical calculation of the configurations of the $[\text{M}^{n+}\cdots\text{CHHP}]$ transition states and the pathways of the decomposition of such complexes to radicals and molecular products. We found that the formation of the $[\text{metal ion}-\text{CCHP}]$ complexes of type A and B is most likely (Figs. 2 and 3). Calculations were performed using the MNDO method [49] with complete optimization of the structures by the gradient method assuming the mechanism for the formation of cyclohexane oxidation products in the presence of the Co^{2+} and Cr^{3+} catalysts.

Table 3. Heats of formation and decomposition and the activation energies of the decomposition of the $[M^{n+}\dots\text{CHHP}]$ complexes of type **A** and **B** via pathways 1 and 2 of reaction (XIX)

Complex	Pathway	A		B		
		ΔH	E_a	ΔH	E_a	
			(303.0 K)		303.0 K	341.5 K
cyclo- $\text{C}_6\text{H}_{11}\text{OOH} \cdot \text{Co}^{2+}$	1	56.1	77.4	146.5	58.6	57.8
	2	49.4	70.7	186.3	35.6	29.7
cyclo- $\text{C}_6\text{H}_{11}\text{OOH} \cdot \text{Cr}^{3+}$	1	53.2	108.4	94.6	136.0	135.6
	2	44.0	88.7	200.5	45.6	32.2

Note: The ΔH and E_a values are expressed in kJ/mol. The ΔH values were calculated from the difference in the heats of formation of the decomposition products (cyclo- $\text{C}_6\text{H}_{11}\text{O}^\cdot$ and $M^{n+}(\text{OH})$) and the corresponding initial complexes $[M^{n+}\dots\text{cyclo-}\text{C}_6\text{H}_{11}\text{OOH}]$. The activation energies of the thermal decomposition of cyclohexyl hydroperoxide via (1') homogeneous and (2') heterogeneous pathways are 229.0 and 249.5 kJ/mol, respectively:

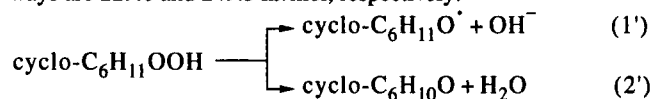
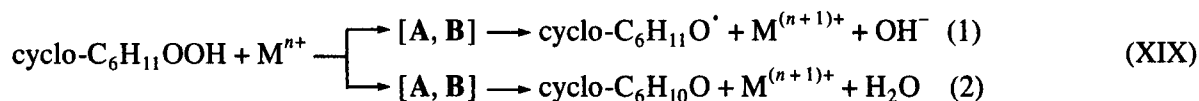


Table 3 presents the most important kinetic and thermodynamic parameters of the transition states of the

$[M^{n+}\dots\text{CHHP}]$ complexes and their decomposition via pathways 1 and 2 of reactions (XIX).

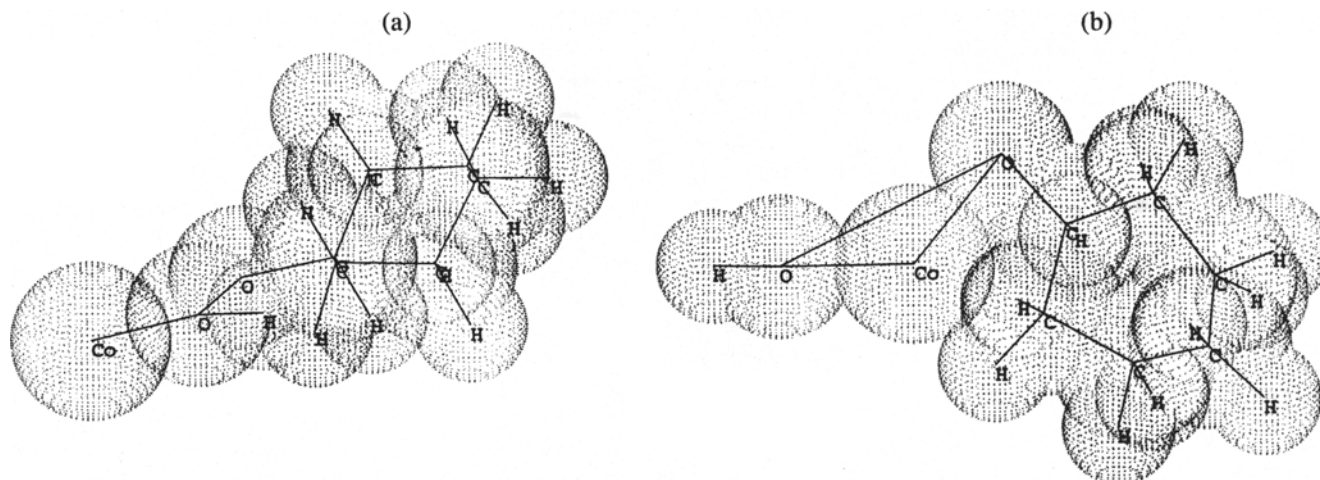


As follows from the above data, the formation and further decomposition of metal-containing transition complexes is thermodynamically and kinetically preferable to the thermal decomposition of cyclohexyl hydroperoxide (see note to Table 3). The structure of the transition complex of type B, which is characterized by the formation of a three-membered cycle, is energetically preferable to the classical structure of type A, where the metal ion is removed from the hydrocarbon ring and directly bound to the terminal oxygen atom. The formation of an intermediate structure of type B is confirmed by the formation of hydrogen peroxide via

the decomposition of this peroxy complex, as was observed experimentally [50].

Moreover, the formation of the complex of type B also explains the much higher rate of the process in the presence of the Co^{2+} catalysts as compared to that in the presence of Cr^{3+} compounds.

It is well known that the overall rate of oxidation is determined by the rate of formation of free radicals, most of which are generated in the course of the catalytic decomposition of cyclohexyl hydroperoxide by reaction (XIX).

**Fig. 2.** Structures of the possible transition states of the Co^{2+} -CHHP complexes (a computational model).

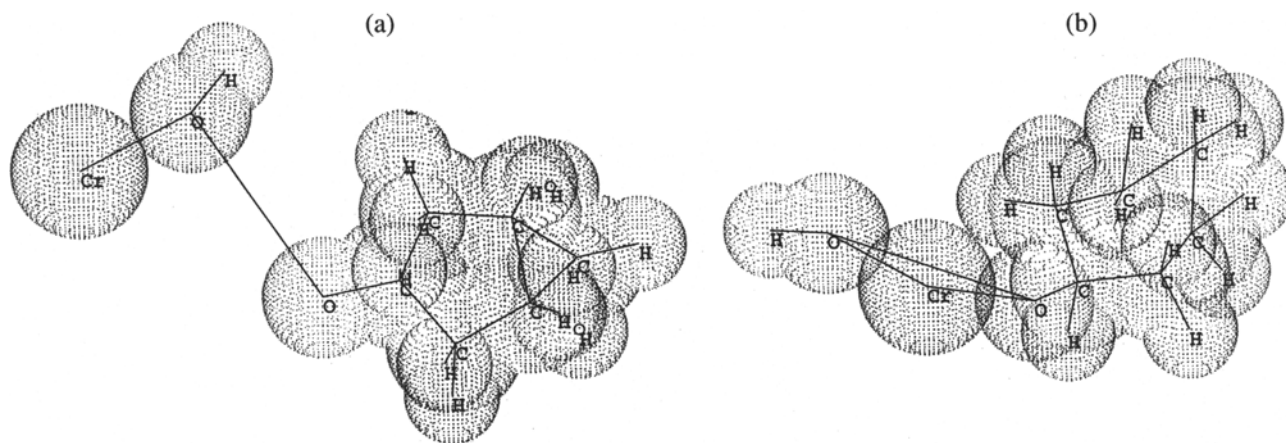


Fig. 3. Structures of the possible transition states of the Cr^{3+} -CHHP complexes (a computational model).

As follows from our quantum-chemical calculations (Table 3), the activation energy of cyclohexyl hydroperoxide decomposition to radicals (pathway 1) at 303 K is by 77.4 kJ/mol lower than the activation energy of the same process involving the Cr^{3+} compounds. For pathway 2 (without free radical generation), this difference is still less pronounced (10.0 kJ/mol). This pattern is also observed when comparing the transition complexes of the Co^{2+} and Cr^{3+} ions with cyclohexyl hydroperoxide formed via pathways 1 and 2 at 341.5 K.

Our quantum-chemical calculations also explain the well-known experimental but still unclear fact, which was confirmed in our previous studies, that cyclohexanone formation dominates over cyclohexanol in the course of cyclohexane oxidation catalyzed by the Cr^{3+} compounds at low temperatures [8].

The temperature dependence of the activation energy of the decomposition of the Co^{2+} and Cr^{3+} complexes with cyclohexyl hydroperoxide suggests that pathway 2 of the decomposition of the $[\text{Cr}^{3+}\cdots\text{CHHP}]$ complex is energetically more favorable when the temperature increases from 303.0 to 341.5 K (the E_a values decrease by 13.4 kJ/mol). The gain in energy in the reactions involving the Co^{2+} compounds with an increase in temperature is only 2.1–5.9 kJ/mol (Table 3).

The use of the MNDO method ensures a rather good agreement between the calculated and experimental data and suggests a model for cyclohexyl hydroperoxide decomposition, the detailed mechanism of which may be studied later.

CONCLUSION

(1) The activity of variable-valence metal salts is determined by the rate of homolysis of peroxide compounds, which to a first approximation correlates with the redox potential of the metal ion (Tables 1 and 2).

(2) The oxidation rate and yield of target products are proportional to the rate of initiation and inversely

proportional to the efficiency of chain termination on the ions of the cyclohexane metal. The competition of these two pathways determines the cyclohexane activity in the process under consideration.

(3) Aldehyde mainly acts as a primary initiator of the chain process by reactions (I) and (XIV). Then, the required stable concentration of the highly reactive acyloxy and acylperoxy radicals is maintained by the same reactions, as well as reactions (X), (XI), and (XIII).

REFERENCES

- Sheldon, R.A. and Kochi, J.K., *Metal-Catalyzed Oxidations of Organic Compounds*, New York: Academic, 1981.
- Hill, C.L., *Activation and Functionalization of Alkanes*, New York: Wiley, 1989.
- Selective Hydrocarbon Oxidation and Functionalization*, Davis, J.A., Watson, P.L., and Grenberg, A., Eds., New York: VCH, 1990.
- Meunier, B., *Chem. Rev.*, 1992, vol. 92, p. 1411.
- Ellis, P.E., Jr. and Lyons, J.E., *Coord. Chem. Rev.*, 1990, vol. 105, p. 181.
- US Patent 367 188.
- Pokutsa, A.P., *Cand. Sci. (Chem.) Dissertation*, Lvov: Lvov Polytechnic Institute, 1990.
- Solyanikov, V.M., *Doctoral (Chem.) Dissertation*, Chernogolovka: Institute of Chemical Physics, 1985.
- Parshall, G.W. and Ittel, S.D., *Homogenous Catalysis*, New York: Wiley, 1992, Ch. 10.
- Kucher, R.V., Pokutsa, A.P., and Timokhin, V.I., *Dokl. Akad. Nauk SSSR*, 1990, vol. 310, no. 3, p. 642.
- Kucher, R.V., Pokutsa, A.P., and Timokhin, V.I., *Kinet. Katal.*, 1990, vol. 31, no. 5, p. 1141.
- USSR Inventor's Certificate no. 1659391.
- Timokhin, V., Lisovska, M., Zaborovskiy, A., et al., *12th Conf. on Physical Organic Chemistry*, Padova, 1994, p. 261.

14. Lisovska, M., Timokhin, V., and Pocutsa, A., *Third Eur. Congr. on Catalysis "EuropaCat-3"*, Krakow, 1997, vol. 1, p. 195.
15. Murahashi, S.-I., Oda, Y., and Naota, T., *J. Am. Chem. Soc.*, 1992, vol. 114, p. 7913.
16. Murahashi, S.-I., Oda, Y., Naota, T., *et al.*, *J. Chem. Soc., Chem. Commun.*, 1993, p. 139.
17. Murahashi, S.-I. and Naota, T., *Bull. Chem. Soc. Jpn.*, 1996, vol. 69, p. 1805.
18. Punniyamurthy, T., Bhatia, B., Reddy, M.M., *et al.*, *Tetrahedron*, 1997, vol. 53, no. 22, p. 7641.
19. Mandal, A.K. and Igbal, J., *Tetrahedron*, 1997, vol. 53, no. 22, p. 7641.
20. Battioni, P., Iwanejko, R., Mansuy, D., *et al.*, *J. Mol. Catal. A: Chem.*, 1996, vol. 109, no. 1, p. 91.
21. Einhorn, C., Einhorn, J., Marcadal, C., *et al.*, *J. Chem. Soc., Chem. Commun.*, 1997, p. 447.
22. Bravo, A., Bjorsvik, H.-R., Fontana, F., *et al.*, *J. Org. Chem.*, 1996, vol. 61, no. 26, p. 9409.
23. Tsepalov, V.F., *Zavod. Lab.*, 1964, no. 1, p. 111.
25. Pokutsa, A.P., Timokhin, V.I., and Suprun, V.Ya., *Zh. Anal. Khim.*, 1989, vol. 44, no. 3, p. 570.
26. Antonovskii, V.L. and Buzlanova, M.M., *Analyticheskaya khimiya organicheskikh peroksidnykh soedinenii* (Analytical Chemistry of Organic Peroxide Compounds), Moscow: Khimiya, 1978, p. 309.
27. Chernyak, B.I. and Andrianova, L.A., *Zh. Org. Khim.*, 1975, vol. 11, no. 9, p. 1800.
28. Timokhin, V.I., *Doctoral (Chem.) Dissertation*, Lvov: Lvov Polytechnic Institute, 1991.
29. Korcek, S., Cheneir, J.H.B., Howard, J.A., *et al.*, *Can. J. Chem.*, 1972, vol. 50, no. 14, p. 285.
30. *Handbook of Chemistry and Physics*, Boca Raton, FL: CRC, 1987/1988, 68th ed., p. 178.
31. Paronikyan, D.G., Oganessian, Em.A., Vardanyan, I.A., *et al.*, *Khim. Fiz.*, 1982, no. 10, p. 1357.
32. Semenchenko, A.E., Solyanikov, V.M., and Denisov, E.T., *Neftekhimiya*, 1971, vol. 11, no. 4, p. 555.
33. Garbuzyuk, I.A., Levush, S.S., and Shevchuk, V.N., *Ukr. Khim. Zh.*, 1976, vol. 42, no. 6, p. 620.
34. Turetskaya, E.A., Skakovskii, E.D., Rykov, S.V., *et al.*, *Dokl. Akad. Nauk BSSR*, 1980, vol. 24, no. 1, p. 57.
35. Chateaneuf, J., Luszyk, J., and Ingold, K.U., *J. Am. Chem. Soc.*, 1988, vol. 110, no. 9, p. 2886.
36. Opeida, I.A., Timokhin, V.I., Simonov, M.A., *et al.*, *VINITI*, 1983, no. 2356.
37. Marta, F., Boga, E., and Matik, M., *Disc. Faraday Soc.*, 1968, no. 46, p. 173.
38. Ariko, N.G., Mitskevich, N.I., and Koval'nov, V.D., *Teoriya i praktika zhidkofaznogo okisleniya* (Theory and Practice of Liquid-Phase Oxidation), Moscow: Nauka, 1974, p. 147.
39. Bawn, C.E.H. and Jolley, J.E., *Proc. Royal Soc. (London)*, 1956, vol. 236, p. 297.
40. Druliner, J.D., Hobbs, F.W., and Seidel, W.C., *J. Org. Chem.*, 1988, vol. 53, no. 3, p. 700.
41. Bawn, C.E.H., Hobin, T.P., and Raphael, L., *Proc. Royal Soc. (London)*, 1956, vol. 237, p. 313.
42. Govindarao, M.H. and Gurumurthy, C.V., *J. Appl. Chem. Biotechnol.*, 1973, vol. 23, p. 465.
43. Sheredin, V.P. and Denisov, E.T., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1967, p. 1428.
44. Matienko, L.I., Goldina, L.A., Skibida, I.P., *et al.*, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1975, p. 287.
45. Pustarnakova, G.F. and Solyanikov, V.M., *Neftekhimiya*, 1975, vol. 15, p. 124.
46. Pustarnakova, G.F., *Cand. Sci. (Chem.) Dissertation*, Chernogolovka: Institute of Chemical Physics, 1976.
47. Gol'dberg, V.M. and Obukhova, L.K., *Uspekhi khimii organicheskikh perekisnykh soedinenii i avtookisleniya* (Advances in Chemistry of Organic Peroxides and Autooxidation), Moscow: Khimiya, 1969, p. 160.
48. Maizus, Z.K., Skibida, I.P., and Emanuel', N.M., *Dokl. Akad. Nauk SSSR*, 1965, vol. 164, p. 374.
49. Clark, T.A., *Handbook of Computational Chemistry*, New York: Wiley, 1985, p. 375.
50. Skibida, I.P., Sakharov, A.M., and Emanuel', O.N., *Itogi Nauki Tekh., Ser.: Kinet. Katal.*, 1986, vol. 15, p. 10.