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CATALYSIS

Catalytic Oxidation of Cyclohexane with Ozone–Oxygen Mixtures

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Abstract—Selective oxidation of cyclohexane with ozone in the presence of chromium(0) hexacarbonyl and sodium naphthenates–Cr(III) mixtures was studied.

Since cyclohexane is an intermediate of caprolactam oxidation, an increase in the selectivity of cyclohexane oxidation to cyclohexanone [1] is an urgent problem.

Previously we showed [2] that noncatalytic oxidation of cyclohexane to cyclohexanone with ozone is more selective that industrial oxidation of cyclohexane with atmospheric oxygen to form a mixture of cyclohexanol and cyclohexanone.

The selectivity of oxidation of alkanes and cycloalkanes to the corresponding carbonyl compounds appreciably increases in the presence of catalysts of heterolytic decomposition of hydroperoxides, such as chromium(III) and chromium(VI) compounds [3–5]. The catalytic effect in the course of high-temperature liquid-phase oxidation of alkanes and cycloalkanes in manifested mainly in the step of hydroperoxide decomposition. When the process is performed at low temperature in the presence of a strong oxidizing agent (O_3 and O_2), variable-valence metal compounds can appreciably affect the mechanism of chain initiation, propagation, and termination and the contribution of radical and nonradical pathways. To control the selectivity of these processes, the features of the mechanism of these steps should be determined.

The procedures for oxidizing cyclohexane and for analyzing the reaction products were described previously [2, 3].

Cyclohexane ozonolysis was performed at 20–60°C in the presence of 2×10^{-2}–2×10^{-3} M stearates, naphthenates, and acetylacetonates of Co(II), Co(III), Cr(III), Mn(II), and $Cr(CO)_6$ as catalysts. The typical kinetic curves of accumulation of the oxidation products are shown in Fig. 1. The classes of compounds formed in this reaction are identical to those formed in oxidation of cyclohexane with ozone–oxygen mixtures. The kinetics of the overall cyclohexane consumption is of the first order irrespective of the catalyst (Figs. 2, 3). This is confirmed by the constancy of the accumulation rates of cyclohexanol, cyclohexanone, cyclohexyl hydroperoxide, and the acids in cyclohexane ozonolysis in the presence of cobalt(II) stearate (Fig. 1). Hence, the selectivity of formation of the target product (cyclohexanone) is almost constant

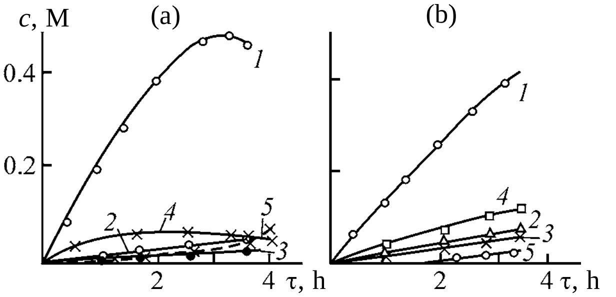

Fig. 1. Kinetic curves of accumulation of (*1*) cyclohexanone, (*2*) cyclohexanol, (*3*) cyclohexyl hydroperoxide, (*4*) acids, and (*5*) esters in catalytic oxidation of cyclohexane with ozone in the presence of (a) $Cr(CO)_6$ and (b) $Co(St)_2$. 40°C, $[O_3]$ = 4 vol %, [cat] = 2×10^{-4} M; the same for Fig. 2. (*c*) Concentration of reaction product and (τ) time.

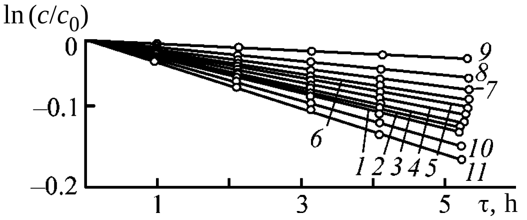

Fig. 2. Kinetic curves of cyclohexane consumption. (c_0, c) Initial and current cyclohexane concentrations and (τ) time; the same for Fig. 3. (*1*) $Cr(CO)_6$; (*2*) $Co(acac)_2$; (*3*) no catalyst; (*4*) $Cr(St)_3$; (*5*) $[Cr(CO)_6] = 2 \times 10^{-5}$ M; (*6*) $Mn(acac)_3$; (*7*) $Co(St)_2$; (*8*) $Cr(CO)_6$, $[O_3]$ = 3 vol %; (*9*) $Cr(CO)_6$, $[O_3]$ = 2 vol %; (*10*) cyclohexane; and (*11*) cyclohexanol ($[Cr(CO)_6] = 2 \times 10^{-4}$ M).

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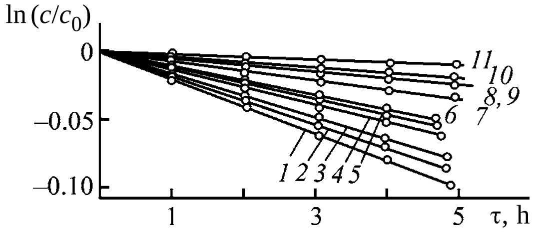


Fig. 3. Kinetic curves of cyclohexane consumption $\{[O_3] = 2–4$ vol %; $[Cr(CO)_6] = 2 \times 10^{-5}–2 \times 10^{-3}$ M$\}$. $[O_3]$, vol %: (*1–9*) 4 and (*10, 11*) 20. *T*, °C: (*1–3, 7–10*) 60 and (*4–6, 11*) 2. $[Cr(CO)_6]$, M: (*1, 6, 7*) 2×10^{-3}, (*2, 5, 8, 11*) 2×10^{-4}, (*4, 9*) 2×10^{-5}, and (*3, 10*) 0.

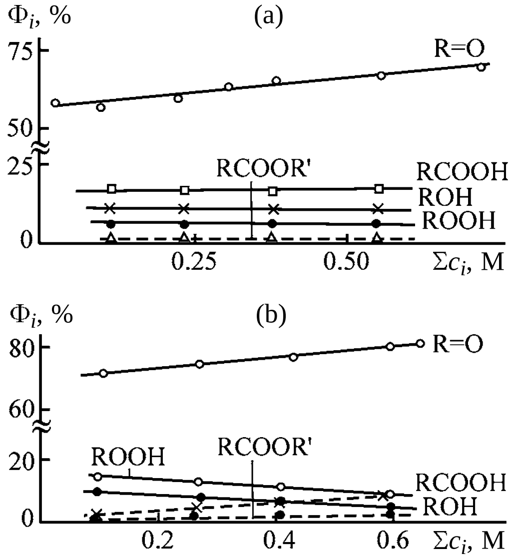


Fig. 4. Total selectivity Φ_i of formation of cyclohexane oxidation products as a function of cyclohexane conversion. 40°C; $[O_3]$ = 4 vol %; (a) $[Cr(St)_3] = 2 \times 10^{-4}$ and (b) $[Cr(CO)_6] = 2 \times 10^{-4}$ M. (Σc_i) Total concentration of the oxidation products.

in the examined conversion range (~10%). In the presence of $Cr(CO)_6$, the accumulation rates of the hydroperoxide, alcohol, and ketone are also constant in the first oxidation steps (Figs. 1–3). The kinetic curve of accumulation of the acids is nonlinear. However, since the content of these acids in less than 0.05 M, the contribution of this pathway is insignificant and has small effect on the kinetic curve of cyclohexane consumption.

Chromium hexacarbonyl catalyzes the oxidation, whereas $CoSt_2$, $Mn(acac)_3$, and $CrSt_3$ appreciably inhibit the cyclohexane ozonolysis. Clearly, this is not due to homolytic or heterolytic catalytic decomposition of cyclohexyl hydroperoxide. First, at 20–40°C cyclohexyl hydroperoxide is relatively stable to thermocatalytic decomposition [4, 5]. Second, the steady-state concentration of cyclohexyl hydroperoxide in the course of cyclohexane ozonolysis is low owing to its fast consumption in the reaction with ozone (catalysis of this reaction is possible). The inhibiting effect is most likely due to reaction of the peroxy radicals with the catalyst. The rate constant of the reaction between the peroxy radicals and 3*d*-metal compounds is high [6]. The catalysis with $Cr(CO)_6$ and $Co(acac)_3$ can be related to their reaction with ozone, cyclohexane, and its oxidation products.

The selectivity of cyclohexanone formation is maximal in the presence of $Cr(CO)_6$. We studied the rate and selectivity of cyclohexane ozonolysis as influenced by the temperature, ozone concentration, and catalyst. The apparent activation energies of the overall cyclohexane consumption and cyclohexanone formation, determined by varying the reaction temperature in the range 20–60°C, are 34.5 ± 3 and 27.5 ± 2.5 kJ mol^{-1}, respectively, and are close to those of the noncatalytic process. The noticeable difference in the activation energies under conditions of consecutive and parallel reactions suggests a strong temperature effect on the reaction selectivity, which is confirmed experimentally (Figs. 4a, 4b).

The experimental kinetic curves measured at different concentrations of ozone and the catalyst and at different temperatures are shown in Figs. 2 and 3, respectively. The ozone concentration and the temperature have the strongest effect on the reaction rate. As the ozone concentration increases by a factor of 2 (from 2 to 4 vol %), the cyclohexane consumption accelerates by a factor of 2.4 $\{20°C, [O_3] = 2–4$ vol %, $[Cr(CO)_6] = 2 \times 10^{-4}$ M$\}$. Hence, bimolecular nonchain reaction of cyclohexane with ozone [1] is accompanied by chain oxidation of cyclohexane or decomposition of ozone with acceleration of initiation and progress of cyclohexane ozonolysis. The dependence of the rate of cyclohexane (RH) oxidation with ozone in CCl_4 at 22°C on [RH], $[O_3]$, and $[O_2]$ is described by the equation [7]

$$v = 3.2 \times 10^{-3}[RH][O_3] + 0.3[RH]^{1/2}[O_3]^{3/2} + 0.75[RH][O_3]^2/[O_2]_{gas}.$$

The third component of this equation is responsible for chain decomposition of O_3 [7] under the action of cyclohexyl radicals. The chain propagates by the equation $R^\cdot + O_3 \rightarrow RO^\cdot + O_2$, $RO^\cdot + RH \rightarrow ROH + R^\cdot$ and is terminated by the reaction $R^\cdot + O_2 \rightarrow RO_2^\cdot$ provided that the reaction between two cyclohexylperoxy radicals is faster than the reaction of RO_2 with ozone. In this case (no solvent, bubbling reactor, $[RH] \gg [O_3] \sim [O_2]$), cyclohexyl radicals are almost quantitatively oxidized to cyclohexylperoxy radicals. However, in the first steps of cyclohexane ozonolysis [7], the major oxidation product, cyclohexanol, is rapidly converted into cyclohexanone by the nonchain mechanism. The reaction of cyclohexylperoxy radicals with ozone and quadratic chain termination with the peroxy radicals should be taken into account in the kinetic equation of cyclohexane consumption by the chain mechanism. The experimental kinetic curves of cyclohexane consumption in $\ln(c/c_0)$–τ coordinates (c_0 and c are the initial and current cyclohexane concentrations, respectively; τ is the reaction time), measured in the first reaction step at low cyclohexane conversion (up to 8%) and small contribution of the chain pathway, are almost linear (Figs. 2, 3). The effect of $Cr(CO)_6$ concentration is significantly weaker. As $[Cr(CO)_6]$ increases from 2×10^{-5} to 2×10^{-3} M (20 – 60°C), the rate of cyclohexane consumption increases by more than 30% as compared to the noncatalytic reaction. As shown above, the mechanism of ozonolysis of saturated hydrocarbons is radical chain.

Catalytic oxidation of cyclohexane with ozone occurs also by the radical chain pathway. To gain insight into the mechanism of this process, we studied accumulation of the main reaction products. To determine the influence of various catalysts [mainly $Cr(CO)_6$] on the yield of each product, we measured the dependence of the selectivity of its formation on the hydrocarbon conversion. The reaction selectivity was taken as the ratio of the concentration of a definite reaction product to the total concentration of the reaction products.

The dependences of the total selectivity of formation of each product on the hydrocarbon conversion in catalytic ozonolysis of cyclohexane at $[O_3]$ = 4 vol %, 40°C, and the catalyst concentration of 2×10^{-4} M are shown in Figs. 4a and 4b. As the conversion increases, the selectivity of formation of the hydroperoxide and cyclohexanol linearly decreases, as a rule, and that of cyclohexanone formation increases owing to conversion of cyclohexanol and cyclohexyl hydroperoxide into the ketone. When the conversion is lower than 10%, the selectivity of cyclohexanone formation ranges from 69 to 73% without catalyst and reaches 81% in the presence of $Cr(CO)_6$. In addition, in the presence of $Cr(CO)_6$, the yield of cyclohexyl hydroperoxide and cyclohexanol decreases more sharply with increasing cyclohexane conversion. Hence, $Cr(CO)_6$ catalyzes the conversion of these compounds into cyclohexanone. An ozone–chromium(III) stearate system also exhibits high catalytic activity with respect to cyclohexanone (Fig. 4a). In this case, the ketone yield is as high as 70% at 6.5% conversion. When chromium(III) acetate poorly soluble in the reaction mixture is used, the selectivity of the ketone formation does not exceed 31%, but the selectivity of the hydroperoxide formation reaches 48%.

The catalytic effect of ozone–$CoSt_2$, ozone–$Co(acac)_3$, and ozone–$Mn(acac)_3$ systems on the selectivity is considerably lower than that of the ozone–chromium(III) and ozone–chromium(0) systems. In the presence of $Mn(acac)_3$, cyclohexane is rapidly converted into the acids and ε-caprolactone and the total yield of peroxides grows with increasing cyclohexane conversion. This dependence passes through a maximum.

Although the selectivity of cyclohexanone formation is maximal in the presence of the ozone–$Cr(CO)_6$ catalytic system, the selectivity and rate of the reaction considerably change in the examined temperature range (20 – 60°C). Cyclohexane ozonolysis with ozone–air mixtures containing 2% ozone is slow. In 4 h, the hydrocarbon conversion is as low as 2.2%, and the selectivity of cyclohexanone formation reaches 42–51%. Under these conditions, the catalyst affects the ratio of the main classes of the ozonolysis products. The selectivity of the cyclohexanone formation in the presence of 2×10^{-5} M $Cr(CO)_6$ is relatively high (up to 65%). The total yield of the hydroperoxides slightly grows with increasing catalyst concentration.

This is the case at elevated temperatures (60°C). Under these conditions, the selectivity of cyclohexanone formation is no higher than 60%. At 60°C, the conversion of cyclohexanol and cyclohexyl hydroperoxide into cyclohexanone and parallel conversion of cyclohexanone into the acids and lactone are accelerated. The almost optimal conditions of catalytic ozonolysis of cyclohexane are as follows: $[O_3]$ = 4 vol %, 40°C, $[Cr(CO)_6] = 2 \times 10^{-4}$ M, cyclohexane conversion 7–10%. The ketone yield reaches 81%. Ozone–sodium naphthenate, chromium(III) naphthenate, and ozone–chromium(III) naphthenate catalytic systems [8, 9] provide 85–90% selectivity of the ketone formation at the cyclohexane conversion of 5.3–6.5%.

Thus, as the cyclohexane conversion increases, the selectivity of formation of the main reaction products (R'C=O, ROOH, and ROH) is constant, decreases, or increases depending on the reaction conditions (temperature, concentrations of ozone and the catalyst). At low temperature (20°C), the selectivity of formation of these products decreases with increasing ozone concentration owing to acceleration of the consumption of the alcohol and hydroperoxide. The selectivity of the ketone formation grows with increasing cyclohexane concentration. At 60°C, cyclohexanone oxidation is accelerated and the selectivity of its formation remains constant in the whole examined conversion range. The selectivity of formation of acids and esters increases. In the course of cyclohexane ozonolysis at 40°C in the presence of the ozone–$Cr(CO)_6$ catalytic system, the total selectivity of cyclohexanone formation regularly increases, the selectivity for the hydroperoxide and alcohol decreases, and the selectivity for the acids is constant. In the presence of ozone–NaNph–$Cr(Nph)_3$ (Nph is the naphthenate anion) catalytic system, the total selectivity of formation of cyclohexanol and cyclohexanone mixture is high [10]. To gain deeper insight into the mechanism of cyclohexane oxidation, let us consider the transformation of the catalyst, hydroperoxide, alcohol, and ketone under these conditions.

The rate constant of reaction of ozone with Co(II), Fe(II), Mn(II), and Cr(III) acetates is higher by 2–3 orders of magnitude than that of reaction of ozone with cyclohexyl hydroperoxide [1, 3, 11]. Ozone reacts with the catalysts by the reaction [12]

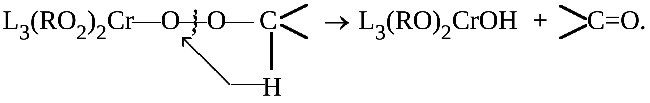
$$O_3 + M(II) \rightarrow M(III) + O_2 + O^- \ (\text{or } O_3^-).$$

Negatively charged oxygen atom rapidly reacts with a proton of the acid present in the reaction mixture to form $^{\cdot}OH$ radical. In addition, the reaction of a saturated hydrocarbon with ozone [1] yields $R^{\cdot}$ and $^{\cdot}OH$ radicals. Hydroxy radicals oxidize the reduced form of a variable-valence metal:

$$^{\bullet}OH + M(II) \rightarrow M(III) + {}^{-}OH.$$

The oxidation potential of Me(III)/Me(II) is sufficient for Me(III) to oxidize hydroperoxides, alcohols, and ketones. If the activation energy of the reaction of the initial or intermediate compound with the oxidized form of the catalyst is high, more active $^{\cdot}OH$ radical can initiate the oxidation. In addition, in the course of cyclohexane oxidation with an ozone–air mixture, variable-valence metal carboxylates in the oxidized or reduced forms coordinate the oxygen-containing reaction products (ROOOH, ROH, R'C=O). The overall rate of catalytic ozonolysis of cyclohexane should depend on the stability of these complexes, and the selectivity of ketone formation, on the ratio of the rates of formation and consumption of these complexes. The main sources of cyclohexanone in noncatalytic ozonolysis of cyclohexane are unstable hydrotrioxide, cyclohexanol, cyclohexyl hydroperoxide, and $RO_2^{\cdot}$ radical [1].

Let us consider the influence of $Cr(CO)_6$ catalyst on the conversion of the above intermediates of cyclohexane ozonolysis. In the presence of chromium compounds, cyclohexyl hydroperoxide is selectively converted into cyclohexanone mainly by the nonradical mechanism [4]. Indictor *et al.* showed [5] that Cr(III) is oxidized with the hydroperoxide to Cr(VI). Antonovskii suggests [13] that the O–O bond of the peroxy ester is homolytically ruptured to form the ketone



As found in [4], decomposition of *tert*-butyl hydroperoxide in the presence of Cr(III) acetylacetonate is described by the scheme

$$Cr(III) + y t\text{-}BuOOH \rightleftarrows \text{Complex},$$

$$\text{Complex} \rightarrow Cr(III + l) + y(t\text{-}BuO^{\cdot} + {}^{-}OH),$$

$$Cr(III + l) + Cr(III) \rightarrow Cr(VI) + Cr(l),$$

where y is the stoichiometric coefficient, and l is an integer equal to the change in the chromium oxidation state.

Bibichev [14] also suggests that the selective conversion of a secondary hydroperoxide into the ketone in the presence of chromium(III) stearate also passes through formation of the complex $Cr(St)_3 \cdot nROOH$, where $n > 1$. When a hydroperoxide molecule is coordinated to the Cr(III) atom, the electron density from the α-oxygen atom of the hydroperoxide is transferred to the d orbital of Cr(III). As a result, the O–O bond of the hydroperoxide is weakened and then homolytically ruptured to form alkoxy and hydroxy radicals. The liberated OH radical, without escaping into the bulk of solution, can attack the C–H bond of the coordinated hydroperoxide to form the ketone and water by the molecular (cryptoradical) mechanism.

The apparent rate constant of cyclohexyl hydroperoxide decomposition in the presence of 2×10^{-4} M $Cr(CO)_6$ is $7.6 \times 10^7 \exp(-67\,000 \pm 2000)/RT$ min^{-1}. If the steady-state concentration of ROOH is 0.1 M, the rate constant of cyclohexanone formation from hydroperoxide at 40°C is 0.0046 mol l^{-1} h^{-1}. Hence, the contribution of the catalytic decomposition of cyclohexyl hydroperoxide to cyclohexanone formation is no higher than 2 and 8.2% at 40 and 60°C, respectively, i.e., is low.

The steady-state concentration of hydrotrioxide at 20°C is 2.2×10^{-3} M. The strength of the O–O bond in this compound is close to that in cyclohexyl hydroperoxide. Hence, the contribution of the catalytic decomposition of the hydrotrioxide to the overall process can be neglected. Both inner- and outer-sphere coordination of cyclohexyl hydroperoxide is typical of 3*d* transition metals [15]; however, coordination-saturated $Cr(CO)_6$ can form only outer-sphere complexes with ROOH $[Cr(CO)_6 \cdot ROOH]$. Chromium hexacarbonyl is stable up to 120–140°C. Since carbonyl groups in $Cr(CO)_6$ are substituted by the dissociative mechanism with a high activation energy (ΔE_a = 163 kJ mol^{-1}), occurrence of these reactions under our conditions is unlikely.

Carbonyl ligands are strongly bonded to the chromium atom in $Cr(CO)_6$. The donor–acceptor σ bond in carbonyls is formed by interaction of the *d* orbital of the metal, e.g., $d_{x^2-y^2}$, with *n* electrons of CO on the *sp*-hybrid σ_n orbital. The carbonyl group donates the α-electron pair localized on the carbon atom. The dative π bond in carbonyls is formed by donation of the electron density form *d* orbitals of the metal, e.g., d_{xy}, to unoccupied antibonding π orbitals of CO.

However, zero-valent chromium in $Cr(CO)_6$ is rapidly oxidized with ozone to Cr(III) and Cr(VI). A sharp band at 336 nm typical for Cr(III) appears in the electronic absorption spectra of $Cr(CO)_6$ solutions in $CHCl_3$ and cyclohexane (1.2×10^{-3} M) after bubbling of an ozone–oxygen mixture for 0.5–1 min ($[O_3]$ = 4 vol %, 25°C). As determined by ESR, the steady-state concentration of Cr^{5+} [18] is very low. Hexavalent chromium was qualitatively determined by the reaction with diphenylcarbazide [19].

The overall process of $Cr(CO)_6$ oxidation with ozone can be described by the following reactions:

$$Cr(CO)_6 + mO_3 \xrightarrow[-CO,\ -CO_2,\ -O_2]{} Cr(III)L_3 + 3O^{\dot{-}},$$

$$O^{\dot{-}} + H^+ \overset{K_e}{\rightleftarrows} {}^{\cdot}OH, \quad K_e = 10^{12} \text{ [3]},$$

$$^{\bullet}OH + Cr(III) \rightarrow Cr(IV) + {}^{-}OH,$$

$$^{-}OH + H^+ \rightleftarrows H_2O,$$

$$Cr(III) + RO_2^{\bullet} \rightarrow Cr(IV) + RO_2^-,$$

$$Cr(IV) + O_3 \rightarrow Cr(V) + O^- + O_2,$$

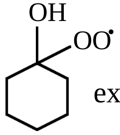
$$Cr(III) + O_3 \rightarrow Cr(IV) + O^- + O_2,$$

$$Cr(V) + O_3 \xrightarrow[-O_2]{} Cr(VI) + O^-,$$

$$RO_2^- + H^+ \rightarrow ROOH.$$

It is known [20] that Cr(VI) selectively oxidizes alcohols to carbonyl compounds:

$$Cr(VI) + ROH \rightarrow R{=}O + Cr(IV).$$

Probably, Cr(IV) is reduced to Cr(III) with cyclohexanol hydroxy hydroperoxide or the hydroxyperoxy radical 

exhibiting redox properties [6]. In addition, reactions between chromium atoms in different oxidation states are also possible. The steady-state concentration of cyclohexanol in the products of catalytic ozonolysis of cyclohexane is low (Fig. 4). The cyclohexanol yield in the course of the ozonolysis decreases owing to its conversion into cyclohexanone [21, 22].

Probably, the fact that the total yield of cyclohexanol and cyclohexanone and the concentration ratio of these products vary a wide range (Fig. 4) is due not only to the catalysis of the alcohol oxidation to the ketone with Cr(VI). Special experiments show slow consumption of cyclohexanol and cyclohexanone in the course of cyclohexane ozonolysis catalyzed with $Cr(CO)_6$ in a bubbling reactor. Slow consumption of cyclohexanol is caused by its self-accociation. We suggest that the increased cyclohexanol yield in the presence of chromium-containing catalysts is due to a change in the reactivity of the peroxide and alkoxy radicals in the chromium(III) coordination sphere. The transformations of these radicals in the course of cyclohexane ozonolysis are discussed in [1].

CONCLUSION

Ozone–chromium(0) hexacarbonyl, ozone–chromium(III) naphthenate–sodium naphthenate, and chromium(0) hexacarbonyl–cyclohexyl hydroperoxide systems are catalytically active in cyclohexane oxidation. In the presence of these catalysts, the selectivity of formation of cyclohexanol–cyclohexanone mixture and of the target product, cyclohexanone, is high.

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