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Mild Oxidation of Cyclohexane Catalyzed by Cobalt(II) Acetate and Initiated by H_2O_2 in the Acetic Acid Medium

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Abstract—The homogeneous catalytic oxidation of cyclohexane by molecular oxygen and hydrogen peroxide in a solution of acetic acid (HOAc) in the presence of cobalt(II) acetate $Co(OAc)_2$ is studied. The high yields of cyclohexanol, cyclohexanone, and cyclohexyl hydroperoxide (0.10–0.15 mol/l) and the high rate of the process ($w = 10^{-5}$–10^{-4} mol l^{-1} s^{-1}) are explained by (1) mild conditions of oxidation in the medium of the HOAc solvent and (2) efficient initiation of the process due to the fast kinetics-controlled dissociation of H_2O_2 into radicals in the studied reaction medium under the action of cobalt cations. Quantitative relationships are found for the cyclohexane oxidation rate, the yield of target products, and the ratio of reactants participating in the process. The effect of hydrogen hydroperoxide additives on the concentrations of reduced and oxidized forms of the catalyst is studied by spectrophotometry in model mixtures. Quantum chemistry is employed to calculate the probabilities of some key elementary reactions. Calculated data agree well with the experiment.

INTRODUCTION

The homogeneous catalytic liquid-phase oxidation of cyclohexane by oxygen in the presence of transition metal compounds (mostly Co, Cr, and Ce stearates and naphthenates) is currently the principal method for obtaining cyclohexanol and cyclohexanone, which are initial products for the synthesis of polyamide fibers [1–4]. However, although the first papers on the commercial use of this process were published about half a century ago [5, 6], it is still far from perfect from the standpoint of the conversion and selectivity, which are lower than 5–10 and 75–80%, respectively [2, 3]. Recent studies have been devoted to new homogeneous catalytic systems [7–10] for cyclohexane oxidation, the effect of a catalyst [9, 10], and that of a solvent [11–15] on the process. Cyclohexane oxidation in the medium of solvents (acetonitrile [12], a mixture of acetonitrile and dichloromethane [13], pyridine [11], and a mixture of pyridine and acetic acid [14]) containing dissolved porphyrin and other nitrogen-containing transition metal complexes [11, 13–15] favor the highly selective transformation of cyclohexane into the target products up to high conversions of cyclohexane. However, it is too early to consider the commercialization of the cited systems due to several shortcomings: (1) the concentration of cyclohexane in the reaction mixture has to be low (1–10%) and, therefore, the reactor space is misused; (2) the cost of catalysts and solvents is high; and (3) oxidants for the process ($KHSO_5$ and PhIO) are expensive and exotic [13–16]. The existence of the above shortcomings stimulates a further search for new, cheaper, and efficient catalytic systems for cyclohexane oxidation. In our opinion, the system containing relatively cheap HOAc as a solvent and cheap H_2O_2 as a promoter are the most promising. Acetic acid readily dissolves both initial reactants and products and favors efficient heat removal from the microzones of the reaction, while H_2O_2 efficiently initiates the process by generating highly active hydroxy radicals. Therefore, the goal of this work was to study the kinetics of cyclohexane oxidation in the solution of HOAc in the presence of H_2O_2 and $Co(OAc)_2$.

EXPERIMENTAL

The kinetics of product accumulation in the process of cyclohexane oxidation in a solution of HOAc containing H_2O_2 and $Co(OAc)_2$ was studied in a thermostated glass cell with a volume of 25 ml. This cell was equipped with a bubbler for purging with O_2 and a Teflon-covered magnetic stirrer to homogenize the reaction medium. Most of the runs were carried out at 303 ± 0.1 K to prevent the carryover of volatile reactants (cyclohexane in the first place). The total volume of the reaction mixture was 10 ml. After 7 h from the start of oxidation, stirring was interrupted and the samples of solutions were withdrawn for thin-layer (TLC) and gas-liquid (GLC) chromatographic analyses and for chemical analysis.

Peroxy compounds were qualitatively analyzed by TLC by comparing their retention indices (R_f) with those for individual peroxides. Silufol plates were used together with a 1 : 1 mixture of toluene and ethyl acetate as an eluent and a saturated solution of NaI in acetone as a developer). Quantitative analyses were carried out using an LKhM-80 chromatograph with a flame-

Table 1. Dependence of the mixture composition in cyclohexane oxidation on the initial concentration of cyclohexane in the mixture with HOAc. $[Co(OAc)_2]_0 = 2.0 \times 10^{-3}$ mol/l, 303 K, 7 h, $v(O_2) = 10$ ml/min

Initial conditions		H_2O_2 consumption, %	Reaction products*			
$[\text{cyclohexane}]_0$	$[H_2O_2]_0$		$[\text{cyclohexanol}]_U/[\text{cyclohexanol}]_L$	$[\text{cyclohexanone}]_U/[\text{cyclohexanone}]_L$	$[\text{cyclohexyl hydroperoxide}]_U/[\text{cyclohexyl hydroperoxide}]_L$	$\Sigma[\text{hydroperoxide}]_U/\Sigma[\text{hydroperoxide}]_L$
mol/l			$\times 10^2$, mol/l			
0.93	1.00	83	1.50	2.20	3.60	30.0
1.86	1.00	81	0.13/0.54	0.19/2.40	1.30/5.62	2.10/23.50
2.06	2.00	76	0.30/2.20	0.30/2.60	0.60/2.20	2.50/35.00
2.24	1.00	78	0.30/2.20	0.32/2.60	1.00/4.00	–
2.79	1.00	85	0.30/2.80	0.26/3.80	1.16/2.80	4.05/25.92
3.80	2.00	73	0.02/0.70	0.08/1.40	0.84/3.20	0.60/75.00
4.18	1.00	75	0.03/2.02	0.06/3.85	1.40/2.30	3.90/45.00
5.57	1.00	75	0.20/2.40	0.10/3.75	1.00/2.50	1.24/64.00
6.50	1.00	76	0.01/0.30	0.06/2.30	1.00/2.40	0.02/90.00
7.43	1.00	74	0.01/1.00	0.03/0.60	0.40/0.80	2.50/130.00

* Subscripts U and L refer to the concentrations of products in the upper and lower layers of the mixture, respectively.

ionization detector and a stainless steel column (4 m × 3 mm packed with Chromaton N–AW with a Silicon OV-351 (5%) stationary phase). Toluene was used as an internal standard. To determine the true concentrations of cyclohexanol and cyclohexanone in the presence of cyclohexyl hydroperoxide, the solution samples were treated with triphenylphosphine. Calculations were performed according to the method described in [17]. The concentration of unreacted H_2O_2 was found as a difference between the total concentration of peroxy compounds determined by iodometric titration and the concentration of cyclohexyl hydroperoxide.

Spectrophotometric measurements were carried out using a double-beam SF-20 spectrophotometer and quartz cell with a width of 1 cm.

Cyclohexane and HOAc were purified according to the method described in [18]. Hydrogen peroxide (30%) and $Co(OAc)_2 \cdot 4H_2O$ (Fluka) were used in the runs without additional purification.

RESULTS AND DISCUSSION

Tables 1 and 2 show that the main, and practically the only, oxidation products are cyclohexanol, cyclohexanone, cyclohexyl hydroperoxide ($R_f = 0.90$), and unreacted H_2O_2 ($R_f = 0.11$). The efficiency of the catalytic system studied estimated as a yield of target products for the same period of time depends on both the cyclohexane/HOAc ratio and on the concentrations of the catalyst and promoter. In the absence of H_2O_2 in the reaction system cyclohexane + $Co(OAc)_2$ + HOAc, cyclohexane is not oxidized by molecular oxygen at 303–323 K. The addition of hydrogen peroxide substantially intensifies the process, which is reflected in an increase in the yield of target products. No noticeable temperature effect was observed. The reaction orders with respect to cyclohexane and $Co(OAc)_2$ were 0.3 and 0.5, respectively. Figure 1a presents a plot of the overall yield of target products on the catalyst concentration in the reaction mixture. It is seen that it has a maximum.

Because the redox potential (E_0) of hydrogen peroxide (1.77 V) is somewhat lower than the potential of the Co^{2+}/Co^{3+} system (1.84 V) [19], Co(III) is capable of oxidizing hydrogen peroxide in the acidic medium via the following reactions:

$$H_2O_2 - 2e^- \longrightarrow 2H^+ + O_2, \qquad \text{(I)}$$

$$[Co(III)OH]^{2+} + e^- + H^+ \longrightarrow Co^{2+} + H_2O, \qquad \text{(II)}$$

$$Co^{2+} + H_2O_2 \longrightarrow [Co(III)OH]^{2+} + HO^{\bullet}, \qquad \text{(III)}$$

$$[Co(III)OH]^{2+} + H_2O_2 \longrightarrow Co^{2+} + HO_2^{\bullet} + H_2O. \qquad \text{(IV)}$$

Table 2. Dependence of the mixture composition in cyclohexane oxidation on the initial concentration of the catalyst in the initial mixture; $[\text{cyclohexane}]_0 = 1.86$ mol/l, $[H_2O_2]_0 = 1.00$ mol/l, 303 K, 7 h, $v(O_2) = 10$ ml/min

Initial concentration of $Co(OAc)_2 \cdot 4H_2O \times 10^3$, M	H_2O_2 consumption, %	Reaction products*			
		$[\text{cyclohexanol}]_U/[\text{cyclohexanol}]_L$	$[\text{cyclohexanone}]_U/[\text{cyclohexanone}]_L$	$[\text{cyclohexyl hydroperoxide}]_U/[\text{cyclohexyl hydroperoxide}]_L$	$\Sigma[\text{hydroperoxide}]_U/\Sigma[\text{hydroperoxide}]_L$
		$\times 10^2$, mol/l			
0.2	91.0	0.01/0.58	0.09/1.45	1.52/3.12	1.8/11.5
0.4	93.0	0.03/2.12	0.12/2.79	1.56/2.52	1.6/9.0
1.0	90.0	0.27/1.15	3.00/2.40	0.74/3.80	2.1/13.0
2.0	82.0	0.13/0.54	0.19/2.40	1.30/5.62	2.5/23.5
4.0	96.0	0.44/2.53	0.59/3.22	0.90/1.88	0.7/5.0
6.0	98.0	0.42/1.91	0.52/2.63	0.62/1.64	0.8/3.0
8.0	99.6	0.20/1.57	0.34/2.41	0.70/1.16	–/0.5
10.0	99.6	0.14/1.61	0.24/2.03	0.14/0.40	–/0.5
12.0	99.6	0.17/1.63	0.35/1.98	0.60/1.08	–/0.5
14.0	99.6	0.18/1.36	0.28/1.74	0.50/1.05	–/0.5

* Subscripts U and L refer to the concentrations of products in the upper and lower layers of the mixture, respectively.

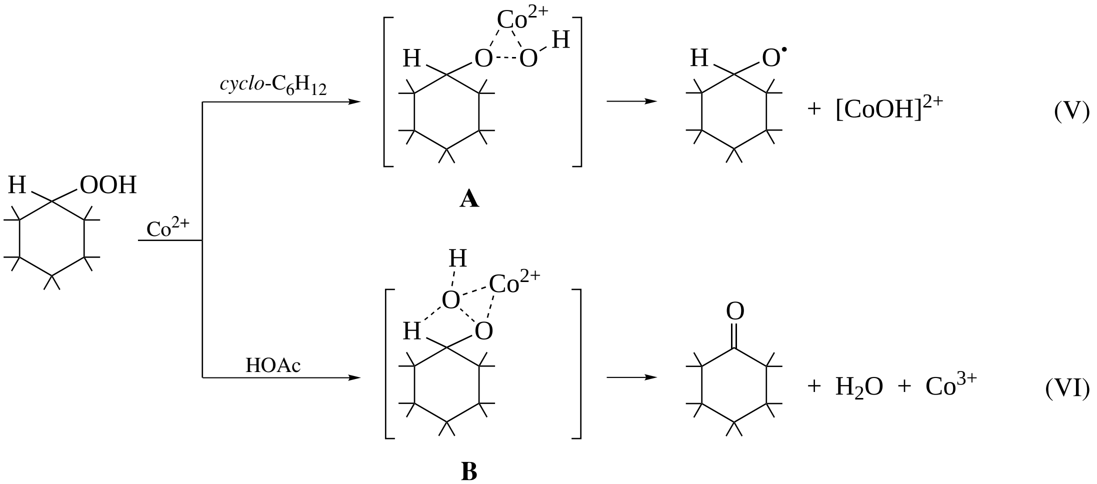
The electrochemical potential of the one-electron reduction of H_2O_2 to H_2O and $^{\bullet}OH$ in water (0.80 V, pH 0 [20]) is much lower than for direct two-electron oxidation to H_2O and O_2 under the same conditions (1.77 V). This means that, in the presence of oxidants stronger than H_2O_2, the mechanism of hydrogen peroxide transformation to the decomposition products may include two competing pathways: (1) generating hydroxy radicals via reactions (III) and (IV) and (2) without the formation of species with free valences via reactions (I) and (II). Thus, by increasing the concentration of the cobalt salt in the reaction mixture higher than the optimal value, we intensify the consumption of H_2O_2 via the two-electron mechanism that excludes peroxide homolysis. Experimental data on the possibility of hydrogen peroxide decomposition in such systems without free radicals were reported in [21].

The dependence of the overall concentration of target products on the concentration of cyclohexane in the initial mixture is also characterized by the presence of a maximum (Fig. 1b). This effect is explained by the existence of some optimal cyclohexane/HOAc ratio, which corresponds to the hydrocarbon concentration belonging to the range 2.5–3.5 mol/l, when the concentration of hydrogen peroxide and the catalyst provide the maximal rate of the process and the decrease in the amount of the reacted hydrocarbon in the lower (acid) layer is compensated by its transfer from the upper (cyclohexane) layer.

To determine the effect of hydrogen peroxide concentration in the mixture on the concentration of the oxidized and reduced forms of the catalyst, we studied absorption spectra in the UV–VIS region for the model mixtures of the catalyst and H_2O_2 in acetic acid. Successive additives of hydrogen peroxide cause a proportional decrease in the heights of absorption bands for both Co^{2+} and Co^{3+}. Note that the additives of water with analogous volume had almost no effect on the heights of absorption peaks of Co^{2+} in the range studied. Interconversions of these two cationic forms of the metal were not detected, and there were no changes in the absorption spectra in the visible region with time. However, on thoroughly examining the dependences of absorption spectra of catalyst solutions in HOAc on the amount of H_2O_2 added one can see a weak hypsochromic shift of the absorption maximum for $Co(OAc)_2$ (Fig. 2a). The additive of H_2O_2 to the solution of the cobalt(III) acetylacetonate $Co(AcAc)_3$ and to the mixture $Co(OAc)_2 + Co(AcAc)_3$ in HOAc (Figs. 2b and 2c) cause a bathochromic shift of the absorption maximum. These insignificant interconversions of the oxidation states of cobalt in the presence of hydrogen peroxide are explained by the competitive reactions (II)–(IV). At the same time, a drastic decrease in the intensities of Co^{2+} and Co^{3+} absorption caused by the additives of

H_2O_2 can be explained by the formation of cation–H_2O_2 complexes that are transparent in the visible spectrum. The mathematical modeling using the ZINDO/1 method was used to determine that the probability of formation of the $[Co(III)OH]^{2+}$ species, and the region of their absorption was found to be 214 nm. This explains the absence of the band of this cation in the visible spectrum of the $Co(OAc)_2 + H_2O_2 + HOAc$ solution. However, this hypothesis could not be verified because of the complete absorption by acetic acid in the UV region.

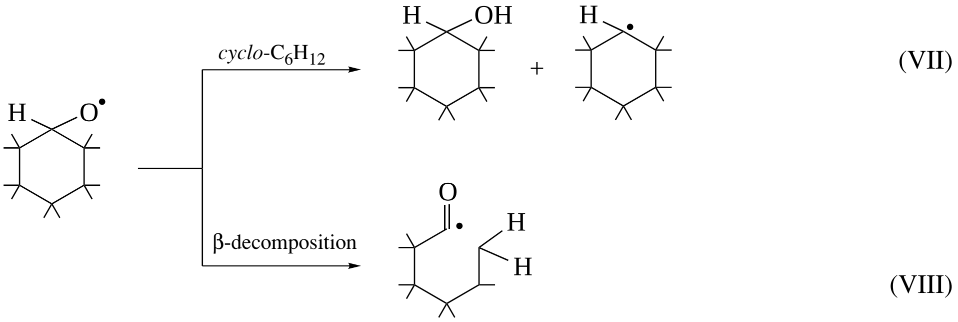
In the presence of $Co(OAc)_2$, cyclohexane oxidation under mild conditions results in the preferred formation of cyclohexanone (the cyclohexanone/cyclohexanol ratio is 1.2–2.3, see Table 1), whereas this ratio is 0.5–0.7 in industrial conditions [3].



Scheme 1

Evaluative quantum chemical calculation of the formation of hypothetical transition states **A** and **B** (Scheme 1) formed in the reaction of cyclohexyl hydroperoxide and $Co(OAc)_2$ in the gas phase showed that the probability of complex **B** formation is higher (E_a = 20.04 kcal/mol). Complex **B** decomposes with the formation of cyclohexanone, whereas the decomposition of complex **A** (E_a = 24.10 kcal/mol) leads to the formation of cyclic alcohol.

On the other hand, an increase in the cyclohexanone/cyclohexanol ratio in the system under study can be explained by the competitive reactions occurring according to Scheme 2.



Scheme 2

Note that the formation of adipic acid was not observed under the conditions of oxidation. That is, there was no noticeable consumption of cyclohexyloxy radicals via reaction (VIII).

To calculate the rate constants of reaction (VIII) and estimate the rates of competitive reactions (VII) and (VIII), we used the following reference data [22]: $k_7 = 8.9 \times 10^5$ l mol^{-1} s^{-1}, $E_{a,8}$ = 12.0 kcal/mol, $A_8 = 10^{12}$ s^{-1}.

Then,

$$k_8 = 10^{12}\exp(-12.0/RT) \cong 1.5 \times 10^3 \text{ s}^{-1} \text{ (303 K)}.$$

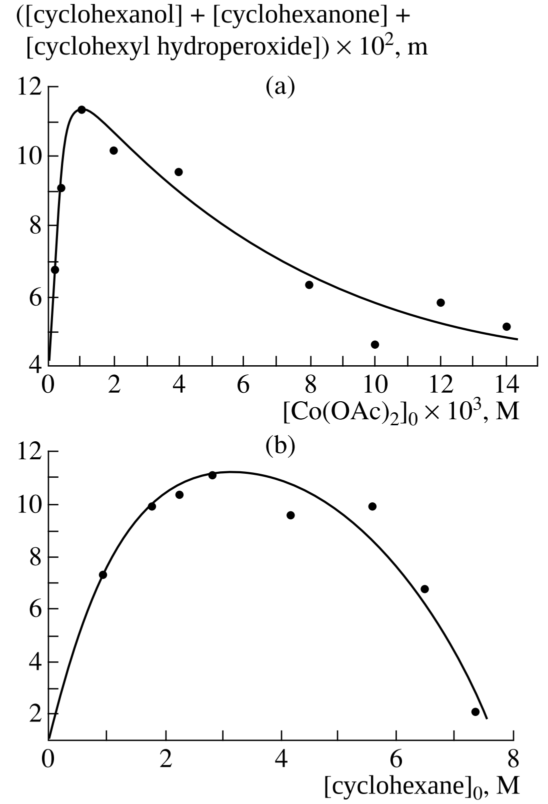


Fig. 1. Dependence of the overall yield of target products ([cyclohexanol] + [cyclohexanone] + [cyclohexyl hydroperoxide]) of cyclohexane oxidation on (a) the initial concentration of the catalyst and (b) the initial concentration of cyclohexane in the reaction mixture (a) $[\text{cyclohexane}]_0$ = 1.86 mol/l, (b) $[\text{Co(OAc)}_2]_0 = 2 \times 10^{-3}$ mol/l, $[\text{H}_2\text{O}_2]_0$ = 1.00 mol/l; the volume of the reaction mixture, 10.0 ml; 303 K; 30% H_2O_2.

When the reaction was carried out in the medium of pure cyclohexane (in the absence of solvents), $[\text{cyclohexane}]_0 = 9.25$ mol/l.

Then,

$$w_7/w_8 = \frac{8.9 \times 10^5 \times 9.25[\mathrm{RO}^{\bullet}]}{1.5 \times 10^3[\mathrm{RO}^{\bullet}]} \cong 5.5 \times 10^3.$$

It can be seen from this formula that the contribution of pathway (VIII) to the overall rate of cyclohexyloxy radical consumption is at most 0.5%. However, it increases if the oxidation is carried out in the medium of a more polar solvent than cyclohexane. According to [23], k_8 may reach a value of 10^6 s^{-1} and w_8 becomes comparable with w_7 in water, which is a more polar solvent than HOAc and cyclohexane. In our case, when we work with HOAc, this value should be much lower and this is confirmed by the above calculation.

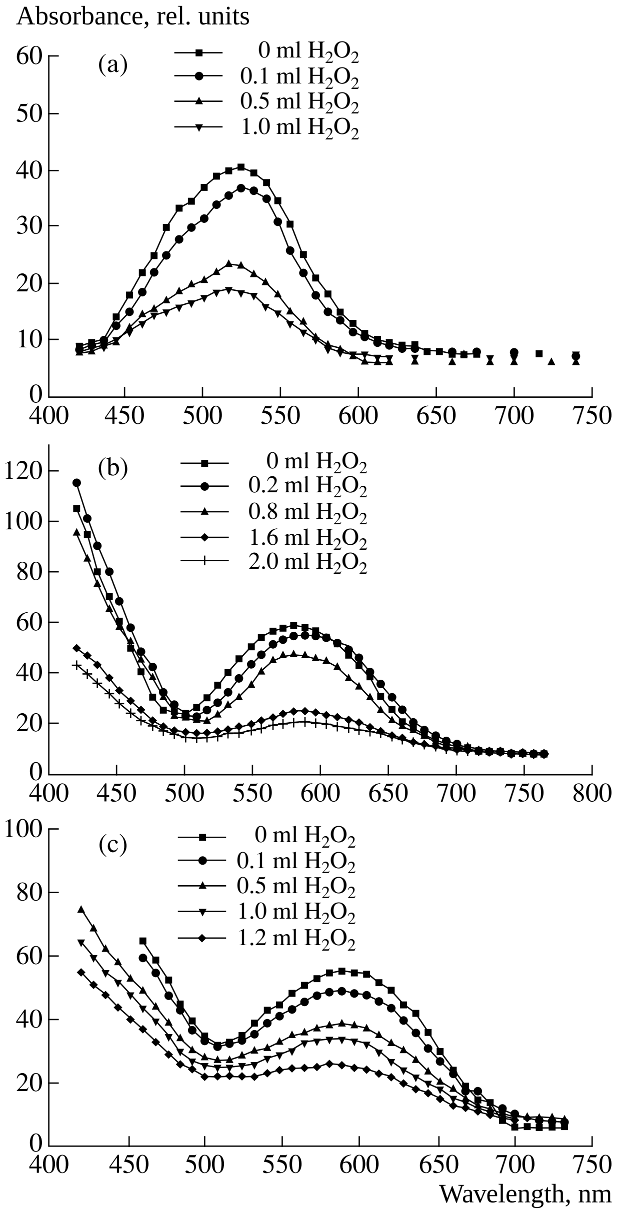


Fig. 2. Electron absorption spectra of acetic acid solutions of (a) Co(OAc)_2, (b) Co(AcAc)_3, and (c) Co(OAc)_2 + Co(AcAc)_3 containing various amounts of 30% H_2O_2 (shown in figures): (a) $[\text{Co(OAc)}_2]_0 = 2.0 \times 10^{-5}$ mol/l; (b) $[\text{Co(AcAc)}_3]_0 = 2.0 \times 10^{-5}$ mol/l; (c) $[\text{Co(OAc)}_2]_0 = 6.0 \times 10^{-5}$ mol/l, $[\text{Co(AcAc)}_3]_0 = 2.0 \times 10^{-5}$ mol/l. The volume of acetic acid solutions of cobalt salts in each run is 5.0 ml; 303 K.

Another specific feature of the system under study is the accumulation of cyclohexyl hydroperoxide in substantial amounts in parallel with cyclohexanol and cyclohexanone (Tables 1 and 2). This feature makes the process substantially different from the commercial process, in which the maximal concentrations of alcohol and ketone are achieved only after the complete consumption of cyclohexyl hydroperoxide. Therefore, we conjectured that this effect is due to both the parallel formation of these three products from a common precursor ($\mathrm{ROO}^{\bullet}$) and the prevalence of cyclohexyl hydro-

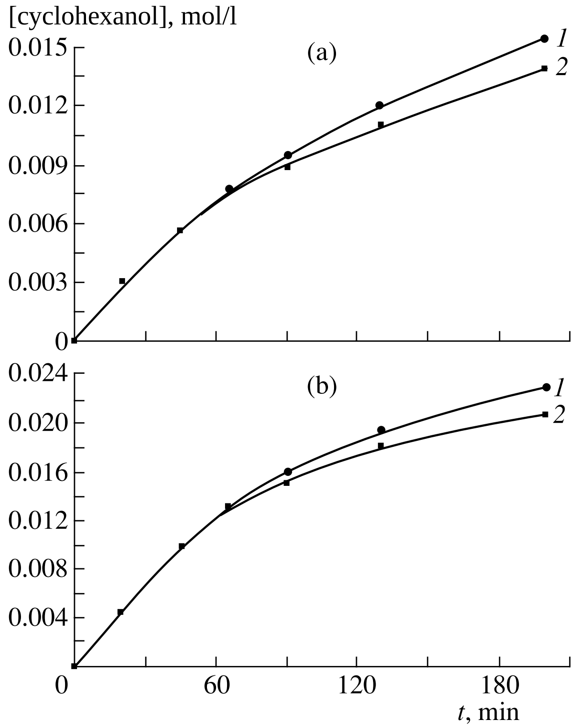


Fig. 3. Kinetics of (a) cyclohexanol and (b) cyclohexanone accumulation in the course of cyclohexane oxidation by (*1*) oxygen and (*2*) hydrogen peroxide in the medium of HOAc: $[Co(OAc)_2]_0 = 7.0 \times 10^{-4}$ mol/l, $[\text{cyclohexane}]_0 = 1.2$ mol/l, $[H_2O_2]_0 = 0.80$ mol/l, 303 K, P = 1 atm.

peroxide formation over its decomposition. To quantitatively check this hypothesis, we carried out calculations using the main equations of formation and consumption of cyclohexyl hydroperoxide under the conditions considered.

(a) Generating cyclohexyl radicals:

$$RH + {}^{\bullet}OH \longrightarrow R^{\bullet} + H_2O,$$
$$w_9 = 4 \times 10^{9} \times 10^{-10} \times 4.2 \cong 1.7 \text{ mol l}^{-1}\text{ s}^{-1}, \qquad \text{(IX)}$$

where 4×10^9 l mol^{-1} s^{-1} is the rate constant [24], 10^{-10} mol/l is the quasi-steady-state concentration of ${}^{\bullet}OH$ radicals in the Fenton system [25] (it was taken as a basis in this calculation), and 4.2 mol/l is the chosen concentration of cyclohexane in the system under study.

(b) O_2 addition:

$$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet},$$
$$w_{10} = 1 \times 10^{10} \times 1 \times 10^{-7} \times 1 \times 10^{-2} \qquad \text{(X)}$$
$$= 10.0 \text{ mol l}^{-1}\text{ s}^{-1},$$

where 1.0×10^{10} l mol^{-1} s^{-1} is the rate constant of diffusion-controlled O_2 addition to the radical, (1.0–10.0) × 10^{-7} mol/l is the concentration of cyclohexyl radicals in the oxidized cyclohexane [3], and 1×10^{-2} mol/l is the equilibrium concentrations of O_2 in alkanes at 303 K, mol/l [25].

(c) Chain propagation:

$$ROO^{\bullet} + RH \longrightarrow ROOH + R^{\bullet},$$
$$w_{11} = 1.8 \times 10^{-2}[ROO^{\bullet}] \times 4.2 \qquad \text{(XI)}$$
$$= 7.5 \times 10^{-2}[ROO^{\bullet}] \text{ mol l}^{-1}\text{ s}^{-1},$$

where 1.8×10^{-2} l mol^{-1} s^{-1} is the rate constant at 303 K [19] and 4.2 mol/l is the concentration of cyclohexane.

(d) Degenerate decomposition of cyclohexyl hydroperoxide:

$$ROOH + Co^{2+} \longrightarrow RO^{\bullet} + Co^{3+} + {}^{-}OH,$$
$$w_{12} = 4.9 \times 2 \times 10^{-4} \times 2.3 \times 10^{-2} \qquad \text{(XII)}$$
$$= 2.2 \times 10^{-5} \text{ mol l}^{-1}\text{ s}^{-1},$$

where 4.9 l mol^{-1} s^{-1} is the rate constant [19]; 2.0 × 10^{-4} mol/l is the concentration of $Co(OAc)_2$; 2.3×10^{-2} is the concentration of cyclohexyl hydroperoxide, which was determined experimentally for the runs with [cyclohexane] = 4.2 mol/l.

It follows from Eqs. (XI) and (XII) that, for the cyclohexyl hydroperoxide concentration in the solution not to decrease, the concentration of $ROO^{\bullet}$ radicals should be higher than $> 10^{-4}$ mol/l. Because the rates of cyclohexyl radical generation (w_9) and cyclohexylperoxy radical generation (w_{10}) are five to six orders of magnitude higher than the rate of cyclohexyl hydroperoxide decomposition (w_{12}), we can affirm that $w_{11} > w_{12}$ and that cyclohexyl hydroperoxide accumulates in the course of the reaction. This is in fact observed in the experiments. The above calculation also confirms the hypothesis that three cyclohexane oxidation products (cyclohexanol, cyclohexanone, and cyclohexyl hydroperoxide) are formed from the same precursor, which is probably the cyclohexylperoxy radical.

The effect of oxygen on the yield of target products is shown in Fig. 3. As follows from the plots, oxygen bubbling has no effect on the yield of target products. A small increase in the yield can be assigned to the experimental error. The nature of kinetic curves is the same for all target products. This also suggests that they are formed from the same common precursor, which is probably the $ROO^{\bullet}$ radical.

Note that the conversion of H_2O_2 in the runs with different cyclohexane concentrations in the reaction mixture is almost the same and does not affect the yield of target products. A decrease in the fraction of HOAc in the mixture (Table 1) leads to an increase in the concentration of H_2O_2 in the acid layer, and this in turn leads to the unproductively fast hydrogen peroxide decomposition as in the case when the catalyst concentration is higher than 2.0×10^{-3} mol/l (Table 2, Fig. 2).

CONCLUSIONS

(1) In an HOAc solution containing H_2O_2 and $Co(OAc)_2$, cyclohexane is oxidized at room temperature and forms cyclohexanol, cyclohexanone, and cyclohexyl hydroperoxide. The high yields of cyclic alcohol, ketone, and hydroperoxide are due to the efficient initiation of $^{\bullet}OH$ radicals generated by hydrogen hydroperoxide via its homolysis in the catalytic system studied.

(2) The higher cyclohexanone/cyclohexanol ratio in the oxidation mixture than in the commercial process is explained by the intramolecular rearrangement of cyclohexyl hydroperoxide leading to the preferred formation of cyclohexanone.

(3) In contrast to the commercial process, cyclohexyl hydroperoxide is accumulated in the studied catalytic system during the whole period of oxidation. This fact lets us assume that all the three target products are formed in parallel from the same precursor, which is probably the $ROO^{\bullet}$ radical. A change in the temperature in the range 303–323 K has no noticeable effect on the yield of these products. The assumption that they are partly formed via a nonradical pathway is confirmed by the existence of the maximum on the plot of the overall yield of cyclohexanol, cyclohexanone, and cyclohexyl hydroperoxide vs. the catalyst concentration.

(4) The existence of the maximum on the plot of the yield of target products vs. the concentration of cyclohexane in the reaction mixture is associated with a decrease in the HOAc/cyclohexane ratio with an increase in the fraction of cyclohexane. As a consequence, the catalyst exhibits more pronounced inhibiting properties, which are characteristic of its high concentrations.

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