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Reactivity of Cyclohexanol CH Bonds toward the *tert*-Butylperoxy Radical

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Abstract—The effect of the hydroxy group on the partial rate constants of the reactions of the *tert*-butylperoxy radical with CH bonds in cyclohexanol at 333 K was studied by the Howard–Ingold method. The overall reaction rate constant increased with decreasing alcohol concentration in chlorobenzene because of complex effects of hydrogen bonds at the steps of chain growth and termination. The hydroxy group activates the α-CH bond and deactivates the β- and γ-CH bonds. The reactivity of δ-CH bonds is close to the reactivity of CH bonds in cyclohexane.

INTRODUCTION

Secondary alcohols are formed along with ketones in the liquid-phase oxidation of aliphatic and alicyclic hydrocarbons with molecular oxygen at the step of decomposition of secondary hydroperoxides [1–3]. Their subsequent reactions are usually associated with chain radical oxidation at an activated CH bond at the α-position with respect to the functional group. According to published data [4], the reactivity of the α-CH bond in 2-propanol toward the "standard" *tert*-butylperoxy radical at 303 K is higher than that of secondary CH bonds in *n*-hexane at the 2- and 3-positions by factors of 16 and 26, respectively. At 353 K, this radical reacted with the α-CH bond in cyclohexanol 50 times more rapidly than with the secondary CH bond of cyclohexane [4, 5]. The reactivity of more distant CH bonds in secondary alcohols was not studied; usually, it is assumed to be equal to the reactivity of corresponding CH bonds in hydrocarbons. At the same time, the electron-acceptor properties of the hydroxy group suggest the deactivation of CH bonds at the β- and γ-positions by analogy with the effect of the acetyl group on the reactivity of CH bonds in the cyclohexyloxy moiety of cyclohexyl acetate [6].

The aim of this work was to study the reactivity of CH bonds in cyclohexanol toward the *tert*-butylperoxy radical. It is believed that these data will be useful for understanding the formation of degradation products in the liquid-phase oxidation of cyclohexane and cyclohexanol.

EXPERIMENTAL

Cyclohexanol of analytical grade was purified sequentially by azeotropic distillation of impurities with water, treatment with a saturated sodium bisulfite solution, and vacuum rectification in an argon flow for the removal of ethers and cyclohexanone. According to GLC data, the purity of the resulting compound was 99.5 ± 0.1%; the concentrations of cyclohexanol ethers (GLC) and cyclohexanone (spectrophotometric determination as 2,4-dinitrophenylhydrazone) were no higher than 0.01 and lower than 0.003%, respectively.

tert-Butyl hydroperoxide (TBHP) was synthesized according to the published procedure [7]. The compound contained 99.3 ± 0.2% hydroperoxide as determined by iodometry.

Cyclohexane of reagent grade and toluene of analytical grade were purified by rectification in an argon flow; the concentrations of cyclohexanol and benzyl alcohol (GLC) in the compounds were no higher than 0.01 and 0.005%, respectively.

The procedures used for the purification of azobisisobutyronitrile (AIBN) and chlorobenzene were reported elsewhere [6, 8].

The kinetics of gas consumption in the oxidation of cyclohexanol with molecular oxygen was measured in a manometric system in the kinetic region of oxygen consumption under conditions of mixed initiation with AIBN and TBHP, as described previously [6, 8]. Oxidized alcohol samples for studying the composition of products were obtained under the same conditions.

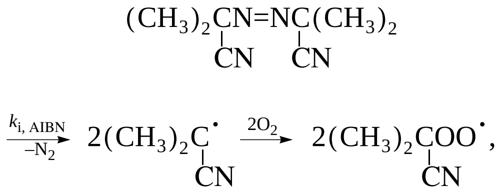
Cyclohexanone in oxidized cyclohexanol was determined by spectrophotometry after derivatization to 2,4-dinitrophenylhydrazone and by GLC. The conditions of determination were described previously [6]. To determine isomeric *cis*- and *trans*-2-, 3-, and 4-hydroxycyclohexyl hydroperoxides, the oxidized alcohol was preconcentrated at a reduced pressure. Peroxide compounds were reduced by treatment with a 50% potassium iodide solution in 0.1 M hydrochloric acid, extracted with 1,2-dichloroethane, and dried with anhydrous magnesium sulfate. The extractant was distilled off, and diols were converted into diacetates by treatment with an acetic anhydride–pyridine mixture (1 : 1) at 373 K for 2 h [9]. The identification and GLC determination of the diacetates of isomeric diols were described elsewhere [6].

Cyclohexyl and benzyl alcohols in the cooxidation products of cyclohexane with toluene were determined after acetylation with the use of a column (2000 × 3 mm) packed with 5% SP-2100 on Chromaton N-AW-Super at 398 K. Cyclohexanone and benzyl alcohol (cyclohexanol and toluene cooxidation products) were determined (also after the treatment with an acetic anhydride–pyridine mixture) on a column (3000 × 3 mm) packed with 5% OV-210 silicone on Chromaton N-AW-Super under conditions of temperature programming.

The optimum values of $k^{\mathrm{overall}}(2k_t)^{-0.5}$ and $w_{\mathrm{i,\,ROOH}}$ were found from the dependence of $w_{\mathrm{O_2}}$ on [AIBN] at a constant value of [TBHP] on a personal computer using a program based on the least-squares technique [6].

RESULTS AND DISCUSSION

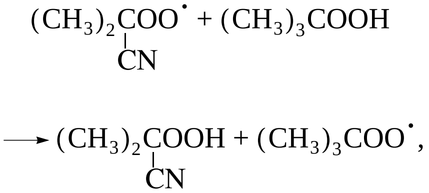
The radical chain oxidation of cyclohexanol ($\mathrm{R_2CHOH}$) initiated by AIBN and TBHP under conditions of the Howard–Ingold method is described by the following reaction scheme:



$$\mathrm{(CH_3)_2\underset{CN}{C}N{=}N\underset{CN}{C}(CH_3)_2 \xrightarrow[-N_2]{k_{i,\,AIBN}} 2(CH_3)_2\underset{CN}{C^{\bullet}} \xrightarrow{2O_2} 2(CH_3)_2\underset{CN}{C}OO^{\bullet}}, \qquad \mathrm{(I)}$$

$$\mathrm{2(CH_3)_3COOH \xrightarrow{k_{i,\,TBHP}} (CH_3)_3CO^{\bullet} + (CH_3)_3COO^{\bullet} + H_2O}, \qquad \mathrm{(II)}$$

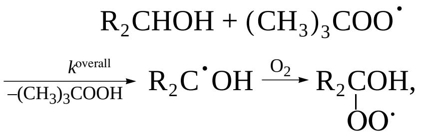
$$\mathrm{(CH_3)_3COOH + R_2CHOH \xrightarrow{k'_{i,\,TBHP}} (CH_3)_3CO^{\bullet} + R_2CHO^{\bullet} + H_2O}, \qquad \mathrm{(III)}$$



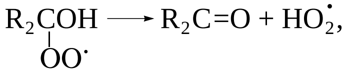
$$\mathrm{(CH_3)_2\underset{CN}{C}OO^{\bullet} + (CH_3)_3COOH \longrightarrow (CH_3)_2\underset{CN}{C}OOH + (CH_3)_3COO^{\bullet}}, \qquad \mathrm{(IV)}$$

$$\mathrm{(CH_3)_3CO^{\bullet} + (CH_3)_3COOH \longrightarrow (CH_3)_3COH + (CH_3)_3COO^{\bullet}}, \qquad \mathrm{(V)}$$

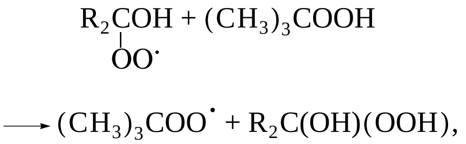
$$\mathrm{R_2CHO^{\bullet} + (CH_3)_3COOH \longrightarrow R_2CHOH + (CH_3)_3COO^{\bullet}}, \qquad \mathrm{(VI)}$$



$$\mathrm{R_2CHOH + (CH_3)_3COO^{\bullet} \xrightarrow[-(CH_3)_3COOH]{k^{overall}} R_2C^{\bullet}OH \xrightarrow{O_2} R_2\underset{OO^{\bullet}}{C}OH}, \qquad \mathrm{(VII)}$$



$$\mathrm{R_2\underset{OO^{\bullet}}{C}OH \longrightarrow R_2C{=}O + HO_2^{\bullet}}, \qquad \mathrm{(VIII)}$$



$$\mathrm{R_2\underset{OO^{\bullet}}{C}OH + (CH_3)_3COOH \longrightarrow (CH_3)_3COO^{\bullet} + R_2C(OH)(OOH)}, \qquad \mathrm{(IX)}$$

$$\mathrm{HO_2^{\bullet} + (CH_3)_3COOH \longrightarrow (CH_3)_3COO^{\bullet} + HOOH}, \qquad \mathrm{(X)}$$

$$\mathrm{2(CH_3)_3COO^{\bullet} \xrightarrow{k_t} (CH_3)_3COOC(CH_3)_3 + O_2}, \qquad \mathrm{(XI)}$$

$$\mathrm{2(CH_3)_3COO^{\bullet} \xrightarrow{k'} 2(CH_3)_3CO^{\bullet} + O_2}. \qquad \mathrm{(XII)}$$

In this case, the rate of radical chain oxidation (w_{v}) can be expressed by the equation [10]

$$w_{\mathrm{v}} = k^{\mathrm{overall}}(2k_{\mathrm{t}})^{-0.5}[\mathrm{CHOH}] \times (w_{\mathrm{i,\,AIBN}} + w_{\mathrm{i,\,TBHP_1}} + w_{\mathrm{i,\,TBHP_2}})^{0.5}, \qquad (1)$$

where k^{overall} is the rate constant of the overall reaction of the *tert*-butylperoxy radical with cyclohexanol; this rate constant is related to the partial rate constants ($k_{\mathrm{i}}^{\mathrm{H}}$) of hydrogen atom abstraction from CH bonds at different positions of the alcohol and to the number (n) of hydrogen atoms by the equation

$$k^{\mathrm{overall}} = \sum n_{\mathrm{i}} k_{\mathrm{i}}^{\mathrm{H}}; \qquad (2)$$

k_{t} is the rate constant of the colligation of *tert*-butylperoxy radicals with chain termination; and $w_{\mathrm{i,\,AIBN}}$, $w_{\mathrm{i,\,TBHP_1}}$, and $w_{\mathrm{i,\,TBHP_2}}$ are the rate constants of initiation by reactions (I), (II), and (III), which can be calculated using Eqs. (3)–(5), respectively.

$$w_{\mathrm{i,\,AIBN}} = k_{\mathrm{i,\,AIBN}}[\mathrm{AIBN}], \qquad (3)$$

$$w_{\mathrm{i,\,TBHP_1}} = k_{\mathrm{i,\,TBHP}}[\mathrm{TBHP}]^2, \qquad (4)$$

$$w_{\mathrm{i,\,TBHP_2}} = k'_{\mathrm{i,\,TBHP}}[\mathrm{TBHP}][\mathrm{CHOH}]. \qquad (5)$$

In the calculation of $w_{\mathrm{i,\,TBHP_1}}$, we used the value of $k_{\mathrm{i,\,TBHP}}$ equal to 4.0×10^{-8} l mol^{-1} s^{-1}, which was obtained from published data [6] by Eq. (4) with the use of the value $w_{\mathrm{i,\,TBHP}} = 1.0 \times 10^{-8}$ l mol^{-1} s^{-1} (333 K; [TBHP] = 0.5 M).

The constant $k_{\mathrm{i,\,AIBN}}$ is related to the rate constant of decomposition of the initiator ($k_{\mathrm{d,\,AIBN}}$) and to the factor that characterizes radical escape from a solvent cage (e) by the equation [10]

Table 1. Effect of TBHP concentration on the parameter $k^{\text{overall}}(2k_t)^{-0.5}$ in the oxidation of cyclohexanol

[TBHP], mol/l	$w_{O_2} \times 10^7$, mol l^{-1} s^{-1}	$w_{i,\,TBHP_1} \times 10^8$, mol l^{-1} s^{-1}	$w_{i,\,TBHP_2} \times 10^8$, mol l^{-1} s^{-1}	$w_v \times 10^7$, mol l^{-1} s^{-1}	ν**	$k^{\text{overall}}(2k_t)^{-0.5} \times 10^3$, $l^{0.5}$ $mol^{-0.5}$ $s^{-0.5}$
0.25	5.60	0.25	1.25	8.02	14.7	3.4 ± 0.1
0.5	8.10	1.00	2.50	11.43	15.3	4.2 ± 0.2
0.7	11.80	1.96	3.50	16.02	17.0	5.3 ± 0.2
0.9	12.50	3.24	4.50	17.80	15.2	5.3 ± 0.2
1.35	14.20	7.29	6.75	22.33	12.4	5.3 ± 0.2

Note: Solvent, chlorobenzene; T = 333 K; [R_2CHOH] = 1.0 mol/l; [AIBN] = 2.1×10^{-3} mol/l.

* $w_{i,\,TBHP_2}$ was obtained by solving Eq. (9).

** $\nu = \dfrac{w_v}{w_{i,\,AIBN} + w_{i,\,TBHP_1} + w_{i,\,TBHP_2}}$ is the chain length.

$$k_{i,\,AIBN} = 2ek_{d,\,AIBN}. \quad (6)$$

The following well-known relations (from [4] and [10], respectively) were used for calculating $2k_t$ and $k_{d,\,AiBN}$:

$$\log 2k_t = 10.15 - \frac{5138.4}{2.303T}, \quad (7)$$

$$\log k_{d,\,AIBN} = 15.0 - \frac{15186.5}{2.303T}. \quad (8)$$

At 333 K, $2k_t = (2.90 \pm 0.05) \times 10^3$ l mol^{-1} s^{-1} and $k_{i,\,AIBN} = 1.89 \times 10^{-5}$ s^{-1} (at $e = 0.6$ [8]).

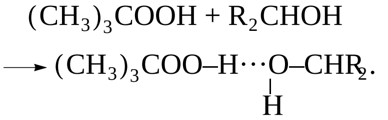
Taking into account corrections for the nonchain consumption of oxygen and for the release of nitrogen in reaction (I), as well as for the release of oxygen in reactions (XI) and (XII), w_v is related to the experimentally measured rate of gas consumption (w_{O_2}) by the expression [8, 10]

$$\begin{aligned} w_v = {} & w_{O_2} + 0.5w_{i,\,AIBN}(k'/k_t - 1) + 0.5w_{i,\,AIBN}/e \\ & + 0.5(w_{i,\,TBHP_1} + w_{i,\,TBHP_2})(1 + k'/k_t), \end{aligned} \quad (9)$$

where k'/k_t is the ratio between the rate constants of reactions (XI) and (XII)—the combination of *tert*-butylperoxy radicals with and without chain termination, respectively (the value k'/k_t(323 K) = 8.1 was used [11]).

An important prerequisite for the correct use of Eqs. (1) and (9) is the completeness of exchange of foreign peroxy and oxy radicals for *tert*-butylperoxy radicals by reactions (IV)–(VI), (IX), and (X); this is usually achieved at a reasonably high hydroperoxide concentration [2, 5, 6, 8].

It is well known that, in the presence of alcohols, the attack of peroxy and, evidently, oxy radicals at the OH bond of the hydroperoxide molecule is hindered because of associate formation due to the hydrogen bonding



$$\begin{aligned} & (CH_3)_3COOH + R_2CHOH \\ & \longrightarrow (CH_3)_3COO\text{–}H\cdots\underset{\displaystyle H}{\underset{|}{O}}\text{–}CHR_2. \end{aligned} \quad \text{(XIII)}$$

Thus, at the first stage, we studied the effect of TBHP concentration on the completeness of exchange of the above radicals at the highest concentration of cyclohexanol equal to 1.0 mol/l. Table 1 summarizes the experimental data.

Data given in Table 1 indicate that, at [TBHP] = 0.7 mol/l or higher, the value of $k^{\text{overall}}(2k_t)^{-0.5}$ reached a constant (maximum) value. This fact suggests almost complete exchange of foreign peroxy and oxy radicals for *tert*-butylperoxy radicals [6, 8].

It is well known [2, 5] that in the oxidation of alcohols the parameter $k^{\text{overall}}(2k_t)^{-0.5}$ can depend on substrate concentration. Therefore, we studied the dependence of the rate of chain-radical oxidation of cyclohexanol in a chlorobenzene solution in the presence of TBHP ([TBHP] = 1.0 mol/l) on AIBN and substrate concentrations (Table 2).

It can be seen in Table 2 that the parameter $k^{\text{overall}}(2k_t)^{-0.5}$ decreases with alcohol concentration. According to Hendry *et al.* [5], this is due to the incomplete exchange of $HO_2^{\bullet}$, which is the most active radical among oxidation chain-propagating radicals, for *tert*-butylperoxy radicals. In the majority of publications summarized in monograph [2], it is believed that a decrease in the parameter of oxidizability with increasing [R_2CHOH] is due to a decrease in the reactivities of the alcohol and peroxy radicals in chain propagation and termination reactions, which are analogous to (VII)–(XII), because of solvation effects.

Data on the AIBN-initiated oxidation of cyclohexanol in the absence of TBHP (Table 3, figure) indicate that the above decrease in $k^{\text{overall}}(2k_t)^{-0.5}$ with increasing alcohol

Table 2. Effects of AIBN and substrate concentrations on the rate of cyclohexanol oxidation in the presence of TBHP

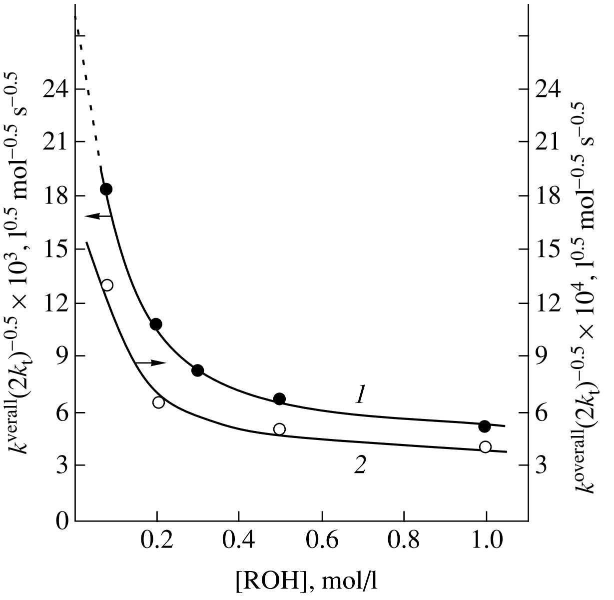
$[R_2CHOH]$, mol/l	$w_{i,\,AIBN} \times 10^8$, mol l^{-1} s^{-1}	$w_{O_2} \times 10^7$, mol l^{-1} s^{-1}	$w_\nu \times 10^7$, mol l^{-1} s^{-1}	$w_{i,\,TBHP} \times 10^8$, mol l^{-1} s^{-1}	ν	$k^{overall}(2k_t)^{-0.5} \times 10^3$, $l^{0.5}$ $mol^{-0.5}$ $s^{-0.5}$
0.1	3.96	0.43	3.70	3.32	5.95	19.1 ± 0.9
	8.05	0.98	5.98		5.24	
	11.87	1.21	7.97		5.24	
	15.80	1.50	9.96		5.20	
0.2	3.96	1.57	5.00	3.74	6.50	10.9 ± 0.5
	8.05	1.65	6.83		5.85	
	11.87	1.84	8.75		5.60	
	15.80	2.08	10.70		5.48	
0.3	3.96	2.60	6.23	4.17	7.67	8.8 ± 0.4
	8.05	3.24	8.60		7.12	
	11.87	3.80	10.90		6.79	
	15.80	3.95	17.80		6.39	
0.5	3.96	4.60	9.42	5.02	10.50	6.8 ± 0.4
	8.05	6.20	11.96		9.24	
	11.87	6.61	14.49		8.57	
	15.80	7.40	16.58		7.95	
1.0	3.96	12.30	17.30	7.14	15.60	5.3 ± 0.4
	8.05	13.20	20.40		13.60	
	11.87	14.60	23.10		12.12	
	15.80	17.40	27.60		12.02	

Note: Solvent, chlorobenzene; $T = 333$ K; $[R_2CHOH] = 0.1–1.0$ mol/l; $[AIBN] = (2.1–8.4) \times 10^{-3}$ mol/l; $[TBHP] = 1.0$ mol/l.

Table 3. Experimental data on the AIBN-initiated oxidation of cyclohexanol

$[R_2CHOH]$, mol/l	$w_{i,\,AIBN} \times 10^8$, mol l^{-1} s^{-1}	$w_{O_2} \times 10^7$, mol l^{-1} s^{-1}	$w_\nu \times 10^7$, mol l^{-1} s^{-1}	ν	$k^{overall}(2k_t)^{-0.5} \times 10^3$, $l^{0.5}$ $mol^{-0.5}$ $s^{-0.5}$
0.1	0.38	0.11	0.08	2.11	1.30 ± 0.05
0.3	0.94	0.24	0.17	1.81	0.60 ± 0.02
0.5	3.96	0.81	0.53	1.34	0.50 ± 0.01
1.0	15.80	2.86	1.75	1.11	0.40 ± 0.01

Note: Solvent, chlorobenzene; $T = 333$ K; $[R_2CHOH] = 0.1–1.0$ mol/l; $[AIBN] = (0.2–8.4) \times 10^{-3}$ mol/l.



A plot of the parameter $k^{\rm overall}(2k_t)^{-0.5}$ vs. the concentration of substrate in the oxidation of the cyclohexanol solution in chlorobenzene at $T = 333$ K (*1*) in the presence of *tert*-butyl hydroperoxide and (*2*) without it; (*1*) [TBHP] = 1.0 M, [AIBN] = (2.1–8.4) × 10^{-3} M; (*2*) [AIBN] = (0.20–8.4) × 10^{-3} M.

concentration also occurs in a similar manner without TBHP. That is, the exchange process cannot play a decisive role in the phenomenon under consideration.

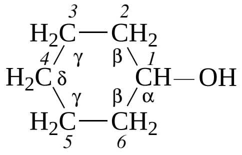
Because the known value of $2k_t$ for the *tert*-butylperoxy radical was determined in the absence of an alcohol, we used the value $k^{\rm overall}(2k_t)^{-0.5} = (28.0 \pm 1.0) \times 10^{-3}$ $l^{0.5}$ $mol^{-0.5}$ $s^{-0.5}$, which was found by the extrapolation of curve *1* (figure) to the zero concentration of cyclohexanol, for calculating $k^{\rm overall}$. At $T = 333$ K, $k^{\rm overall} = 1.51 \pm 0.08$ l mol^{-1} s^{-1}. A comparison of the obtained value of $k^{\rm overall}$ with an analogous value for cyclohexane ($k^{\rm overall}_{\rm cyclihexane} = 12k^{\rm H}_{\rm cyclihexane}$; $k^{\rm overall}_{\rm cyclihexane}(333\ {\rm K}) = 0.046$ l mol^{-1} s^{-1}) calculated by the equation [12]

$$\log k^{\rm H}_{\rm cyclihexane} = 10.4 - \frac{9831.5}{2.303T}, \qquad (10)$$

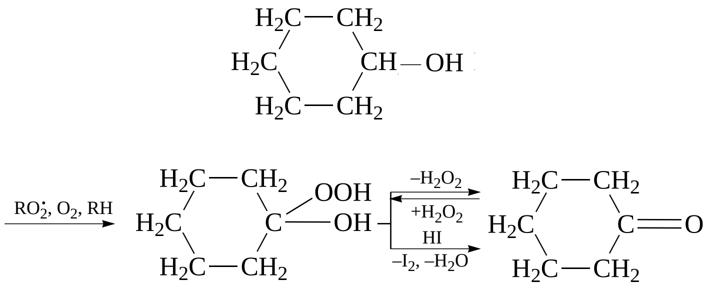
indicates that, in the reaction with the *tert*-butylperoxy radical, the cyclohexanol molecule is more highly reactive than the cyclohexane molecule by a factor of ~30. This fact is consistent with data on the reactions of cyclohexanol and cyclohexane with the *tert*-butylperoxy radical at 353 K [5].

The partial rate constants of the reactions of *tert*-butylperoxy radicals with various CH bonds in cyclohexanol can be evaluated based on $k^{\rm overall}$ and the analysis of oxidation product composition. In this case, it is reasonable to convert primary oxidation products (isomeric hydroxyhydroperoxides) into more stable nonperoxide compounds by reduction [13].

The cyclohexanol molecule contains 11 CH bonds of the following four types: one α-CH bond (1-position), four β-CH bonds (2- and 6-positions), four γ-CH bonds (3- and 5-positions), and two δ-CH bonds (4-position).

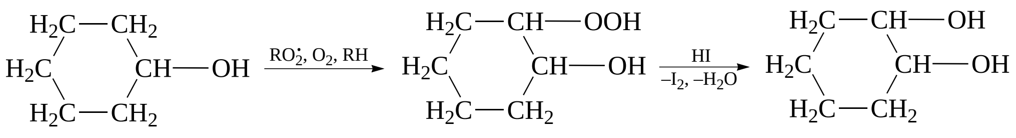


The oxidation of cyclohexanol at the α-CH bond results in 1-hydroxycyclohexyl hydroperoxide, the dissociation or reduction of which results in cyclohexanone [13]:



(XIV)

The interaction of the *tert*-butylperoxy radical with the β-, γ-, or δ-CH bonds of cyclohexanol gives isomeric 2-, 3-, or 4-hydroxycyclohexyl hydroperoxide, the reduction of which results in 1,2-, 1,3-, or 1,4-cyclohexanediol, respectively, for example:



(XV)

Table 4. Effect of substrate conversion (*x*) on the composition of cyclohexanol oxidation products (after reduction and acetylation)

Determined products	*x*, %					
	3.3		5.3		6.4	
	$C \times 10^4$, mol/l	*C*, mol %	$C \times 10^4$, mol/l	*C*, mol %	$C \times 10^4$, mol/l	*C*, mol %
Cyclohexanone	320.0 ± 0.3	97.5	520.0 ± 0.5	97.5	620.0 ± 0.6	97.5
cis-1,2-Diacetoxycyclohexane	0.38 ± 0.02	0.26*	0.58 ± 0.03	0.24*	0.68 ± 0.04	0.24*
trans-1,2-Diacetoxycyclohexane	0.46 ± 0.02		0.70 ± 0.04		0.82 ± 0.05	
cis-1,3-Diacetoxycyclohexane	0.43 ± 0.02	0.30*	0.66 ± 0.03	0.30*	0.89 ± 0.04	0.32*
trans-1,3-Diacetoxycyclohexane	0.55 ± 0.03		0.91 ± 0.05		1.18 ± 0.06	
cis-1,4-Diacetoxycyclohexane	1.60 ± 0.08	1.90*	2.50 ± 0.12	1.89*	2.80 ± 0.14	1.89*
trans-1,4-Diacetoxycyclohexane	4.70 ± 0.20		7.60 ± 0.40		9.30 ± 0.50	

Note: $T = 333$ K; [R_2CHOH] = 1.0 mol/l; [TBHP] = 1.0 mol/l; [AIBN] = 2.1×10^{-3} mol/l.

* Total concentration of *cis* and *trans* isomers.

Table 5. Effect of substrate concentration on the composition of cyclohexanol oxidation products in a chlorobenzene solution at conversions from 1.9 to 4.3%

Determined products	[R_2CHOH], mol/l							
	1.0		1.5		2.0		4.35	
	$C \times 10^4$*, mol/l	*C**, mol %	$C \times 10^4$, mol/l	*C*, mol %	$C \times 10^4$, mol/l	*C*, mol %	$C \times 10^4$, mol/l	*C*, mol %
Cyclohexanone	320.0 ± 0.3	97.5	630.0 ± 0.6	97.5	710.0 ± 0.6	97.6	780.0 ± 0.7	97.5
cis- and *trans*-1,2-diacetoxycyclohexane	0.84 ± 0.04	0.25	1.55 ± 0.08	0.24	1.75 ± 0.09	0.24	1.92 ± 0.09	0.24
cis- and *trans*-1,3-diacetoxycyclohexane	0.98 ± 0.05	0.31	2.00 ± 0.10	0.31	2.26 ± 0.10	0.31	2.48 ± 0.12	0.31
cis- and *trans*-1,4-diacetoxycyclohexane	6.30 ± 0.30	1.90	12.30 ± 0.60	1.90	13.80 ± 0.70	1.90	15.20 ± 0.80	1.90

Note: $T = 333$ K; [R_2CHOH] = 1.00–4.35 mol/l; [TBHP] = 1.0 mol/l; [AIBN] = 2.1×10^{-3} mol/l.

* Average value according to data in Table 4.

Indeed, the presence of cyclohexanone and the *cis* and *trans* isomers of 1,2-, 1,3-, and 1,4-diacetoxycyclohexanes was found in a study of the product composition in the oxidation of a 1.0 M cyclohexanol solution in chlorobenzene initiated by AIBN (0.021 mol/l) in the presence of TBHP (1.0 mol/l) at 333 K after the reduction of oxidation products with KI and acetylation (Table 4).

It can be seen in Table 4 that the composition of oxidation products is almost independent of cyclohexanol conversion. Consequently, isomeric hydroxycyclohexyl hydroperoxides, which are formed in competing parallel reactions, did not undergo decomposition under the experimental conditions. The analysis of oxidation products at different cyclohexanol concentrations in chlorobenzene demonstrated that the composition of the products was almost independent of substrate concentration (Table 5).

The partial rate constants k_i^H of hydrogen abstraction by the *tert*-butylperoxy radical from CH bonds of different types in cyclohexanol at a concentration of cyclohexanol approaching zero were calculated from

Table 6. Partial rate constants of the reactions of various types of CH bonds in cyclohexanol, cyclohexyl acetate, and cyclohexane with the *tert*-butylperoxy radical at $T = 333$ K

Type of CH bonds	Cyclohexanol			Cyclohexyl acetate**		Cyclohexane***
	$k_{\mathrm{i}}^{\mathrm{H}} \times 10^3$, l mol^{-1} s^{-1}	$k_{\mathrm{i}}^{\mathrm{H}}/k_{\mathrm{cyclohexane}}^{\mathrm{H}}$	$k_{\mathrm{i}}^{\mathrm{H}}/k_{\mathrm{cyclohexane}}^{\mathrm{H}}$ *	$k_{\mathrm{i}}^{\mathrm{H}} \times 10^3$, l mol^{-1} s^{-1}	$k_{\mathrm{i}}^{\mathrm{H}}/k_{\mathrm{cyclohexane}}^{\mathrm{H}}$	$k_{\mathrm{cyclohexane}}^{\mathrm{H}} \times 10^3$, l mol^{-1} s^{-1}
α	1470 ± 20	387.6	101.9	18.2 ± 1.5	4.90	3.8
β	0.90 ± 0.06	0.24	0.074	0.31 ± 0.05	0.082	
γ	1.17 ± 0.09	0.31	0.095	0.52 ± 0.07	0.14	
δ	14.3 ± 0.5	3.78	1.15	3.70 ± 0.40	0.97	

* According to experimental data on cooxidation.

** According to published data [6].

*** According to published data [12].

k^{overall} and the average yields of products for [R$_2$CHOH] = 1.0 mol/l (Table 6).

A comparison of the resulting $k_{\mathrm{i}}^{\mathrm{H}}$ with the partial rate constants of the reactions of the *tert*-butylperoxy radical with CH bonds in cyclohexane (Table 6) demonstrates that the hydroxy group considerably increases the reactivity of the α-CH bond and, to a smaller degree, δ-CH bonds and considerably decreases the reactivity of β- and γ-CH bonds.

A similar effect of functional groups was observed previously in a study of the reaction of cyclohexyl acetate with the *tert*-butylperoxy radical [6]. The exception is provided by the δ-CH bonds, whose reactivity is almost equal to the reactivity of CH bonds in cyclohexane (Table 6).

Additional data on the relative reactivity of various types of CH bonds in cyclohexanol, as compared with CH bonds in cyclohexane, in the reaction with the *tert*-butylperoxy radical were obtained using the method of competing reactions [6, 12]. This method is based on a study of the ratio between the yields of substrate conversion products in cooxidation. Because cyclohexyl hydroperoxide (after reduction, cyclohexanol) is the product of cyclohexane oxidation under conditions of the Howard–Ingold method, we studied the cooxidation of binary mixtures of cyclohexane with toluene at the first stage and of toluene with cyclohexanol at the second stage.

Toluene ([toluene] = 2.1 mol/l) and cyclohexane ([cyclohexane] = 4.4 mol/l) in chlorobenzene with AIBN (0.01 mol/l) at 333 K were oxidized in the presence of TBHP (1.0 mol/l) for 390 min. The reaction mixture after reduction and acetylation contained benzyl acetate and cyclohexyl acetate in the ratio [benzyl acetate] / [cyclohexyl acetate] = 0.84 ± 0.02. Based on these data, we calculated the ratio between the rate constants of overall reactions of the *tert*-butylperoxy radical with toluene and cyclohexane ($k_{\mathrm{toluene}}^{\mathrm{overall}}/k_{\mathrm{cyclohexane}}^{\mathrm{overall}}$) = 1.77 ± 0.04 with the use of the equation [6]

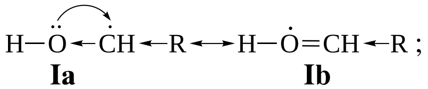
$$\frac{k_{\mathrm{toluene}}^{\mathrm{overall}}}{k_{\mathrm{cyclohexane}}^{\mathrm{overall}}} = \frac{[\text{benzyl acetate}][\text{cyclohexane}]}{[\text{cyclohexyl acetate}][\text{tolyene}]}. \quad (11)$$

In the oxidation of a mixture of cyclohexanol ([R$_2$CHOH] = 1.17 mol/l) and toluene ([toluene] = 5.17 mol/l) in chlorobenzene under the specified conditions for 350 min, after an analogous treatment, we found that the ratio of the total yield of alcohol oxidation products (cyclohexanone and the monoacetates of isomeric diols) to the yield of benzyl acetate equals 1.29 ± 0.03. The ratio between the rate constants of overall reactions of the *tert*-butylperoxy radical with cyclohexanol and toluene ($k_{\mathrm{cyclohexanole}}^{\mathrm{overall}}/k_{\mathrm{toluene}}^{\mathrm{overall}}$) is 5.70 ± 0.06.

Based on the above values of $k_{\mathrm{toluene}}^{\mathrm{overall}}/k_{\mathrm{cyclohexane}}^{\mathrm{overall}}$ and $k_{\mathrm{cyclohexanole}}^{\mathrm{overall}}/k_{\mathrm{toluene}}^{\mathrm{overall}}$ and on the data on the composition of cyclohexanol oxidation products, which were used previously for calculating $k_{\mathrm{i}}^{\mathrm{H}}$ (Table 4), we found the ratios of the partial rate constants of reactions of the *tert*-butylperoxy radical with various types of CH bonds in cyclohexanol to the partial rate constant of the reaction of this radical with cyclohexane (Table 6). It follows from the above ratios that, under comparable conditions, the *tert*-butylperoxy radical reacts with the δ-CH bond of cyclohexanol at almost the same rate as with the CH bond of cyclohexane. Previously [6], such a behavior was observed in a study of the interaction of cyclohexyl acetate with this radical.

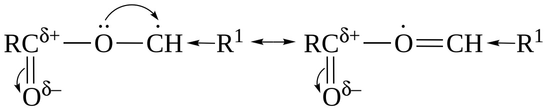
The oxidation of cyclohexanol, as well as of the alkoxy moiety of the cyclohexyl acetate molecule, is a case of homolytic substitution at a hydrocarbon chain bound to an electron-acceptor substituent. Because of the polar effect (inductive effect + field effect) of such a substituent, the electron density at the hydrogen atom of the attacked CH bond decreases. Thus, the probability of reactions with electrophilic peroxy radicals decreases [14]. Moreover, an electron-acceptor substituent destabilizes the transition state and the carbon-centered radicals that are formed when cyclohexanol attacks CH bonds in the β- and γ-positions.

In the reaction of a peroxy radical with the α-CH bond, along with the destabilization of the transition state and hydroxyalkyl radical **I** due to the inductive effect, they are significantly stabilized by the conjugation of an unpaired electron with lone electron pairs of the hydroxy group. Obviously, this stabilization is higher in cyclohexanol than in cyclohexyl acetate (cf. **I** and **II**); in the latter compound, the rate constant of the reaction of the *tert*-butylperoxy radical with the α-CH bond is much lower than that for the α-CH bond of cyclohexanol (Table 6).



$$\mathrm{H{-}\ddot{O}\leftarrow\dot{C}H\leftarrow R \longleftrightarrow H{-}\dot{O}{=}CH\leftarrow R\ ;}$$

Ia **Ib**



$$\mathrm{R\underset{\overset{\|}{O^{\delta-}}}{C^{\delta+}}{-}\ddot{O}{-}\dot{C}H\leftarrow R^{1} \longleftrightarrow R\underset{\overset{\|}{O^{\delta-}}}{C^{\delta+}}{-}\dot{O}{=}CH\leftarrow R^{1}}$$

IIa **IIb**

It is important that, as in the reaction of the *tert*-butylperoxy radical with cyclohexyl acetate, the deactivating effect of an electron-acceptor substituent applies not only to β-CH bonds but also to more distant γ-CH bonds.

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