The Reactivity of C–H Bonds in the Cyclohexyloxy Moiety of Cyclohexyl Acetate toward the *tert*-Butylperoxy Radical

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Abstract—The effect of the functional group on the partial rate constants of the reactions of the *tert*-butylperoxy radical with CH bonds in the cyclohexyloxy moiety of cyclohexyl acetate at 333 K was studied by the Howard–Ingold method. The ester group activates the CH bond at the 1-position and deactivates the CH bonds at the 3-position and, especially, the 2-position. The reactivity of CH bonds at the 4-position is close to the reactivity of CH bonds in cyclohexane.

INTRODUCTION

The esters of secondary alcohols belong to the main group of ester by-products formed in the liquid-phase oxidation of organic compounds with molecular oxygen [1–3]. A considerable number of publications, which were summarized in a monograph [1], a handbook [4], and a review [5], were devoted to the transformation of esters in autoxidation reactions. Nevertheless, the problems of the effect of the functional group on the relative reactivity of CH bonds at various positions of an alkoxy moiety of the molecule are still unclear and poorly studied, especially, in the case of the esters of secondary alcohols. Data on the reaction rates of "standard" peroxy radicals with molecules of the esters of secondary alcohols are available for the reactions of the *tert*-butylperoxy radical ($(CH_3)_3COO^\bullet$) with isopropyl acetate [6] and cyclohexyl acetate [7] and of the cumylperoxy radical ($C_6H_5C(CH_3)_2OO^\bullet$) with the isopropyl esters of propionic and adipic acids [1]. At 303 K, the reactivity of the α-alkoxy CH bond of isopropyl acetate toward the *tert*-butylperoxy radical is three times lower than that of the tertiary CH bond in 2-methylbutane and 16 times higher than that of the secondary CH bond of 2-methylbutane. At 353 K, the overall rate constant of the reaction of the above radical with cyclohexyl acetate is lower than that with cyclohexane by a factor of two [7]. This fact indicates that the functional group has a deactivating effect on the majority of CH bonds in the alkoxy moiety. According to data obtained by Agabekov and coauthors, which were summarized in the monograph [1], at 373 K, the rate constants of the reactions of the cumylperoxy radical with the α-CH bond in an isopropyl moiety of the esters of adipic and propionic acids are higher than that of the reaction with secondary CH bonds in *n*-decane by factors of 3.3 and 100, respectively. It is likely that this considerable difference in the reactivity of the same moiety for the esters of adipic and propionic acids is

associated with not only the effect of multidipole interactions of a peroxy radical with esters [8] but also errors in the calculation of corresponding partial constants. This calculation was performed based on the additivity principle; however, it is likely that in the majority of cases this principle does not hold for esters [3, 9]. There is no data on the interactions of standard peroxy radicals with β-, γ-, and more distant CH bonds of the alkoxy moieties in the molecules of esters of secondary alcohols. However, it is well known that, in cyclododecyl acetate oxidation in the presence of boric acid [10], the yield of bifunctional compounds that correspond to attacks on β- and γ-CH bonds is lower than that in the oxidation of CH bonds at more distant positions.

The aim of this work was to study the effect of the ester group on the reactivity of CH bonds in the cyclohexyloxy moiety of cyclohexyl acetate. Cyclohexyl acetate can serve as a convenient model compound for studying general laws of the oxidative transformations of cyclohexyl esters of mono- and dicarboxylic acids; these esters are formed in considerable amounts during the oxidation of cyclohexane and cyclohexanol [2, 3].

EXPERIMENTAL

Cyclohexyl acetate was prepared according to a well-known procedure by the treatment of cyclohexanol with acetic anhydride in an ethyl acetate medium [11]. Perchloric acid was used as a catalyst. The ester was purified by vacuum rectification in an argon flow. The test compound was of 99.5 ± 0.1% purity according to GLC data, the cyclohexanol content was no higher than 0.01% (GLC), and the cyclohexanone content was lower than 0.005% (spectrophotometric determination as the 2,4-dinitrophenylhydrazone).

tert-Butyl hydroperoxide (TBHP) was synthesized according to the procedure [12]. The compound contained 99.3 ± 0.2% hydroperoxide as determined by iodometry.

Azobisisobutyronitrile (AIBN) was purified by recrystallization from ethanol until the rate of oxidation of a model compound (ethylbenzene) in the presence of AIBN no longer increased.

trans-1,2-Cyclohexanediol was prepared by the treatment of cyclohexene with a mixture of hydrogen peroxide and formic acid according to a well-known procedure [13]. The product had a melting point of 102°C, which is characteristic of this compound [13]. *cis*-1,2-Cyclohexanediol was prepared by the oxidation of cyclohexene with potassium permanganate according to the procedure [14].

The kinetics of gas consumption in the oxidation of cyclohexyl acetate with molecular oxygen and in the cooxidation of cyclohexyl acetate with cyclohexane 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 [9]. In this case, *tert*-butylperoxy radicals were generated in the reaction medium by the Howard–Ingold method. Oxidized cyclohexyl acetate samples were obtained under the same conditions, and these samples were subsequently used for examining the composition of products.

Cyclohexanone in oxidized cyclohexyl acetate was determined by spectrophotometry after derivatization to the 2,4-dinitrophenylhydrazone under conditions that prevented the effect of interference from hydroperoxides on analytical results [15, 16]. Cyclohexanone and cyclohexanol were also determined by GLC [15] with the use of a column (2000 × 3 mm) packed with 5% OV-17 silicone on Chromaton N-AW-Super at 380 K; undecane was used as an internal standard.
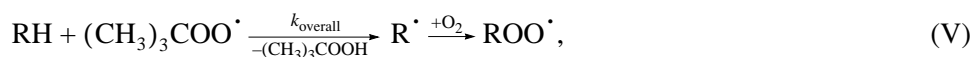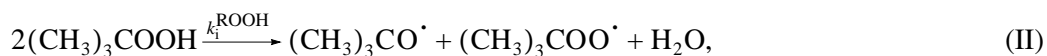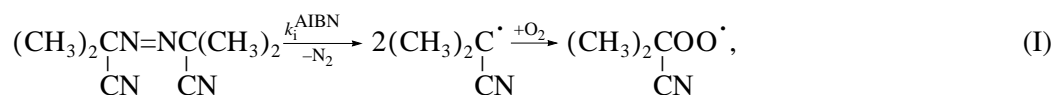
To determine isomeric *cis*- and *trans*-2-, 3-, and 4-acetoxycyclohexyl hydroperoxides, oxidation products were preconcentrated at a reduced pressure. Peroxide compounds were reduced by treatment with a 50% potassium iodide solution in 0.1 M hydrochloric acid, extracted with 1,2-dichloroethane, and dried with anhydrous magnesium sulfate. The extractant was distilled off, 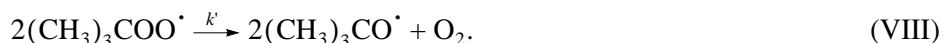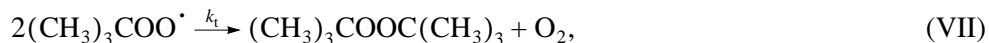and the monoacetates of diols were converted into diacetates by the treatment with an acetic anhydride–pyridine mixture (1 : 1) at 373 K for 2 h [17].

The GLC identification of the diacetates of isomeric diols was performed using both the standard addition method (with the addition of individual products synthesized according to well-known procedures) and the characteristic retention times of identified products on the stationary phases in use [18, 19]. The total concentration of the diacetates of diols was determined on a column (2000 × 3 mm) packed with 5% OV-17 silicone on Chromaton-N-AW-Super at 438 K; dodecyl acetate was used as an internal standard. The following compounds (henceforth, in the order of emergence) were determined on a column (3000 × 3 mm) packed with 20% diethylene glycol succinate on Chromaton-N-AW-HMDS at 458 K: dodecyl acetate (internal standard), *cis*-1,2-diacetoxycyclohexane, *trans*-1,2-diacetoxycyclohexane, *trans*-1,3-diacetoxycyclohexane, *trans*-1,4-diacetoxycyclohexane, and total *cis*-1,3-diacetoxycyclohexane and *cis*-1,4-diacetoxycyclohexane. Finally, the following compounds were determined on a column (1000 × 3 mm) packed with 5% 1,2,3,4,5,6-hexakis(β-cyanoethoxy)hexane on Chromaton N-AW-HMDS at 413 K: dodecyl acetate (internal standard), total *cis*-1,2-diacetoxycyclohexane and *trans*-1,2-diacetoxycyclohexane, total *cis*-1,3-diacetoxycyclohexane and *trans*-1,4-diacetoxycyclohexane, and total *trans*-1,3-diacetoxycyclohexane and *cis*-1,4-diacetoxycyclohexane. The optimum values of $k^{overall}(2k_t)^{-0.5}$ and w_i^{ROOH} were found from w^{O_2}–[AIBN] relationships at a constant value of [TBHP] on a personal computer using a program based on the least-squares technique. The program was developed by Docent I.V. Dvorovenko at the Kuzbass State Technical University.

RESULTS AND DISCUSSION

The radical chain oxidation of cyclohexyl acetate (RH) initiated by AIBN and TBHP under conditions of the Howard–Ingold method can be represented by the following reaction scheme:

$$(CH_3)_2\underset{\underset{CN}{|}}{C}N=N\underset{\underset{CN}{|}}{C}(CH_3)_2 \xrightarrow[-N_2]{k_i^{AIBN}} 2(CH_3)_2\underset{\underset{CN}{|}}{\overset{\bullet}{C}} \xrightarrow{+O_2} (CH_3)_2\underset{\underset{CN}{|}}{C}OO^\bullet, \qquad (I)$$

$$2(CH_3)_3COOH \xrightarrow{k_i^{ROOH}} (CH_3)_3CO^\bullet + (CH_3)_3COO^\bullet + H_2O, \qquad (II)$$

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

$$(CH_3)_3CO^\bullet + (CH_3)_3COOH \longrightarrow (CH_3)_3COH + (CH_3)_3COO^\bullet, \qquad (IV)$$

$$RH + (CH_3)_3COO^\bullet \xrightarrow[-(CH_3)_3COOH]{k_{overall}} R^\bullet \xrightarrow{+O_2} ROO^\bullet, \qquad (V)$$

$$ROO^{\bullet} \xrightarrow[-ROOH]{+(CH_3)_3COOH} (CH_3)_3COO^{\bullet}, \qquad (VI)$$

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

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

Under these conditions, the rate of radical chain oxidation (w_{rc}) is described by the equation [9]

$$w_{rc} = k_{overall}(2k_t)^{-0.5}[RH](w_i^{AIBN} + w_i^{TBHP})^{0.5}, \qquad (1)$$

where $k_{overall}$ is the rate constant of the overall reaction of the *tert*-butylperoxy radical with cyclohexyl acetate; k_t is the rate constant of the colligation of *tert*-butylperoxy radicals with chain termination; and w_i^{AIBN} and w_i^{TBHP} are the rate constants of initiation due to the decomposition of AIBN and TBHP, respectively.

The rate constant $k_{overall}$ is related to the partial rate constants (k^H) of hydrogen abstraction by *tert*-butylperoxy radicals from different positions of the ester and to the numbers (n_i) of hydrogen atoms by the expression

$$k_{overall} = \sum n_i k^H. \qquad (2)$$

In accordance with reactions (I) and (II), w_i^{AIBN} and w_i^{TBHP} are described by the following Eqs. (3) and (4), respectively [9]:

$$w_i^{AIBN} = k_i^{AIBN}[AIBN], \qquad (3)$$

$$w_i^{TBHP} = k_i^{TBHP}[TBHP]^2. \qquad (4)$$

The constant k_i^{AIBN} is related to the rate constant of decomposition of the initiator (k_d^{AIBN}) and to the factor that characterizes radical escape to the bulk (e) by the equation [20]

$$k_i^{AIBN} = 2e k_d^{AIBN}. \qquad (5)$$

The following well-known relations were used for calculating $2k_t$ and k_d^{AIBN} :

$$\log 2k_t = 10.15 - 42.7 \text{ kJ/mol}/2.303RT \text{ [4]}, \qquad (6)$$

$$\log k_d^{AIBN} \\ = 15.0 - 126.2 \text{ kJ/mol}/2.303RT \text{ [20]}, \qquad (7)$$

$2k_t(333 \text{ K}) = (2.90 \pm 0.05) \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$ and $k_i^{AIBN}(333 \text{ K}) = 1.57 \times 10^{-5} \text{ s}^{-1}$ (at $e = 0.6$ [9]).

If 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 (VII) and (VIII), are made, w_{rc} is related to the gas consumption

rate w^{O_2} experimentally measured in the manometric system by the equation [9]

$$w_{rc} = w^{O_2} + 0.5w_i^{AIBN}(k'/k_t - 1) \\ + 0.5w_i^{AIBN}/e + 0.5w_i^{TBHP}(1 + k'/k_t), \qquad (8)$$

where k'/k_t is the ratio between the rate constants of reactions (VII) and (VIII)—the combination of *tert*-butylperoxy radicals with and without chain termination, respectively (the value $k'/k_t(323 \text{ K}) = 8.1$ was used [21]).

An important prerequisite for the correct use of Eqs. (1) and (8) is the completeness of exchange of the peroxy radicals of the oxidized substance and the initiator, as well as of *tert*-butoxy radicals for *tert*-butylperoxy radicals, by reactions (III), (IV), and (VI); this can be accomplished at a reasonably high hydroperoxide concentration. Therefore, at the first stage, we studied the effect of TBHP concentration on the rate of oxygen consumption in cyclohexyl acetate oxidation (333 K, with no solvent) in the presence of 0.002 mol/l AIBN. The $(w^{O_2})^2$–$[TBHP]^2$ plot (Fig. 1) is rectilinear starting from [TBHP] = 0.4 mol/l. At this concentration, the above radicals are almost completely exchanged for the *tert*-butylperoxy radical.

The $k_{overall}(2k_t)^{-0.5}$ parameter was determined from experiments on cyclohexyl acetate oxidation (333 K, with no solvent) at a constant concentration of TBHP (0.5 mol/l) and under changes in the concentration of AIBN within the range 0.0021–0.0084 mol/l. Table 1 summarizes the experimental data and the results of their treatment using Eqs. (1) and (8).
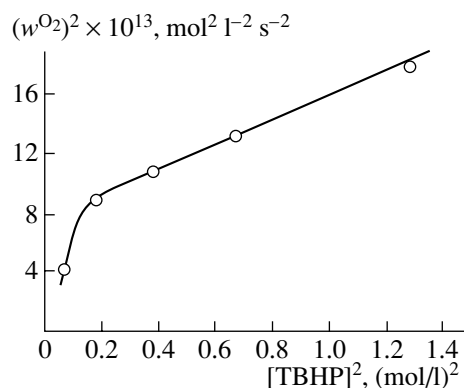

Fig. 1. Rate of oxygen consumption in the initiated oxidation of cyclohexyl acetate as a function of concentration of added *tert*-butyl hydroperoxide (333 K; [AIBN] = 0.002 mol/l).

Table 1. Experimental results on the oxidation of cyclohexyl acetate in the presence of *tert*-butyl hydroperoxide and azobisisobutyronitrile (333 K; [RH] = 6.83 mol/l; [TBHP] = 0.5 mol/l)

$w_i^{AIBN} \times 10^7$, mol l^{-1} s^{-1}	$w_{O_2} \times 10^7$, mol l^{-1} s^{-1}	$w_{rc} \times 10^7$, mol l^{-1} s^{-1}	$w_i^{TBHP} \times 10^7$, mol l^{-1} s^{-1}	v^*	$k_{overall}$, l mol^{-1} s^{-1}
0.40	9.37	8.56	0.10	17.1	0.03
0.80	13.30	11.80	"	13.1	"
1.19	15.70	13.60	"	10.5	0.03
1.58	18.70	16.00	"	9.5	0.03

$* \; v = \dfrac{w_{rc}}{w_i^{AIBN} + w_i^{TBHP}}$ is the chain length.
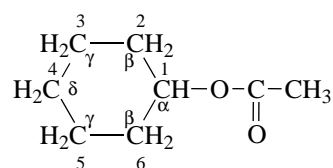
A comparison between the obtained value of $k_{overall}$ and an analogous value for cyclohexane ($k_{overall}^{cyclohexane} = 12k^{H,\,cyclohexane}$; $k_{overall}^{cyclohexane}$ (333 K) = 0.046 l mol^{-1} s^{-1}) calculated by the equation [9]

$$\log k^{H,\,cyclohexane} = 10.4 - 81.7 \text{ kJ/mol}/2.303RT, \quad (9)$$

demonstrates that the cyclohexyl acetate molecule is less reactive toward the *tert*-butylperoxy radical than the cyclohexane molecule by a factor of ~1.5. This fact indicates that a considerable number of CH bonds in the cyclohexyloxy moiety of the test ester are deactivated.
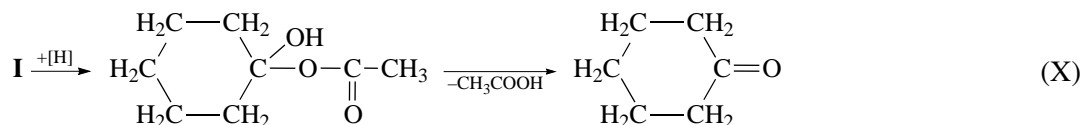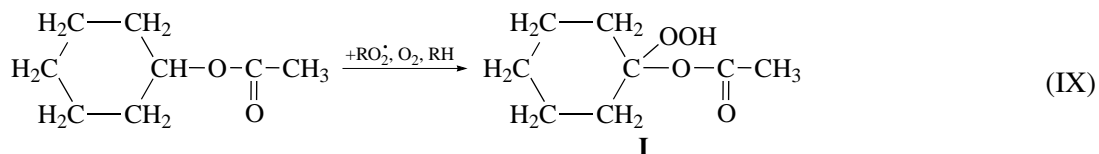
The partial rate constants of the interaction of peroxy radicals with various types of CH bonds in cyclohexyl acetate can be evaluated by studying the composition of its oxidation products. Because the quantitative determination of isomeric hydroperoxides (primary oxidation products) is associated with considerable experimental difficulties, the conversion of

hydroperoxides into stable compounds, for example, by reduction, seems reasonable [17]. The molecular structure of cyclohexyl acetate suggests that its alkoxy moiety 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).
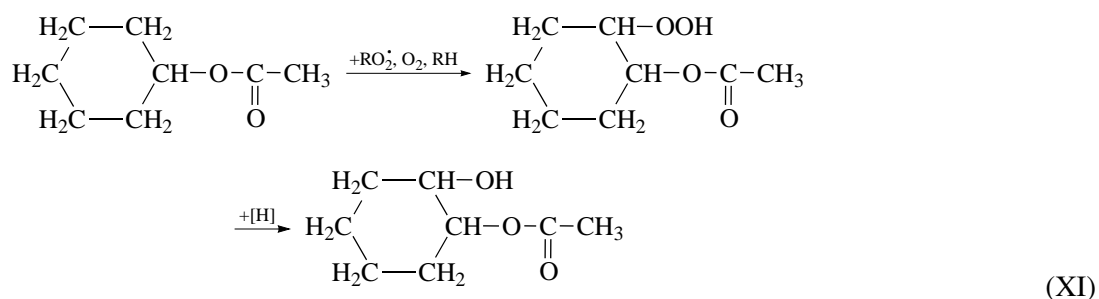

Cyclohexyl acetate oxidation at α-CH bonds results in 1-acetoxycyclohexyl hydroperoxide (**I**).

It is well known [17] that such hydroperoxides are converted into ketones upon reduction as follows:

(IX)

(X)

However, the interaction of the *tert*-butylperoxy radical with the ester at β-, γ-, or δ-CH bonds results in the formation of isomeric 2-, 3-, or 4-acetoxycyclohexyl hydroperoxides, respectively. The reduction of these compounds results in the monoacetates of corresponding diols, for example:

(XI)

Indeed, in a study of the products of cyclohexyl acetate oxidation initiated by AIBN (0.05 mol/l) in the presence of TBHP (1.5 mol/l) at 333 K after the reduction with KI and acetylation, we detected cyclohexanone and *cis*- and *trans*-isomers of 1,2-, 1,3-, and 1,4-diacetoxycyclohexanes (Fig. 2, Table 2).

In this case, cyclohexyl glycolate and the acetates of α-, β-, and γ-ketoalcohols were not detected in the reduced oxidation products. This fact is indicative of the low reactivity of CH bonds in the CH_3 group of the acyl unit. This fact also suggests an insignificant role of the decomposition of isomeric acetoxy hydroperoxides under the experimental conditions and of the conversion of the corresponding peroxy radicals into the acetates of ketoalcohols, for example:
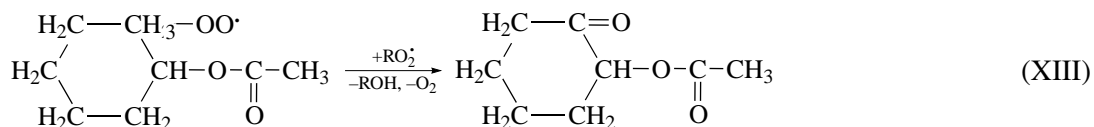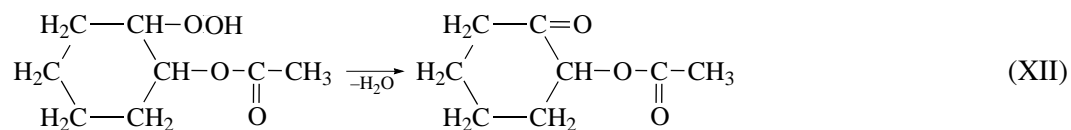
(XII)

(XIII)

Figure 2 demonstrates that under the test conditions the analyte concentrations are linear functions of cyclohexyl acetate conversion. This fact indicates that the products are formed in competing parallel reactions, and k^H can be calculated from $k_{overall}$ and the average yields of products (Table 2).

For a more correct consideration of the effect of the ester group on the reactivity of CH bonds in a cyclo-

Table 2. Composition of the determined products of cyclohexyl acetate oxidation and rate constants of reactions of the *tert*-butylperoxy radical with various types of CH bonds of the cyclohexyloxy moiety (333 K; [RH] = 6.83 mol/l; [TBHP] = 1.5 mol/l; [AIBN] = 0.05 mol/l)

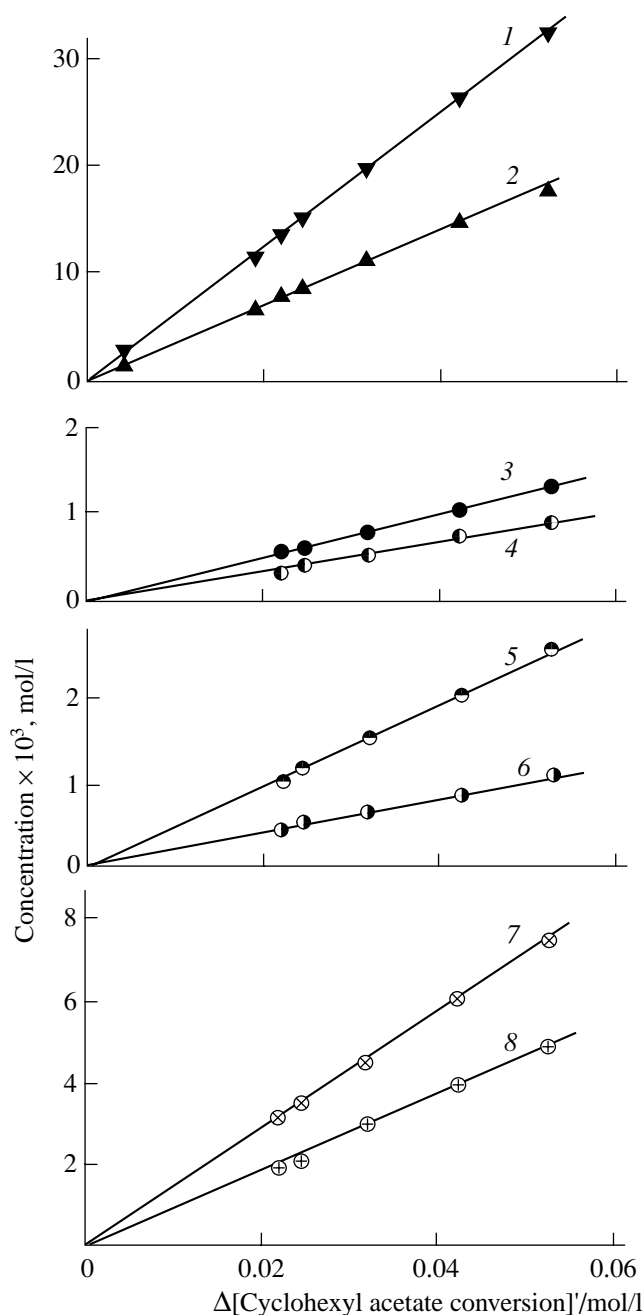| Type of CH bonds	Number of CH bonds	Determined products	Yield, mol %	$k^H \times 10^3$, l mol^{-1} s^{-1}
α-	1	Cyclohexanone	63.0 ± 1.4	18.20 ± 1.50
β-	4	*cis*-1,2-Diacetoxycyclohexane	1.7 ± 0.2	0.31 ± 0.05
		trans-1,2-Diacetoxycyclohexane	2.6 ± 0.2	
γ-	4	*cis*-1,3-Diacetoxycyclohexane	3.3 ± 0.5	0.52 ± 0.07
		trans-1,3-Diacetoxycyclohexane	4.9 ± 0.1	
δ-	2	*cis*-1,4-Diacetoxycyclohexane	15.3 ± 0.5	3.70 ± 0.40
		trans-1,4-Diacetoxycyclohexane	10.2 ± 0.3	

Fig. 2. Accumulation of reaction products (after reduction and acetylation) in the initiated oxidation of cyclohexyl acetate in the presence of AIBN and TBHP as a function of cyclohexyl acetate conversion: (*1*) cyclohexanone; (*2*) *cis*- and *trans*-1,2-, 1,3-, and 1,4-diacetoxycyclohexanes (total concentration); (*3*) *trans*-1,2-diacetoxycyclohexane; (*4*) *cis*-1,2-diacetoxycyclohexane; (*5*) *trans*-1,3-diacetoxycyclohexane; (*6*) *cis*-1,3-diacetoxycyclohexane; (*7*) *cis*-1,4-diacetoxycyclohexane; and (*8*) *trans*-1,4-diacetoxycyclohexane.

hexyl moiety, it seemed reasonable to examine the reactivity of CH bonds in cyclohexane under comparable conditions. Because cyclohexanol is the only product of cyclohexane oxidation under conditions of the

Howard–Ingold method followed by reduction, the method of competing reactions can be used for this purpose. A mixture of cyclohexyl acetate ($[R_1H]$ = 3.91 mol/l) and cyclohexane ($[R_2H]$ = 3.91 mol/l) was oxidized at 333 K with 0.05 mol/l AIBN in the presence of 1.5 mol/l TBHP. After reduction, the mixture oxidized for 16.5 h contained cyclohexanone ($\sim 13.3 \times 10^{-3}$ mol/l), monoacetates of isomeric diols ($\sim 5.1 \times 10^{-3}$ mol/l), and cyclohexanol ($\sim 27 \times 10^{-3}$ mol/l).

The ratio between the overall rate constants of the reactions of the *tert*-butylperoxy radical with cyclohexyl acetate and cyclohexane ($k_{\text{overall}}^{\text{cyclohexyl acetate}} / k_{\text{overall}}^{\text{cyclohexane}}$) was calculated from the above data using Eq. (10) to be equal to 1.47 ± 0.07.

$$k_{\text{overall}}^{\text{cyclohexyl acetate}} / k_{\text{overall}}^{\text{cyclohexane}}$$
$$= \frac{[\text{CHO}][R_2H]}{([\text{CHN}] + [\text{CHDOMA}])[R_1H]}. \qquad (10)$$

The values of $k_{\text{overall}}^{\text{cyclohexane}} = (44.5 \pm 5) \times 10^{-3}$ l mol^{-1} s^{-1} and $k^{\text{H, cyclohexane}} = (3.7 \pm 0.04) \times 10^{-3}$ l mol^{-1} s^{-1} were found from this ratio with the use of $k_{\text{overall}}^{\text{cyclohexyl acetate}}$ ace-tate] (Table 1). The latter value is consistent with $k^{\text{H, cyclohexane}} = 3.8 \times 10^{-3}$ l mol^{-1} s^{-1} calculated by Eq. (9).
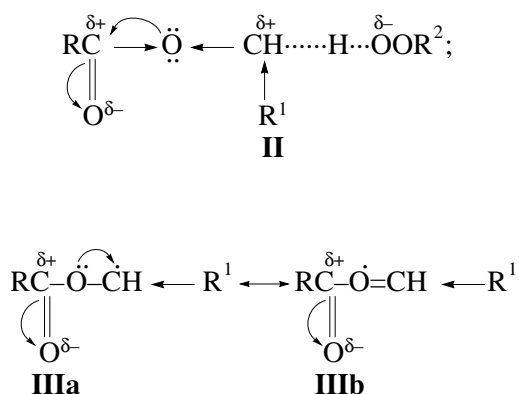
A comparison of $k^{\text{H, cyclohexane}}$ with the partial rate constants of the reactions of the *tert*-butylperoxy radical with CH bonds in the cyclohexyloxy moiety of cyclohexyl acetate (Table 2) demonstrates that the acetyl group increases the reactivity of the CH bond at the 1-position toward the *tert*-butylperoxy radical by a factor of 4.9 and decreases the reactivity of CH bonds at the 2- and 3-positions by factors of 12 and 7.1, respectively. The reactivity of CH bonds at the 4-position remains almost equal to that in cyclohexane.

The oxidation of the alkoxy moiety of an ester molecule is a case of homolytic substitution in a hydrocarbon chain attached to an electron-acceptor substituent RCOO$^-$. Hydrogen abstraction by electrophilic peroxy radicals is the rate-limiting step of this oxidation. In these cases, the reactivity of CH bonds depends on the following three main factors: the electron density at the hydrogen atom of the attacked CH bond, the degree of stabilization of the transition state, and the stability of the resulting carbon-centered radicals [5, 23, 24]. The first factor depends on the polar effect (inductive effect + field effect) of the electron-acceptor substituent, and it is of primary importance for highly reactive radicals such as Cl$^{\cdot}$. Because the polar effect sharply decays, it primarily deactivates α- and β-CH bonds. The second and third factors are activating factors for the reactions of hydrogen abstraction from α-CH bonds of the alkoxy moiety of an ester molecule.

Table 3. Relative reactivity of the CH bonds of butyl acetate and butane in the photochemical chlorination and bromination [24]

Reaction	Substituent X	Reaction conditions	x–CH$_2$–CH$_2$–CH$_2$–CH$_3$			
			α	β	γ	δ
Chlorination	H	Gas phase, 50°C	1.0	3.6	3.6	1.0
	CH$_3$COO–	"	0.1	2.5	4.0	1.0
Bromination	H	Gas phase, 160°C	1.0	80.0	80.0	1.0
	CH$_3$COO–	"	20.0	30.0	70.0	1.0

In accordance with the Hammond principle, transition state **II** for $RO_2^{\cdot}$ radicals, which are less active than the chlorine atom, is closer to the end products [58] and, as with radical **III**, is stabilized by the conjugation

II

IIIa   **IIIb**

In an attack of peroxy radicals on the β-, γ-, and more distant CH bonds of an alkoxy moiety, the ester group cannot exert a stabilizing effect on the transition state and corresponding radicals. Thus, in these cases, the reactivity depends on the deactivating effect of an electron-acceptor substituent [5, 23, 24].

The above consideration is consistent with data on the relative reactivity of CH bonds in butyl acetate and butane in the reactions with electrophilic chlorine and bromine radicals in the course of gas-phase photochemical chlorination and bromination (Table 3).

A comparison of the data given in Table 3 with the results obtained for cyclohexyl acetate (Table 2) indicates that the *tert*-butylperoxy radical exhibits a higher selectivity in the reaction with the CH bonds of the alkoxy moiety of an ester molecule than more reactive Cl$^{\cdot}$ and Br$^{\cdot}$ radicals.

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