ISSN 0023-1584, Kinetics and Catalysis, 2012, Vol. 53, No. 2, pp. 155–161. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © Yu.V. Nepomnyashchikh, S.V. Puchkov, A.L. Perkel', O.I. Arnatskaya, 2012, published in Kinetika i Kataliz, 2012, Vol. 53, No. 2, pp. 163–169.

Reactivity of the C–H Bonds of Methyl Hexanoate toward the *tert*-Butylperoxy Radical

Yu. V. Nepomnyashchikh, S. V. Puchkov, A. L. Perkel'*, and O. I. Arnatskaya
Faculty of Chemical Technology, Kuzbass State Technical University, Kemerovo, 650000 Russia
** e-mail: perkel2@rambler.ru*

Received January 21, 2011

Abstract—The kinetics of oxygen uptake and the kinetics of accumulation of methyl hexanoate oxidation products in the presence of *tert*-butyl hydroperoxide have been investigated to determine the partial rate constants for the interaction of the *tert*-butylperoxy radical with C–H bonds of the ester at 373 K. The ester group deactivates the C–H bonds in the 2- and 3-positions and does not deactivate the same bonds in the 5-position, which are similar in reactivity to the methylenic C–H bonds of hydrocarbons. The C–H bonds of the methoxyl group of methyl hexanoate are substantially more reactive than the C–H bonds of the methyl group.

DOI: 10.1134/S0023158412020085

Carboxylic acid esters resulting from the liquid-phase oxidation of hydrocarbons and their oxygen derivatives [1, 2] can enter into free-radical chain processes involving both the acyl and alkoxyl moieties [1, 3, 4]. The electron-withdrawing functional group affects the mechanisms of formation and transformation of the intermediates (peroxyl radicals and hydroperoxides) and also the reactivity of the C–H bonds nearest to this functional group [1, 3, 4]. It was shown for the reactions of *tert*-butylperoxy radicals with cyclohexyl acetate at 333 K [5] that the ester group activates the α-C–H bonds and substantially deactivates the β- and γ-C–H bonds of the alkoxyl moiety with respect to the peroxyl radicals. Although there have been many works devoted to ester oxidations (see monograph [1] and review [3]), the influence of the functional group on the reactivity of various types of C–H bonds in the acyl moiety remains unclear. The discovery of a new mechanism and new products of the oxidation of carbonyl-containing compounds at the β-C–H bonds [6–8] makes disputable the results of an earlier study [9] in which the relative reactivity of the C–H bonds of methyl hexanoate were determined from the composition of the alcohols that resulted from the reduction of the oxidation products of this ester with lithium aluminum hydride at 413 K.

The purpose of the present work is to determine, using methyl hexanoate as an example, the reactivity of the main types of C–H bonds in the acyl moiety of the ester toward the *tert*-butylperoxy radical at 373 K.

EXPERIMENTAL

Methyl hexanoate (analytical grade) was purified by vacuum distillation in flowing argon. According to GLC data, the product contained 99.5 ± 0.1% methyl hexanoate.

tert-Butyl hydroperoxide (TBHP) was synthesized and purified by a standard procedure [10]. As determined by iodometry, the synthesized compound contained at least 99.3 ± 0.2% hydroperoxide. Peroxide compounds were quantified by a colorimetric method using a reagent containing Fe^{2+} ions and *N*,*N*-dimethyl-*para*-phenylenediamine [11].

The reference substances necessary for gas chromatographic identification of methyl hexanoate oxidation products were synthesized using standard methods. 2-Hydroxyhexanoic acid was obtained by the hydrolysis of 2-bromohexanoic acid [12]. According to GLC data, the 2-hydroxyhexanoic acid content of the product was 99.3 ± 0.2%. Methyl 6-hydroxyhexanoate was obtained by heating ε-caprolactone with water in a sealed tube followed by the esterification of the carboxyl groups with diazomethane. 2-Hexenic acid was synthesized by the Knoevenagel condensation of butanal and propanedioic acid in the presence of pyridine [13] and was purified by consecutive recrystallization from water and an ethanol–water (1 : 1) mixture. The melting point of the product was 32°C (reference value: 32–33°C [13]). 2,3-Epoxyhexanoic acid was obtained by treating 2-hexenic acid with a 30% aqueous solution of hydrogen peroxide in the presence of Na_2WO_4 [14]. The purity of the resulting acid, according to the GLC analysis of its methyl ester, was at least 95.0 ± 0.5%. 2,3-Dihydroxyhexanoic acid was synthesized by the oxidation of 2-hexenic acid with potassium permanganate [15]. According to GLC data, the purity of the product was 99.3 ± 0.2%.

The kinetics of gas uptake in methyl hexanoate oxidation with dioxygen was studied by the Howard–

Ingold method using a manometric setup. The experiments were carried out under kinetically controlled dioxygen uptake conditions. The mixed initiation method was used, in which cumyl peroxide (CP) and *tert*-butyl hydroperoxide served as initiators. The kinetics of the accumulation of methyl hexanoate oxidation products was studied by analyzing oxidized substrate samples.

Prior to performing GLC analysis, isomeric methyl 2-, methyl 4-, methyl 5-, and methyl 6-hydroperoxyhexanoates, as well as methyl 2,3-dihydroperoxyhexanoate, were converted to the corresponding hydroxyl derivatives by treating them with triphenylphosphine [16, 17]. Thereafter, methyl 2-, methyl 4-, and methyl 5-hydroperoxyhexanoates were analyzed on a column packed with 15% silicone rubber Carbowax-6000 on Chromatone N-AW-DMCS using methyl tetradecanoate as the internal standard. Methyl 6-hydroxyhexanoate was determined as methyl 6-acetyloxyhexanoate (after its acetylation with a pyridine–acetic anhydride (1 : 1) mixture) on a column packed with 5% silicone rubber SE-30 on Chromatone N-AW using dimethyl decanedioate as the internal standard. Methyl 2,3-dihydroxyhexanoate was analyzed on a column packed with 5% silicone OV-17 on Chromatone N-AW-super (dimethyl decandioate as the internal standard).

Prior to performing GLC analysis, methyl 2-hexenoate was converted to methyl 2,3-dibromohexanoate via a standard procedure [18]. A column packed with Sp-2100 on Chromatone N-AW-super was used in the analysis (methyl dodecanoate as the internal standard).

Methyl 2,3-epoxyhexanoate was determined in triphenylphosphine-unreduced aliquots of the sample on a column packed with 15% silicone rubber Carbowax-6000 on Chromatone N-AW-DMCS (methyl tetradecanoate as the internal standard).

Prior to GLC determination, free hexanoic acid was extracted from oxidized methyl hexanoate by treating an aliquot of the sample with the AB-17P anion-exchange resin in HCO_3^- form under static exchange conditions [17, 19].Thereafter, the resin was thoroughly washed with hexane to remove methyl hexanoate (with GLC monitoring), and the acid was converted into methyl hexanoate directly on the resin by treating it with a 10% CH_3I solution in hexane [19]. After concentrating in a vacuum created by a water-jet pump, the resulting methyl hexanoate was analyzed on a packed column packed with the 20% diethylene glycol succinate phase on Chromatone N-AW-HMDS (methyl octanoate as the internal standard).

The optimal values of kinetic parameters were determined from the dependence of the O_2 uptake rate on [CP] at a constant [TBHP] value using a least-squares based program. The objective function was optimized by the Fletcher–Reeves conjugate gradient method.

RESULTS AND DISCUSSION

In order to calculate the partial rate constants for the interaction of the *tert*-butylperoxy radical with the C–H bonds of methyl hexanoate, it was necessary to determine the empirical rate constant for the reaction between the *tert*-butylperoxy radical and the ester under Howard–Ingold method conditions and to identify the products so as to determine the direction of oxidation.

The radical chain oxidation of methyl hexanoate (RH) under conditions of mixed initiation with CP and TBHP can be presented as follows:

$$C_6H_5C(CH_3)_2OOC(CH_3)_2C_6H \xrightarrow{k_{d,CP}} 2C_6H_5C(CH_3)_2O^{\bullet}, \tag{I}$$

$$2(CH_3)_3COOH \xrightarrow{w_{i,TBHP}} (CH_3)_3CO^{\bullet} + (CH_3)_3COO^{\bullet} + H_2O; \tag{II}$$

$$C_6H_5C(CH_3)_2O^{\bullet} + (CH_3)_3COOH \rightarrow (CH_3)_3COO^{\bullet} + C_6H_5C(CH_3)_2OH; \tag{III}$$

$$(CH_3)_3CO^{\bullet} + (CH_3)_3COOH \rightarrow (CH_3)_3COH + (CH_3)_3COO^{\bullet}; \tag{IV}$$

$$RH + (CH_3)_3COO^{\bullet} \xrightarrow[-(CH_3)_3COOH]{k_{em}} R^{\bullet} \xrightarrow{+O_2} ROO^{\bullet}; \tag{V}$$

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

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

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

where k_d is the rate constant of the decomposition of the initiator, $w_{i,TBHP}$ is the initiation rate due to the decomposition of TBHP (mol L^{-1} s^{-1}), k_{em} is the empirical rate constant of the reaction between the *tert*-butylperoxy radical and methyl hexanoate (L mol^{-1} s^{-1}), k_t and k' are the rate constants of the recombination of *tert*-butylperoxy radicals with and without chain termination, respectively (L mol^{-1} s^{-1}). At 323 K, $k_t/k' = 8.1$ [20].

Under these conditions, the rate of radical chain oxidation, w_{rc}, is given by the equation

$$w_{rc} = k_{em}(2k_t)^{-0.5}[RH](w_{i,TBHP} + w_{i,CP})^{0.5}, \tag{1}$$

where $w_{i,CP}$ is the initiation rate due to the decomposition of CP (mol L^{-1} s^{-1}).

The constant k_{em} can be expressed in terms of the partial rate constants for the abstraction of hydrogen atoms from different positions in the methyl hexanoate molecule by the *tert*-butylperoxy radical (k^H) and in terms of the number of these atoms (n_i):

$$k_{em} = \Sigma n_i k^H. \tag{2}$$

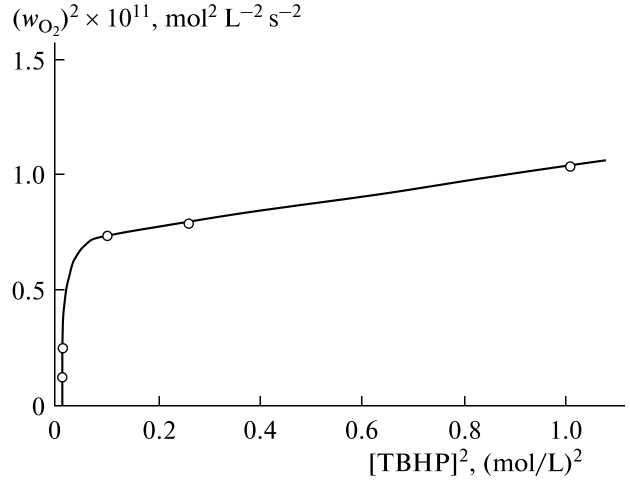


Fig. 1. Oxygen uptake rate in the oxidation of methyl hexanoate initiated by cumyl peroxide and *tert*-butyl hydroperoxide versus the *tert*-butyl hydroperoxide concentration (373 K, [RH] = 6.46 mol/L, [CP] = 0.006 mol/L).

According to reaction (I), $w_{i,CP}$ is described by the equation

$$w_{i,CP} = k_{i,CP}[CP]. \tag{3}$$

The constant $k_{i,CP}$ is related to the initiator decomposition rate constant $k_{d,CP}$ and to the coefficient of radical escape to the bulk, e, by the following equation [21]:

$$k_{i,CP} = 2ek_{d,CP}. \tag{4}$$

A known relationship [22] was used in the calculation of $2k_t$:

$$\log 2k_t = 10.15 - 42.7/2.303RT, \tag{5}$$

where the factor 42.7 has dimensions of kJ/mol. Hence, at 373 K, $2k_t = 14.734 \times 10^3$ L mol^{-1} s^{-1}.

Several temperature dependences of $k_{d,CP}$ have been published [21, 23, 24]. Use of these dependences leads to calculated initiation rates differing by one order of magnitude. The value $w_{i,CP} = 1.78 \times 10^{-8}$ mol L^{-1} s^{-1} was obtained by determining the rate of inhibitor (ionol) consumption in the CP-initiated oxidation of methyl hexanoate (373 K, [RH] = 6.46 mol/L, [CP] = 0.006 mol/L). This value agrees well with $w_{i,CP} = 1.77 \times 10^{-8}$ mol L^{-1} s^{-1} value, which was calculated using the following relationship [23]:

$$\log k_{d,CP} = 14.63 - 144.3/2.303RT, \tag{6}$$

where the factor 144.3 has dimensions of kJ/mol. At 373 K and $e = 0.6$, $k_{i,CP} = 2.94 \times 10^{-6}$ s^{-1} [23].

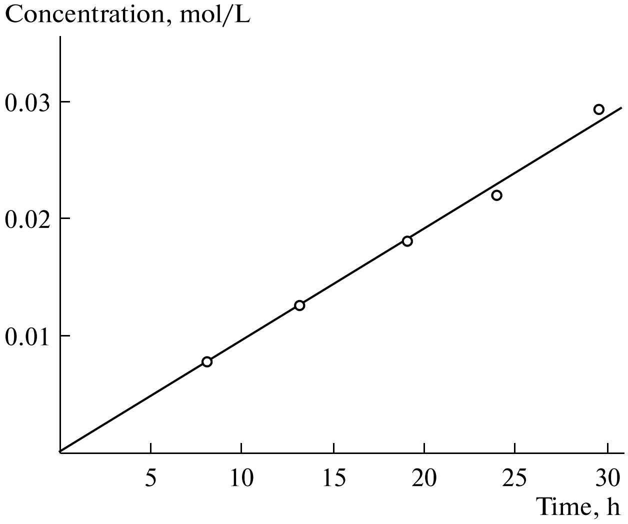


Fig. 2. Kinetics of the accumulation of the sum of the peroxide compounds resulting from methyl hexanoate oxidation initiated by cumyl peroxide ([CP] = 0.006 mol/L) at 373 K ([RH] = 6.46 mol/L).

If corrections for dioxygen evolution in reactions (VII) and (VIII) are applied [21], the constant w_{rc} will be related to the gas uptake rate w_{O_2} by the equation

$$\begin{aligned} w_{O_2} &= k_{em}(2k_t)^{-0.5}[RH](w_{i,TBHP} + w_{i,CP})^{0.5} \\ &\quad - 0.5(w_{i,TBHP} + w_{i,CP})(1 + k'/k_t). \end{aligned} \tag{7}$$

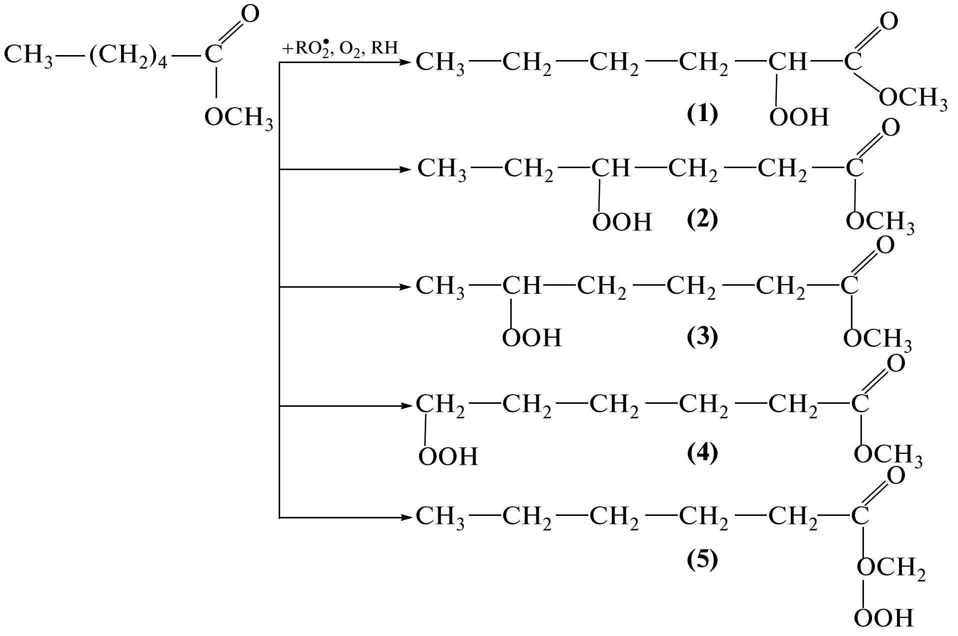
The conditions for correct application of Eqs. (1) and (7) are the complete replacement of the peroxyl radicals of the compound being oxidized, initiator, and *tert*-butyloxy radicals by *tert*-butylperoxy radicals via reactions (III), (IV), and (VI) and the stability of the peroxide products of the oxidized compound (the absence of degenerate branching). It is known that a rather high *tert*-butyl hydroperoxide concentration is necessary to fulfill the first condition. For this reason, we initially studied the influence of the TBHP concentration on the oxygen uptake rate in the oxidation of methyl hexanoate (373 K, [RH] = 6.46 mol/L, [CP] = 0.006 mol/L).

The dependence of $(w_{O_2})^2$ on [THBP]^2 (Fig. 1) is linear starting at [TBHP] = 0.35 mol/L, when the aforementioned radicals are almost completely exchanged for *tert*-butylperoxy radicals.

The kinetics of accumulation of all peroxide compounds formed under the conditions of the CP-initiated oxidation of methyl hexanoate (373 K, [RH] = 6.46 mol/L, [CP] = 0.006 mol/L) was studied to estimate the stability of the peroxide compounds of oxidized methyl hexanoate. It can be seen from Fig. 2 that the concentration of the peroxide compounds depends linearly on the reaction time and, hence, the peroxide products resulting from methyl hexanoate oxidation at 373 K do not decompose at any noticeable rate.

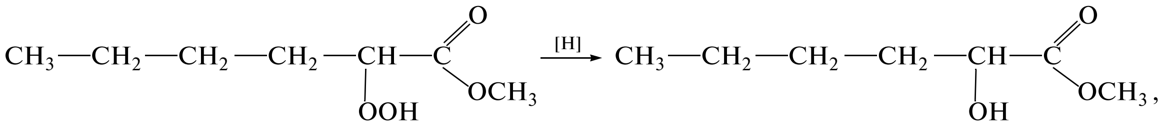
The parameter $k_{em}(2k_t)^{-0.5}$, which is necessary for calculation of the empirical rate constant for the reaction between the *tert*-butylperoxy radical and methyl hexanoate, was determined from the results of experiments on methyl hexanoate oxidation (373 K, [RH] = 6.46 mol/L, [TBHP] = 0.5 mol/L) at CP concentrations varied between 0.001 and 0.006 mol/L. The results of these experiments and the results of data fitting to Eqs. (1) and (7) are presented in Table 1.

The composition of the oxidation products should be known for estimation of the partial rate constants for the interaction of the *tert*-butylperoxy radical with different types of C–H bonds of methyl hexanoate. A methyl hexanoate molecule has six types of C–H bonds (five types in the acyl moiety and one in the alkoxyl moiety). The interaction of the *tert*-butylperoxy radical with the α-, γ-, δ-, and ε-C–H bonds of the acyl moiety of the ester and with the C–H bond of the alkoxyl moiety yields hydroperoxides **1**–**5**:



(IX)

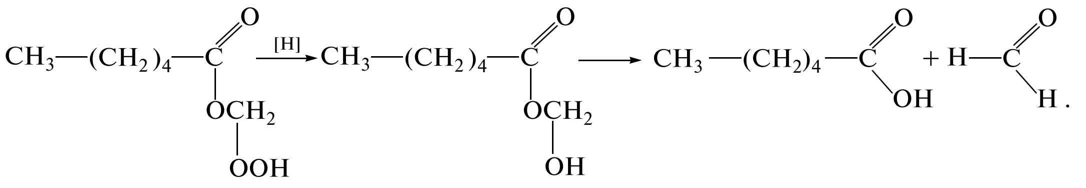
The reduction of products **1**–**4** with triphenylphosphine yields the corresponding hydroxy esters, for example,



$$CH_3-CH_2-CH_2-CH_2-CH(OOH)-C(=O)OCH_3 \xrightarrow{[H]} CH_3-CH_2-CH_2-CH_2-CH(OH)-C(=O)OCH_3,$$

(X)

The reduction of product **5** results in the formation of hexanoic acid and formaldehyde:



$$CH_3-(CH_2)_4-C(=O)-OCH_2-OOH \xrightarrow{[H]} CH_3-(CH_2)_4-C(=O)-OCH_2-OH \longrightarrow CH_3-(CH_2)_4-C(=O)OH + H-C(=O)H.$$

(XI)

It has recently been demonstrated that the oxidation of carbonyl-containing compounds (including esters) at the β-C–H bonds yields α,β-unsaturated compounds [6–8, 25] and their oxides [7, 25]. The oxidation of methyl hexanoate via these mechanisms should result in the formation of methyl 2-hexenoate and methyl 2,3-epoxyhexanoate (routes **a** and **b** in the scheme presented below). The observation of the precursor of these compounds, namely, carbon-centered radical **A** [6–8, 25] suggests the possibility of its transformation (via interaction with oxygen and the substrate) into methyl 2,3-dihydroperoxyhexanoate. The reduction of the latter gives methyl 2,3-dihydroxyhexanoate (route **c**):

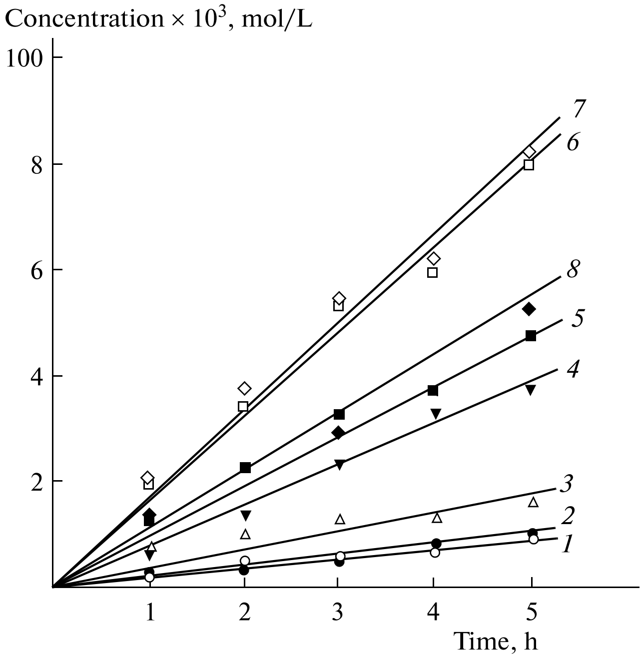
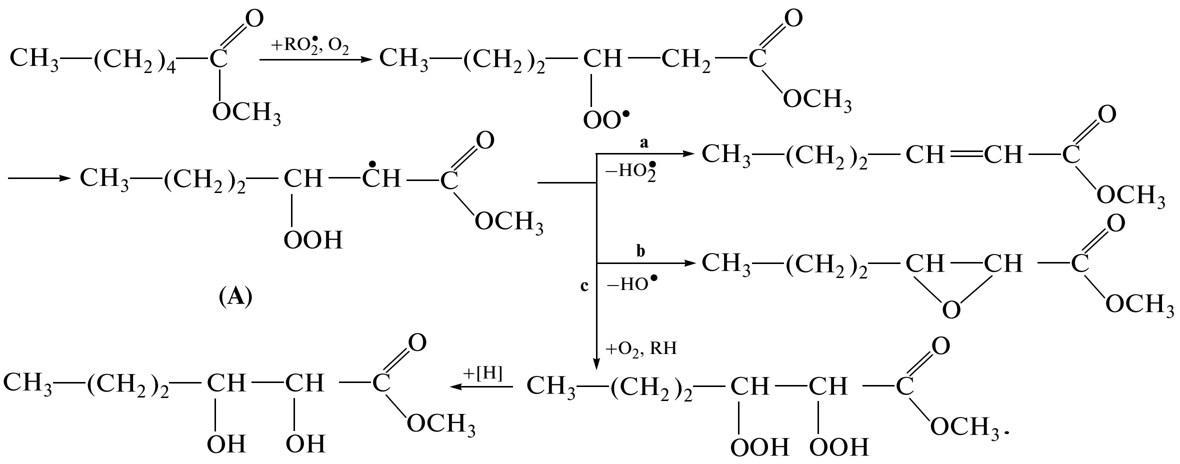


Fig. 3. Kinetics of the accumulation of the products of the CP-initiated oxidation of methyl hexanoate: (*1*) methyl 2,3-dihydroxyhexanoate, (*2*) methyl 6-hydroxyhexanoate, (*3*) methyl 2,3-epoxyhexanoate, (*4*) methyl 2-hexenoate, (*5*) methyl 2-hydroxyhexanoate, (*6*) methyl 4-hydroxyhexanoate, (*7*) methyl 5-hydroxyhexanoate, and (*8*) hexanoic acid. Reaction conditions: 373 K, [RH] = 6.46 mol/L, [CP] = 0.006 mol/L, [TBHP] = 0.5 mol/L.



(XII)

The study of the composition of the products of the CP-initiated oxidation of methyl caproate at 373 K in the presence of RH (6.46 mol/L), TBHP (0.5 mol/L), and CP (0.006 mol/L) after their reduction with triphenylphosphine indeed revealed the presence of the above compounds (Fig. 3). It can be seen from Fig. 3 that, under the conditions examined, the concentrations of all products depend linearly on the reaction time. This means that these products form via competing parallel reactions, making it possible to calculate k^H (Table 2) provided that k_{em} and the average product accumulation rates are known.

The data listed in Table 2 show that k^H for the methylenic α-C–H bonds of the acyl moiety of the methyl hexanoate molecule is almost 1.7 times lower than $k^H = 14.0 \times 10^{-2}$ L mol^{-1} s^{-1} for the δ-C–H bond. The latter value is likely close to k^H for the reactions of the methylenic C–H bonds of saturated hydrocarbons with the *tert*-butylperoxy radical. The values of k^H at 373 K are known for the secondary C–H bonds of cyclohexane (11×10^{-2} L mol^{-1} s^{-1} [26]), methylcyclohexane (15.5×10^{-2} L mol^{-1} s^{-1} for the 3-position and 6.5×10^{-2} L mol^{-1} s^{-1} in the 2-position [26]), and tridecane (9.5×10^{-2} L mol^{-1} s^{-1} [27]). They are close

Table 1. Influence of the CP concentration on the oxygen uptake rate in methyl hexanoate oxidation

[CP], mol/L	$w_{i,CP} \times 10^8$, mol L^{-1} s^{-1}	$w_{O_2} \times 10^6$, mol L^{-1} s^{-1}	$w_{i,TBHP} \times 10^8$, mol L^{-1} s^{-1}	$k_{em}(2k_t)^{-0.5} \times 10^3$, $L^{0.5}$ $mol^{-0.5}$ $s^{-0.5}$	k_{em}, L mol^{-1} s^{-1}	k'/k_t
0.001	0.29	2.10 ± 0.25	1.76	2.48	1.18	15.5
0.002	0.59	2.22 ± 0.17				
0.003	0.88	2.34 ± 0.32				
0.004	1.18	2.58 ± 0.16				
0.006	1.77	2.80 ± 0.24				

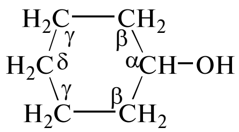
Note: Reaction conditions: 373 K, [RH] = 6.46 mol/L, [TBHP] = 0.5 mol/L.

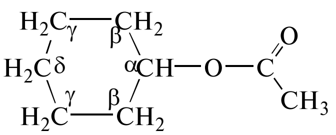
Table 2. Partial oxidation rate constants k^H and the relative reactivities of different types of C–H bonds in methyl hexanoate toward the *tert*-butylperoxy radical

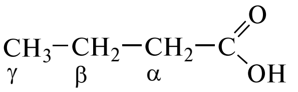
Type of bond	Number of bonds	Product accumulation rate $w \times 10^7$, mol L^{-1} s^{-1}	$k^H \times 10^2$, L mol^{-1} s^{-1}	k^{H_i}/k^{H_z}	
				experiment	data from [9]
Alkoxyl	3	2.8 ± 0.4	6.6 ± 0.9	5.5	–
α	2	2.5 ± 0.5	8.3 ± 1.6	6.9	6.9
β	2	3.4 ± 0.4	11.4 ± 1.3	9.5	2.4
γ	2	4.1 ± 0.7	13.8 ± 2.3	11.5	26.4
δ	2	4.2 ± 0.8	14.0 ± 2.7	11.7	18.3
ε	3	0.52 ± 0.08	1.2 ± 0.2	1.0	1.0

Note: Reaction conditions: 373 K, [RH] = 6.46 mol/L, [CP] = 0.006 mol/L, [TBHP] = 0.5 mol/L.

to the value of k^H obtained for the δ-C–H bond of methyl hexanoate. The bonds in the β-position also have a lower reactivity than the methylenic C–H bonds (Table 2). At the same time, k^H for the methoxyl group is considerably higher than that for the methyl group (Table 2). The influence of electron-withdrawing functional groups on the reactivity of the C–H bonds in the α- and β-positions was observed earlier for the oxidation of cyclohexanol [28], cyclohexyl acetate [5], and butanoic acid [25]:

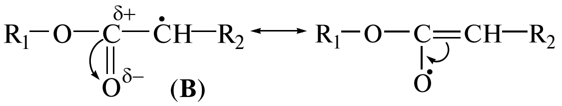


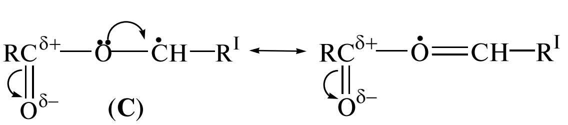




δ	γ	β	α	δ	γ	β	α	γ	β	α
1.0	0.087	0.068	110.5	1.0	0.21	0.087	5.0	1.0	7.4	5.0

All of the experimental data obtained can be explained in terms of the dual effect of electron-withdrawing functional groups on the interaction of the C–H bonds with electrophilic peroxyl radicals [3, 5, 25, 28]. On the one hand, the polar effect (inductive effect + field effect) of the electron-withdrawing functional group decreases the electron density on the hydrogen atom of the attacked C–H bond, thus lowering the probability of interaction with electrophilic peroxy radicals [3]. Naturally, this deactivating effect of the electron-withdrawing functional groups weakens on passing from the α-position to the β- and, particularly, γ-position. On the other hand, electron-withdrawing oxygen-containing groups, due to the conjugation effect, can stabilize the transition state, which is likely closer to the carbon-centered radicals (**B** and **C**). Possibly, the ester group exerts this stabilizing effect on the α-position of both the acyl and alkoxyl moieties of the ester molecule:


(B)


(C)

The reactivity of the C–H bonds in both α positions of the ester molecule is determined by the interplay of the two opposite electronic effects [3]. The conjugation effect cannot stabilize the β- or γ-centered radical, and, hence, only the former (deactivating) affect can alter the reactivity of the C–H bonds in these positions.

The data presented in Table 2 also indicates that the relative reactivity of the β-C–H bonds of methyl hexanoate is substantially higher than was assumed earlier [9]. This is explained by the fact that the products resulting from methyl hexanoate oxidation at the β-C–H bonds were determined more thoroughly in this study.

REFERENCES

1. Denisov, E.T., Mitskevich, N.I., and Agabekov, B.E., *Mekhanizm zhidkofaznogo okisleniya kislorod-soderzhashchikh soedinenii* (Mechanism of the Liquid-Phase Oxidation of Oxygen-Containing Compounds), Minsk: Nauka i tekhnika, 1975.
2. Perkel', A.L., Voronina, S.G., and Freidin, B.G., *Usp. Khim.*, 1994, vol. 63, no. 9, p. 793.
3. Perkel', A.L. and Voronina, S.G., *Russ. J. Appl. Chem.*, 1999, vol. 72, no. 9, p. 1487.
4. Martem'yanov, V.S., *Neftekhimiya*, 1986, vol. 26, no. 6, p. 753.
5. Puchkov, S.V., Perkel', A.L., and Buneeva, E.I., *Kinet. Catal.,* 2001, vol. 42, no. 6, p. 751.
6. Nepomnyashchikh, Yu.V., Nosacheva, I.M., and Perkel', A.L., *Kinet. Catal.*, 2004, vol. 45, no. 6, p. 768.
7. Nepomnyashchikh, Yu.V., Puchkov, S.V., Abdulova, O.V., and Perkel', A.L., *Kinet. Katal.,* 2009, vol. 50, no. 5, p. 609.
8. Gail, S. and Dagaut, P., *Energy Fuels*, 2008, no. 22, p. 1469.
9. Pritzkow, W. and Voerckel, V., *Oxid. Commun.*, 1983, no. 4, p. 223.
10. Karnozhitskii, V., *Organicheskie perekisi* (Organic Peroxides), Moscow: Inostrannaya Literatura, 1961.
11. Perkel', A.L., Voronina, S.G., and Perkel', R.L., *Zh. Anal. Khim.,* 1991, vol. 46, no. 11, p. 2283.
12. *Organisch-chemische Experimentierkunst*, von Hilgetag, G. and Martini, A., Eds., Leipzig: Barth, 1964.
13. *Organikum: Organisch-chemisches Grundpraktikum*, Berlin: Wissenschaften, 1976.
14. Payne, G.B. and Williams, P.H., *Org. Chem.*, 1959, no. 24, p. 54.
15. *Die Methoden der organischen Chemie*, Houben, J., Ed., Leipzig: Thieme, 1949.
16. Hendry, D.G., Gould, C.W., Schuetzle, D., Syz, M.G., and Mayo, F.R., *J. Org. Chem.*, 1976, vol. 41, no. 1, p. 1.
17. Perkel', A.L., Freidin, B.G., and Voronina, S.G., *Zh. Anal. Khim.*, 1993, vol. 48, no. 10, p. 1607.
18. Borkina, G.G., Nepomnyashchikh, Yu.V., and Perkel', A.L., *J. Anal. Chem.*, 2009, vol. 64, no. 11, p. 1120.
19. Perkel', R.L., Melamud, N.L., and Pylina, S.V., *Tr. Vses. NII Zhirov,* 1973, no. 30, p. 49.
20. Mill, T. and Hendry, D.G., *Comprehensive Chemical Kinetics*, vol. 16: *Liquid-Phase Oxidation*, Bamford C.N. and Tipper C.F.H., Eds., Amsterdam: Elsevier, 1980.
21. Denisov, E.T. and Kovalev, G.I., *Okislenie i stabilizatsiya reaktivnykh topliv* (Oxidation and Stabilization of Jet Fuels), Moscow: Khimiya, 1983.
22. *Landolt–Burnstein Lahlwerte und Funktionen aus Natur-wissenschaften und Technik*, Neue Serie, Gruppe II, Berlin: Springer, 1984, vol. 13.
23. Antonovskii, V.L. and Khursan, S.L., *Fizicheskaya khimiya organicheskikh peroksidov* (Physical Chemistry of Organic Peroxides), Moscow: Akademkniga, 2003.
24. Denisov, E.T., *Konstanty skorosti gomoliticheskikh zhidkofaznykh reaktsii* (Rate Constants of Homolytic Liquid-Phase Reactions), Moscow: Nauka, 1971.
25. Nepomnyashchikh, Yu.V., *Extended Abstract of Cand. Sci. (Chem) Dissertation*, Kemerovo: Kemerovo State Univ., 2009.
26. Chenier, J.H.B., Tong, S.B., and Howard, J.A., *Can. J. Chem.*, 1978, vol. 56, no. 24, p. 3047.
27. Korcek, S., Chenier, J.H.B., Howard, J.A., and Ingold, K.U., *Can. J. Chem.*, 1972, vol. 50, no. 14, p. 2285.
28. Puchkov, S.V., Buneeva, E.I., and Perkel', A.L., *Kinet. Catal.,* 2002, vol. 43, no. 6, p. 756.