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Kinetics and Mechanism of the Liquid-Phase Oxidation of *n*-Carboxylic Acids

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Abstract—Short reaction chains participate in the oxidation of C_3–C_6, C_8, C_{10}, and C_{12} *n*-carboxylic acids. The quadratic-law recombination of peroxy radicals occurs both without and with chain termination. The ratio of the rate constants of these reactions increases to $k'/k_t = 4.5$ on passing from propanoic acid to pentanoic acid, and then it decreases almost to zero for dodecanoic acid. The anomalous variation of the k'/k_t ratio is explained by the fact that the radicals resulting from carboxylic acid oxidation at the CH bonds nearest to the functional group make different contributions to the recombination process, depending on the carbon chain length. The cross recombination of secondary hydrocarbon peroxy radicals with the $HO_2^{\bullet}$ radicals resulting from the oxidation of carboxylic acids at the β-C–H bonds proceeds without chain termination.

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INTRODUCTION

Aliphatic carboxylic acids result from the liquid-phase oxidation of paraffinic hydrocarbons by molecular oxygen [1–3]. Naturally, at deep substrate conversions, these compounds can be involved in radical chain process. Long-chain aliphatic carboxylic acids can be oxidized to dicarboxylic acids [1, 2, 4]. It was believed earlier that the oxidation of carboxylic acids at the reactive methylene C–H bonds proceeds in the same way as oxidation at the corresponding bonds in hydrocarbons [1, 2]. Nevertheless, the carboxyl group can influence the reactivity of the C–H bonds in the α- and β-positions, although the result of this influence is ambiguous: there is evidence of some increase [2] and a substantial decrease in their reactivity [2, 5]. It could be assumed that the carboxyl group affects both the reactivity of the nearest C–H bonds and also the mechanisms of the conversion of peroxy radicals and hydroperoxides. Indeed, it was shown [6] that the oxidation of butanoic acid at the β-C–H bonds yields the $HO_2^{\bullet}$ radical and 2-butenoic acid, not 3-hydroxyperoxybutanoic acid, contrary to the expectations. The change in the reaction mechanism and composition of the peroxy radicals should affect the kinetics of radical chain oxidation, especially the oxidation of short-chain carboxylic acids. For these acids, the contribution from the β-C–H bond oxidation route is substantially larger than the same contribution for long-chain acids.

The purpose of this work is to refine the kinetics and mechanism of the liquid-phase oxidation of *n*-carboxylic acids and to estimate the effect of the carbon chain length on this reaction. It is expected that these data will provide a better understanding of the processes occurring at the later stages of paraffinic hydrocarbon oxidation.

EXPERIMENTAL

Prior to oxidation, propanoic, butanoic, pentanoic, and dodecanoic acids (high-purity grade), as well as octanoic and decanoic acids (analytical grade), were fractionated under reduced pressure in flowing argon. The liquid acids were preliminarily kept over anhydrous magnesium sulfate. The purity of the resulting acids was at least 99.0 ± 0.5%, according to GLC analyses of their methyl esters. To purify hexanoic acid (high-purity grade), the acid was converted into its sodium salt. Pentanol and other neutral impurities were multiply extracted with chlorobenzene from an aqueous solution of the sodium salt. Then residual chlorobenzene was removed in vacuo using a water-jet pump, and the sodium hexanoate solution was acidified with sulfuric acid. The resulting hexanoic acid was dried with anhydrous magnesium sulfate and fractionated under reduced pressure in flowing argon. The pentanol content of the purified acid was lower than 0.001%. Chlorobenzene (high-purity grade) was purified by successive treatment with sulfuric acid and a sodium bicarbonate solution [7] and was distilled two times (second time, from P_2O_5). The method of cyclohexanol purification was described earlier [8].

Carboxylic acids were oxidized by molecular oxygen at 373 K using a manometric setup. The reaction, initiated by cumyl peroxide, was carried out under kinetic control. The temperature was maintained with an accuracy of ±0.2 K.

The hydrogen peroxide content was derived from the difference between the total concentration of peroxides and their concentration after the selective decomposition of H_2O_2 by catalase under conditions ruling out the deactivation of the enzyme by carboxylic acid [9]. The amount of peroxide compounds was determined colorimetrically after adding a reagent containing Fe^{2+} ions and *N*,*N*-dimethyl-*para*-phenylenediamine to the sample [10].

To determine the total pentyl hydroperoxide and pentanol content of the product of hexanoic acid oxidation, an aliquot was treated, immediately after sampling, with a 100% molar excess of a triphenylphosphine solution in benzene to reduce the peroxide compounds. Next, a 100% molar excess of acetic anhydride and pyridine (on the basis of the assumed alcohol content) were added to the same aliquot. The sample was heated for 2 h at 373 K, and pentyl hexanoate (which resulted from the esterification of pentanol by a mixture of anhydrides [11]) was quantified by GLC. The GLC analysis was carried out using a column packed with 20% diethylene glycol succinate on Chromaton N-AW-HMDS. If necessary, a correction for the possible formation of pentyl acetate was applied in the calculation of the pentanol content.

The rate constant of reaction initiation by cumyl peroxide (k_i) was determined by the familiar equation [12]

$$\log k_i = 12.89 - \frac{126400}{2.3RT}. \quad (1)$$

RESULTS AND DISCUSSION

According to the task stated, we studied the influence of the initiation rate w_i on the kinetics of oxygen uptake in the oxidation of a number of *n*-carboxylic acids by molecular oxygen at 373 K without a solvent or in chlorobenzene using cumyl peroxide as the initiator. The linear character of the observed kinetics indicated that degenerate branching reactions make an insignificant contribution to the initiation of the process. The rates of oxygen uptake (w_{O_2}) in the oxidation of various substrates were determined by experimental data processing (Table 1).

In all cases, the dependence of w_{O_2} on w_i is described by Eq. (2), derived for the radical chain oxidation of organic compounds with quadratic-law chain termination [12]:

$$w_{O_2} = k_p(2k_t)^{-0.5}[RH]w_i^{0.5} + mw_i, \quad (2)$$

where k_t and k_p are the rate constants of chain termination and propagation, [RH] is the substrate concentration, *m* is the coefficient taking into account the nonchain uptake and/or evolution of oxygen at the chain initiation and termination stages.

In full accord with Eq. (2), the dependences of $w_{O_2}/w_i^{0.5}$ on $w_i^{0.5}$ are linear. The numerical values of the oxidizability parameter of the carboxylic acids ($k_p(2k_t)^{-0.5}$) and the coefficient *m* were determined from these dependences (Table 1). In most cases, *m* is not equal to 0.5, and this is in conflict with the theory of radical chain oxidation using this type of initiator (cumyl peroxide) with quadratic-law chain termination [12], as well as with *n*-decane oxidation data. It also follows from Table 1 that *m* as a function of the number of carbon atoms in the carboxylic acid passes through an extremum. On going from propanoic acid to pentanoic acid, *m* first increases and then decreases, and for the oxidation of dodecanoic acid *m* is almost the same as for *n*-decane oxidation.

A similar effect was observed previously for the oxidation of aromatic esters [13, 14], ketones [15, 16], and benzaldehyde [17]. The effect was explained in terms of the quadratic-law chain termination,

$$2RO_2^{\bullet} \xrightarrow{k_t} \text{molecular products} + O_2, \quad (I)$$

accompanied by peroxy radical recombination reactions without chain termination typical of tertiary peroxy radicals [1, 12, 18]:

$$2RO_2^{\bullet} \xrightarrow{k'} 2RO^{\bullet} + O_2. \quad (II)$$

In the latter case, when cumyl peroxide is used as the initiator [14, 16],

$$m = 0.5(1 + k'/k_t), \quad (3)$$

where *k*' is the rate constant of reaction (II).

The oxidizability parameter $k_p(2k_t)^{-0.5}$ and the ratio k'/k_t determined using Eqs. (2) and (3) for propanoic, butanoic, pentanoic, hexanoic, octanoic, decanoic, and dodecanoic acids are also given in Table 1.

Unlike the oxidation of saturated hydrocarbons and most of their other oxygen-containing derivatives, the corresponding reactions involving carboxylic acids have some specific features. The oxidation of carboxylic acids is accompanied by decarboxylation reactions [2]:

$$R'COOH \xrightarrow[-ROOH]{+RO_2^{\bullet}} R'COO^{\bullet} \xrightarrow[-CO_2]{} R'^{\bullet}. \quad (III)$$

Since short chains form in most cases of carboxylic acid oxidation (Table 1), it is necessary to elucidate whether or not the anomalously large values of *m* are a consequence of reactions of type (III). For this purpose, we studied the kinetics of oxygen uptake, the accumulation of organic peroxides and H_2O_2, and the formation of pentanol + pentyl hydroperoxide under the conditions of cumyl peroxide–initiated hexanoic acid oxidation at 373 K (see Fig. 1, where *C* designates the concentrations of these compounds). The character of the kinetic curves in Fig. 1 indicates that the peroxide compounds decompose insignificantly under the experimental conditions. The source of pentanol

Table 1. Effect of the initiation rate (or substrate concentration) on the kinetics of the cumyl peroxide–initiated oxidation of carboxylic acids, methyl hexanoate, and decane at 373 K

Substrate	[RH], mol/l	$w_i \times 10^8$, mol l^{-1} s^{-1}	$w_{O_2} \times 10^7$, mol l^{-1} s^{-1}	$w_v \times 10^7$, mol l^{-1} s^{-1}	v	$k_p(2k_t)^{-0.5} \times 10^5$, l$^{0.5}$ mol$^{-0.5}$ s$^{-0.5}$	m	k'/k_t
Propanoic acid	13.4	4.22	0.52	0.2	0.47	0.8 ± 0.2	0.8 ± 0.1	0.5
		5.42	0.66	0.24	0.45			
		8.55	0.91	0.26	0.3			
		11.5	1.24	0.37	0.32			
Butanoic acid	10.9	4.22	0.86	0.23	0.54	1.0 ± 0.4	1.5 ± 0.2	2.0
		5.42	1.01	0.19	0.36			
		8.55	1.61	0.32	0.38			
		11.5	2.03	0.30	0.26			
Pentanoic acid	9.2	4.22	1.74	0.58	1.37	3.3 ± 0.5	2.8 ± 0.2	4.5
		5.42	2.18	0.69	1.27			
		8.55	3.3	0.95	1.11			
		11.5	4.19	1.02	0.89			
Hexanoic acid	7.9	4.22	1.52	0.67	1.59	3.8 ± 0.8	2.0 ± 0.2	3.0
		5.42	1.8	0.71	1.31			
		8.55	2.68	0.96	1.12			
		11.5	3.24	0.93	0.81			
Hexanoic acid	1.17	8.55	1.93	0.13	0.15	3.8 ± 0.3	2.10 ± 0.01	3.2
	3.03		2.13	0.33	0.39			
	4.8		2.32	0.53	0.62			
	7.9		2.68	0.88	1.03			
Octanoic acid	6.3	4.22	2.87	2.17	5.13	15.9 ± 0.7	1.7 ± 0.2	2.3
		5.42	3.25	2.35	4.33			
		8.55	4.35	2.93	3.42			
		11.5	5.16	3.25	2.82			
Decanoic acid	5.1	4.22	3.84	3.37	7.98	31.9 ± 0.3	1.1 ± 0.1	1.2
		5.42	4.41	3.80	7.02			
		8.55	5.76	4.80	5.62			
		11.5	6.82	5.53	4.81			
Dodecanoic acid	2.0	4.22	2.09	1.88	4.45	44.0 ± 4.7	0.5 ± 0.3	0
		5.42	2.23	1.96	3.61			
		8.55	3.0	2.57	3.01			
		11.5	3.54	2.97	2.58			
Hexanoic acid + $C_6H_5NO_2$ (0.1 mol/l)	7.9	4.22	1.31	1.10	2.6	6.5 ± 0.3	0.5 ± 0.1	0
		5.42	1.48	1.21	2.23			
		8.55	1.97	1.54	1.8			
		11.5	2.37	1.79	1.56			
Methyl hexanoate	6.8	4.22	7.07	6.16	14.6	44.2 ± 0.1	2.15 ± 0.03	3.3
		5.42	8.15	6.9	12.8			
		8.55	10.6	8.8	10.3			
		11.5	12.6	10.2	8.8			
Dodecanoic acid + $C_6H_{11}OH$ (0.04 mol/l)	2.0	4.22	1.66	1.31	3.1	33.0 ± 1.0	0.83 ± 0.07	0.7
		5.42	1.97	1.52	2.8			
		8.55	2.6	1.89	2.21			
		11.5	3.17	2.22	1.93			
n-Decane	5.1	4.22	2.71	2.3	5.92	24.0 ± 2.0	0.5 ± 0.4	0
		5.42	3.16	2.89	5.33			
		8.55	4.21	3.78	4.42			
		11.5	4.76	4.19	3.64			

Note: w_v is the radical chain oxidation rate, and v is the chain length ($v = w_v/w_i$).

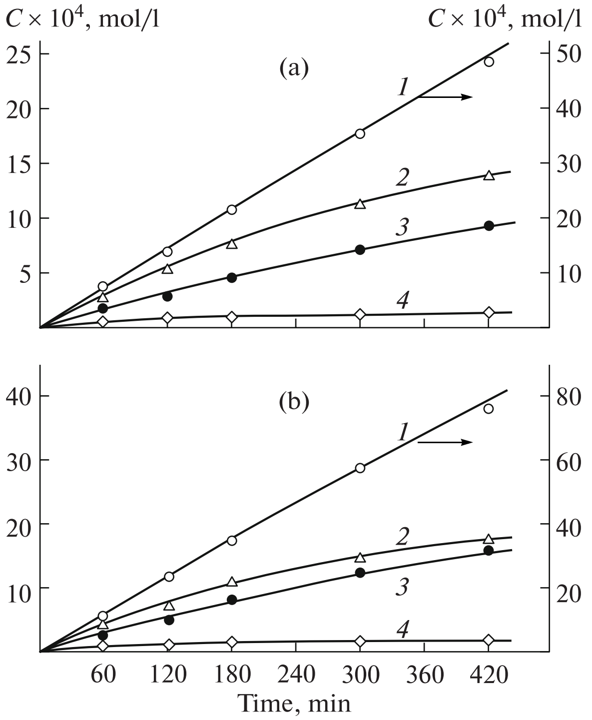


Fig. 1. Kinetics of oxygen uptake and product accumulation in hexanoic acid oxidation initiated by cumyl peroxide at 373 K and initiation rates of (a) 5.42×10^{-8} and (b) 8.55×10^{-8} mol l^{-1} s^{-1}: (*1*) oxygen uptake, (*2*) total concentration of peroxide compounds, (*3*) 1-pentanol accumulation, and (*4*) hydrogen peroxide accumulation.

in the samples reduced by triphenylphosphine can be pentyl hydroperoxide, whose formation is not due to the radical chain conversion of hexanoic acid and is most likely a result of decarboxylation via reaction (III) followed by the interaction of the pentyl radical with oxygen and the substrate:

$$C_5H_{11}^{\bullet} \xrightarrow[-R^{\bullet}]{+O_2, RH} C_5H_{11}OOH. \qquad (IV)$$

Under the assumption that the amount of CO_2 evolved in reaction (III) and the amount of oxygen taken up in reaction (IV) are equal, the net effect of reactions (III) and (IV) on the oxygen uptake kinetics is zero. At the same time, if the decomposition of the peroxide compounds is neglected, the initial rate of accumulation of all hydroperoxides ($w_{HP,0}$) will be equal to the sum of the initial rates of radical chain oxidation (w_v) and pentyl hydroperoxide accumulation ($w_{PHP,0}$):

$$w_{HP,0} = w_v + w_{PHP,0}. \qquad (4)$$

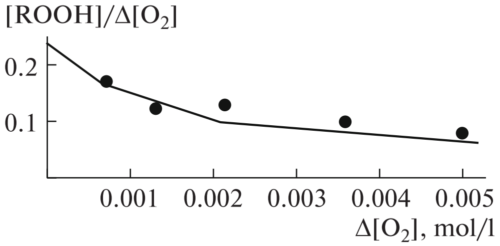


Fig. 2. Dependence of [ROOH]/Δ[O_2] on Δ[O_2] in hexanoic acid oxidation initiated by cumyl peroxide at 373 K ($w_i = 5.42 \times 10^{-8}$ mol l^{-1} s^{-1}).

From the kinetic dependences plotted in Fig. 1, we derived the initial rates of oxygen uptake (w_{O_2}), the initial total hydroperoxide accumulation rate, and the initial pentyl hydroperoxide accumulation rate (Table 2). From these data, using Eqs. (2), (3), and

$$m = \frac{w_{O_2} - (w_{HP,0} - w_{PHP,0})}{w_i}, \qquad (5)$$

we calculated the parameters $k_p(2k_t)^{-0.5}$ and m. Next, the k'/k_t ratio was calculated using the m value (Table 2).

A comparison between the data presented in Tables 1 and 2 indicates that the $k_p(2k_t)^{-0.5}$ and k'/k_t values obtained for hexanoic acid by the two different methods are in satisfactory agreement.

The k'/k_t ratio can also be estimated from the dependence of [ROOH]/Δ[O_2] on Δ[O_2] (Fig. 2), where [ROOH] is the total concentration of peroxide compounds (except pentyl hydroperoxide) and Δ[O_2] is the oxygen uptake. The linear extrapolation of this dependence to Δ[O_2] = 0 using the MathCad 2001i Pro program gives [ROOH]/Δ[O_2] = 0.24 ± 0.03, which is equal to the $\frac{w_v}{w_{O_2}}$ ratio. Therefore, $m = 2.8 \pm 0.1$ and $k'/k_t = 4.6$. The higher values of these param-

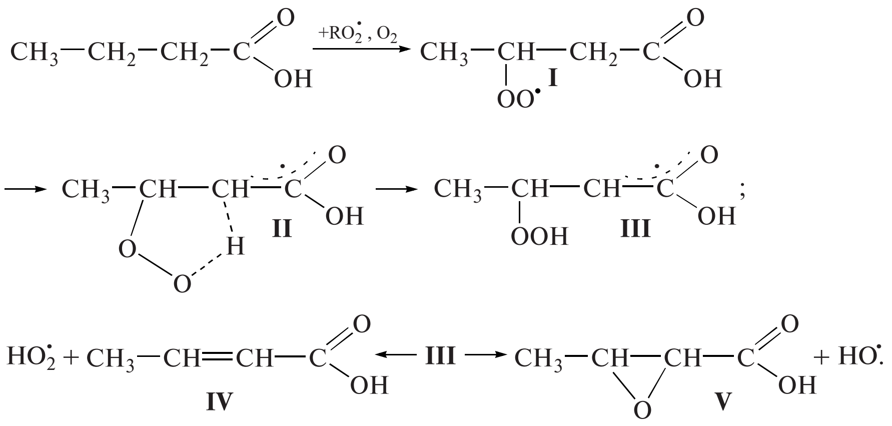
Table 2. Initial rates of product accumulation and the kinetic parameters of hexanoic acid oxidation initiated by cumyl peroxide at [RH] = 7.98 mol/l and 373 K

$w_i \times 10^8$, mol l^{-1} s^{-1}	$w_{O_2} \times 10^7$, mol l^{-1} s^{-1}	$w_{\Sigma ROOH,0} \times 10^7$, mol l^{-1} s^{-1}	$w_{ROH} \times 10^7$, mol l^{-1} s^{-1}	$w_v \times 10^7$, mol l^{-1} s^{-1}	v	$k_p(2k_t)^{-0.5} \times 10^5$, $l^{0.5}$ $mol^{-0.5}$ $s^{-0.5}$	m	k'/k_t
5.42	1.96	1.05	0.35	0.71	1.3	3.8	2.3	3.6
8.55	2.95	1.83	0.74	1.09	1.3	4.7	2.2	3.4
Average value							2.3	3.5

eters can be a consequence of the decomposition of part of the hydrogen peroxide under the experimental conditions (Fig. 1, curve *4*) and, hence, a decrease in the $\frac{w_V}{w_{O_2}}$ ratio with an increase in the extent of oxidation (Fig. 2). The latter circumstance would lead to an increase in the length of the ordinate intercept and, accordingly, to an increase in *m*.

The fact that k'/k_t as a function of the chain length of the carboxylic acid passes through an extremum (Table 1) can be explained under the assumption that the ratio of peroxy radicals of different types in the reaction medium changes. The works cited above indicate that the secondary α-peroxy radicals of aromatic esters, including benzyl benzoate (k'/k_t = 1.5 [13]) and *tert*-butyl phenyl acetate (k'/k_t = 2.2 [14]), and those of ketones, including benzyl phenyl ketone (k'/k_t = 1.5 [15]) and benzyl *para*-chlorophenyl ketone (k'/k_t = 3.89 [16]), can be involved in reactions of type (II). Under the assumption that the secondary α-peroxy radicals of aliphatic carboxylic acids possess the same properties, the largest k'/k_t ratio would be expected of the oxidation of propanoic and butanoic acids. With further elongation of the carbon chain, this ratio would be expected to decrease due to the decrease in the fraction of α-peroxy radicals in the total amount of peroxy radicals. However, this was not proved experimentally. It is natural to assume that not only the α-peroxy radicals but also other peroxy radicals of carboxylic acids can participate in reaction (II). It is impossible to explain the observed phenomenon by the participation of the primary peroxy radicals resulting from acid decarboxylation (reactions (III) and (IV)) in reactions of type (II). Firstly, the fraction of these radicals also should decrease with the elongation of the carboxylic acid chain. Secondly, in the case of methyl hexanoate, which undergoes no noticeable decarboxylation, the k'/k_t ratio is approximately the same as in the oxidation of hexanoic acid (Table 1). The only peroxy radical that forms in larger amounts in carboxylic acid oxidation than in hydrocarbon oxidation is $HO_2^\bullet$.

It was demonstrated that β-carboxyperoxy radical **I** resulting from the oxidation of carbonyl-containing compounds (including carboxylic acids) at the β-C—H bonds decomposes via two parallel routes to yield the $HO_2^\bullet$ radical and an α, β-unsaturated carbonyl-containing compound [6, 19] or the $HO^\bullet$ radical and the corresponding epoxide [19]:



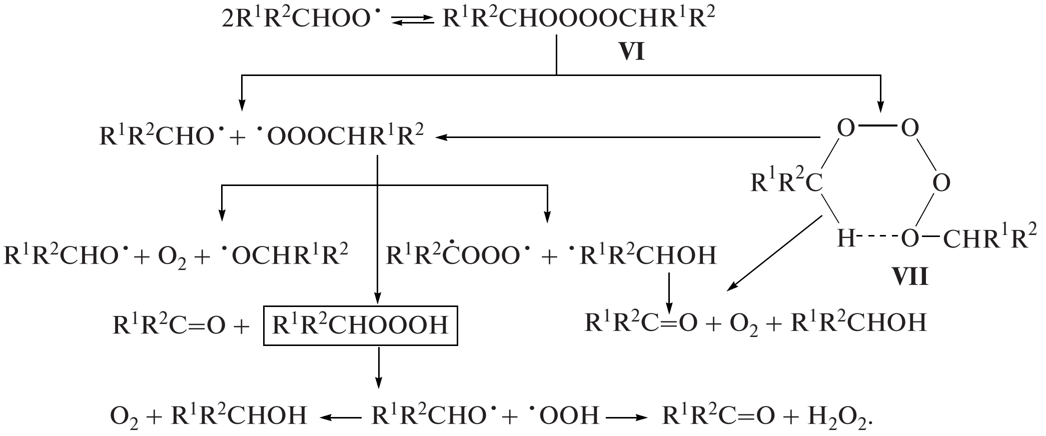
(V)

The formation of compounds **IV** and **V** in similar yields was actually observed for butanoic acid oxidation initiated by cumyl peroxide at 373 K [19]. Quantum chemical calculations [19] showed that the conversion of **I** into **IV** or **V** is, most likely, a two-step process. The activation energy of two consecutive steps of the conversion of **I** into **IV** through transition state **II** (E_a = 78.0 kJ/mol) is substantially lower than that of the direct conversion of **I** into **IV** (E_a = 234.3 kJ/mol). The rate-determining step of the decomposition is the conversion of **III** into **IV**, because the activation energy of the conversion of **I** into **III** is lower than that of the conversion of **III** into **IV** and is 61.4 kJ/mol. The conversion of **II** into **V** is known to be a step in the epoxidation of unsaturated compounds by peroxy radicals [20]. The calculated activation energy of the conversion of **III** into **V** (E_a = 80.63 kJ/mol) is close to that of the conversion of **III** into **IV** [19].

When the reaction medium contains peroxy radicals of two types with different reactivities, the cross recombination of more and less reactive radicals becomes significant [13, 21]. Therefore, a probable mechanism of peroxy radical recombination without chain termination during carboxylic acid oxidation becomes the interaction of the secondary peroxy radicals of carboxylic acids with the $HO_2^\bullet$ radical:

$$HO_2^\bullet + RO_2^\bullet \xrightarrow{k'} RO^\bullet + HO^\bullet + O_2. \qquad \text{(VI)}$$

This cross recombination of the secondary peroxy radicals with the $HO_2^\bullet$ radicals without chain termination is not impossible. The results of the calculation of the preexponential factors for reactions of type (VI) [1, 22] in terms of transition state theory check well with experimental data [23] on the overall rate of the cross recombination of the cyclohexylperoxy radical with $HO_2^\bullet$. It was assumed [1] that the same products can result from the disproportionation of the oxyl radical formed in the solvent cage and from the reaction occurring via Russell's mechanism (see below). As was shown later [18], all known experimental data on the rate and composition of the recombination products of the primary, secondary, and tertiary radicals both with and without chain termination can be explained as follows:



(VII)

Scheme (VII) includes the reversible interaction between two peroxy radicals with the formation of tetraoxide **VI** and the decomposition of the latter. The decomposition can either be molecular, proceeding via transition state **VII** (Russell's mechanism), or occur via the asymmetric homolysis of the O–O bond. This homolytic decomposition can give the same products as the decomposition via Russell's mechanism, namely, equimolar amounts of carbonyl- and hydroxyl-containing compounds and molecular oxygen or two oxyl radicals and molecular oxygen. According to [24, 25], the rate constants of tetraoxide decomposition correlate with the strength of the O–O bond, and, for nonsymmetric decomposition, they depend weakly on the substituent nature.

Reaction (VI) should proceed via the intermediate hydrotetraoxide ROOOOH. The strengths of the two different O–O bonds (D) subjected to the asymmetric cleavage in this intermediate compound are D(ROOO–OH) = 105.0 ± 2.1 kJ/mol and D(RO–OOOH) = 87.0 ± 5.8 kJ/mol [25]. Therefore, ROOOOH will decompose predominantly at the O–O bond nearest to the alkyl radical R:

$$ROOOOH \rightarrow RO^\bullet + {}^\bullet OOOH. \qquad \text{(VIII)}$$

The hydrotrioxy radical formed in reaction (VIII) decomposes to yield the hydroxyl radical and molecular oxygen [26]:

$$HOOO^\bullet \rightarrow HO^\bullet + O_2. \qquad \text{(IX)}$$

Scheme (VII) and the above assumption are in good agreement with recently published experimental data on the composition of the products of the recombination of the $HO_2^\bullet$ radicals with the ethylperoxy ($CH_3CH_2OO^\bullet$), acetylperoxy ($CH_3C(O)OO^\bullet$), and acetonylperoxy ($CH_3C(O)CH_2OO^\bullet$) radicals at 25°C [27] and with the results of quantum chemical calculations and kinetic simulation based on these calculations [28]. According to [27, 28], other reactions can occur along with reaction (VI), but all of them are accompanied by chain termination

$$RO_2^\bullet + HO_2^\bullet \xrightarrow{k_t} ROOH + O_2, \qquad \text{(X)}$$

$$RO_2^\bullet + HO_2^\bullet \xrightarrow{k_t} R'CHO + H_2O + O_2; \qquad \text{(XI)}$$

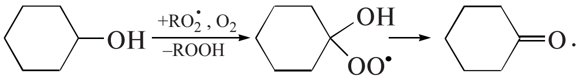
$$RO_2^\bullet + HO_2^\bullet \xrightarrow{k_t} ROH + O_3. \qquad \text{(XII)}$$

The structure of the organic peroxy radical has a substantial effect on the contribution from reaction (VI) to the total yield of the recombination products. In the case of the acetonylperoxy radical, the total yield is as high as 67%, whereas it is 40% in the case of the acetylperoxy radical. No occurrence of reaction (VI) involving the ethylperoxy radical was observed [27]. However, quantum chemical calculations on the recombination of 11 alkylperoxy radicals (including the ethylperoxy and cyclohexylperoxy radicals) with the $HO_2^{\bullet}$ radical show that the contribution from reaction (VI) increases substantially above room temperature [29]. For the recombination of two methylperoxy radicals, the temperature dependence of k'/k_t is expressed by the equation [30]

$$\ln k'/k_t = 3.80 - 1470/T. \qquad (6)$$

According to this equation, the k'/k_t ratio increases by a factor of 2.7 (from 0.32 to 0.86) as the temperature increases from 298 to 373 K.

The occurrence of reaction (VI) under the conditions of carboxylic acid oxidation is evidenced by the data according to which the recombination of peroxy radicals without chain termination in hexanoic acid oxidation is suppressed by nitrobenzene, which is a selective inhibitor binding $HO_2^{\bullet}$ radicals [6, 31, 32] (Table 1). In addition, the role of these recombination reactions increases considerably when the $HO_2^{\bullet}$ radical is additionally generated. For example, in the simultaneous oxidation of dodecanoic acid and cyclohexanol, the radical chain oxidation of the latter is an extra source of these radicals [2, 8]:



(XIII)

It can seen from the data in Table 1 that the k'/k_t ratio reaches a value of 0.7 in this case, whereas almost no recombination of peroxy radicals without chain termination occurs in the absence of alcohol ($k'/k_t = 0$).

Under the assumption that the maximum k'/k_t value corresponds to the ratio of peroxy radicals optimal for reactions of types (II) and (VI), this ratio should decrease both with an increase in the fraction of $HO_2^{\bullet}$ radicals (butanoic acid) and with a decrease in this fraction (decanoic and dodecanoic acids) (Table 1). It is noteworthy that reactions of type (VI) should occur in the oxidation of both *n*-carboxylic acids and saturated hydrocarbons (already at the early stages). In this case, reactions of type (XIII) are the source of the $HO_2^{\bullet}$ radicals. This fact should be taken into account when analyzing the oxidation kinetics of both carboxylic acids and saturated hydrocarbons.

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