

Routes of Formation of Bifunctional C₆ Carboxylic Acids in the Cyclohexane Oxidation Process

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Received March 23, 2018; revised February 9, 2019; accepted February 12, 2019

Abstract—The buildup kinetics of the main and side products during uncatalyzed and cobalt naphthenate-catalyzed oxidation of cyclohexane at 150°C have been studied. 6-Hydroxyhexanoic, 6-oxohexanoic, and adipic acids are accumulated in parallel during the oxidation of cyclohexane, cyclohexanone, and 2-hydroxycyclohexanone. The critical consideration of their known formation pathways and the reactivity of possible precursors gives evidence for the predominant formation of 6-hydroxyhexanoic acid at the step of cyclohexanol oxidation and adipic acid from 2-hydroxycyclohexanol.

Keywords: cyclohexane, cyclohexanone, 2-hydroxycyclohexanone, liquid-phase oxidation, 6-hydroxyhexanoic acid, 6-oxohexanoic acid, adipic acid, formation routes

DOI: 10.1134/S0965544119060136

Bifunctional C₆ carboxylic acids (adipic, 6-hydroxyhexanoic, and 6-oxohexanoic) are one of the main side products in the process of cyclohexane oxidation to cyclohexanol and cyclohexanone [1, 2]. The routes of their formation are still under debate. It is supposed [1, 3–5] that adipic and 6-oxohexanoic acids are formed from cyclohexanone. By measuring the activity of side products in experiments on the co-oxidation of C¹⁴-labeled cyclohexane with an admixture of unlabeled cyclohexanone on one hand and unlabeled cyclohexane with an admixture of C¹⁴-labeled cyclohexanone on the other hand, it was shown that 86–95% adipic acid is produced through cyclohexanone during cyclohexane oxidation [3]. Later, based on the investigation of the kinetics of buildup of side products at the initial steps of uncatalyzed and cobalt(II) and cobalt(III) acetate-catalyzed oxidation of cyclohexane, Hermans and coworkers [6–8] concluded that adipic, 6-hydroxyhexanoic, and 6-oxohexanoic acids are predominantly produced from cyclohexyloxy radicals. This conclusion contradicts the data on a substantial decrease in the selectivity of the cyclohexane oxidation process even at a low conversion as a result of the involvement of the alcohol and ketone into the radical chain process [1, 9]. The hypothetical mechanisms proposed in [6–8] include intramolecular isomerization (chain transfer) through seven- and eight-membered transition states, which is unlikely due to the increase in the entropic barrier in the case of formation of a folded conformation of an alicyclic molecule [10].

This work is devoted to the investigation of the kinetics of buildup of the desired and main side products in the uncatalyzed and cobalt naphthenate-catalyzed liquid-phase oxidation reaction of cyclohexane and discussion of possible routes of the formation of adipic, 6-hydroxyhexanoic, and 6-oxohexanoic acids.

EXPERIMENTAL

Cyclohexane of the chemically pure grade was purified according to the procedure given in [11]. Bp 80.5°C (published value, 80.738°C [11]).

Cyclohexane was oxidized by oxygen in a stainless steel bubble reactor at 150°C and a pressure of 1.47 MPa in the absence of a catalyst and with 8.5 × 10⁻⁴ mol/L cobalt(II) naphthenate. The accuracy of temperature control was ±1°C.

The total concentration of peroxide compounds in oxidized cyclohexane was determined using iodometric titration [12, 13], and the other products were determined by GLC. To prevent the disturbing influence of peroxide compounds on the results of determination of nonperoxide products, the samples were reduced with triphenylphosphine immediately after sampling. 2-Hydroxycyclohexanone was determined after acylation with acetic anhydride in a pyridine medium. Carboxylic acids and monocyclohexyl adipate were transformed to methyl esters by treating with diazomethane prior to the determination. The sample preparation procedures, analysis conditions, and metrological characteristic of the methods are presented in [14] for cyclohexanol, 2-hydroxycyclohexa-

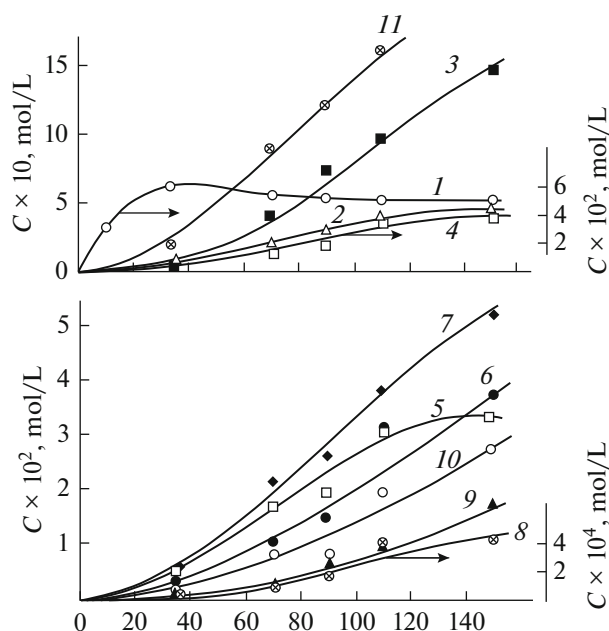


Fig. 1. Buildup rate curves for the products of uncatalyzed oxidation of cyclohexane at 150°C: (1) peroxides, (2) cyclohexanol, (3) cyclohexanone, (4) 2-hydroxycyclohexanone and 2-hydroperoxycyclohexanone, (5) 6-hydroxyhexanoic acid, (6) 6-oxohexanoic acid, (7) adipic acid, (8) adipic anhydride, (9) monocyclohexyl adipate, (10) ϵ -caprolactone, and (11) total oxidation products.

none, and compounds with carboxyl groups; [15] for cyclohexanone; and [16] for adipic anhydride.

RESULTS AND DISCUSSION

In accordance with the set task, the product buildup kinetics in the case of uncatalyzed and cobalt naphthenate-catalyzed oxidation of cyclohexane at 150°C have been studied (Figs. 1, 2). The buildup rate curve for total oxidation products shows the presence of an induction period in the case of uncatalyzed reaction; after this period, cyclohexane is oxidized at an almost constant rate (Fig. 1).

The shape of a similar curve in the cobalt(II) salt-catalyzed reaction indicates the absence of the induction period; the rate of oxidation is higher than in the uncatalyzed process, but no noticeable autoacceleration is observed in this case as well. The absence of autoacceleration in both experiments cannot be explained by the constancy of the rate of reactions of degenerated branching—homolytic decomposition of cyclohexyl hydroperoxide.

On the opposite, their role should increase as a result of the accumulation of oxygen-containing compounds (cyclohexanol, cyclohexanone, 2-hydroxycyclohexanone, etc.), which substantially accelerate the degradation of cyclohexyl hydroperoxide including the homolytic decomposition [5, 17]. Apparently, acceleration due to the increase in the rate of degener-

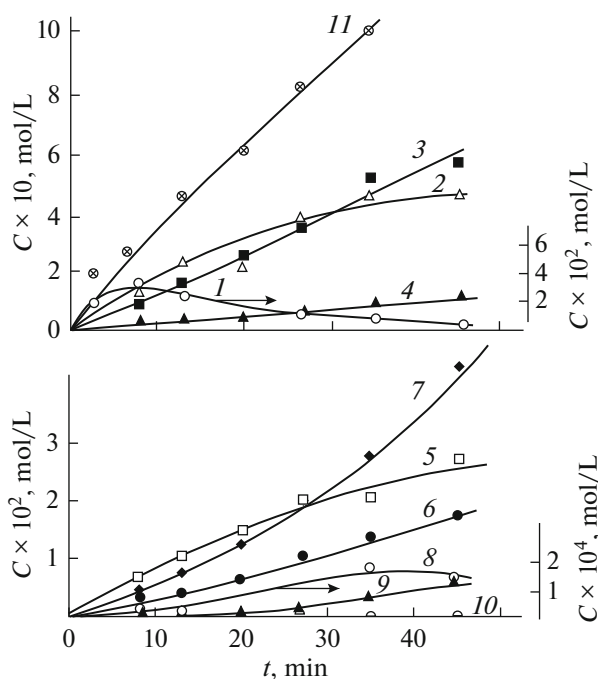


Fig. 2. Buildup rate curves for the products of cyclohexane oxidation at 150°C in the presence of cobalt(II) naphthenate. See Fig. 1 for the designation of the curves.

ated branching is compensated by the factors that decelerate the radical chain process. These include the change in the composition of peroxy radicals due to the involvement of cyclohexanol, cyclohexanone, 2-hydroxycyclohexanone, etc. into the oxidation reaction, as well as a decrease in the activity of peroxy radicals as a result of their solvation by oxygen-containing compounds [5, 17].

The pattern of the buildup rate curves of peroxide compounds and total nonperoxide products (Figs. 1, 2) suggests the predominant formation of the latter from the former products. Apparently, the non-terminating routes of combination of peroxy radicals



revealed in the case of oxidation of cyclohexanol [18] or 2-hydroxycyclohexanone [19] are unimportant during the oxidation of cyclohexane.

At the initial steps of uncatalyzed oxidation, adipic, 6-hydroxyhexanoic, and 6-oxohexanoic acids are accumulated in parallel and in close amounts (Fig. 1). In the cobalt naphthenate-catalyzed reaction, the initial buildup rate of 6-hydroxyhexanoic acid is higher by a factor of 1.8 than that of adipic acid (Fig. 2). The formation rate of 6-hydroxyhexanoic acid decreases in 20 min after the onset of oxidation, whereas that of adipic acid increases and it becomes the main carboxylated product of the reaction. This finding does not contradict the idea advanced by Hermans et al. [6–8] about the formation of 6-hydroxyhexanoic and adipic

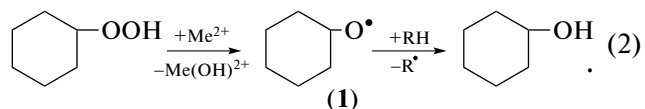
acids from the cyclohexyloxy radical, nor does it prove the preferred formation of adipic acid from 6-hydroxyhexanoic acid, since 6-oxohexanoic acid, the supposed intermediate product of such a transformation, is accumulated in parallel with adipic acid at the beginning of uncatalyzed and catalyzed oxidation (Figs. 1, 2).

It is known that adipic, 6-hydroxyhexanoic, and 6-oxohexanoic acids can be produced not only from the cyclohexyloxy radical [6–8], but also at the steps of oxidation of cyclohexanol [1, 4, 5], cyclohexanone [1, 4, 5, 20, 21], and 2-hydroxycyclohexanone [5, 6, 19, 22]. Because of this, it is reasonable to critically consider all the alternative routes of formation of these compounds.

Formation of Bifunctional C₆ Acids from Cyclohexyloxy Radical

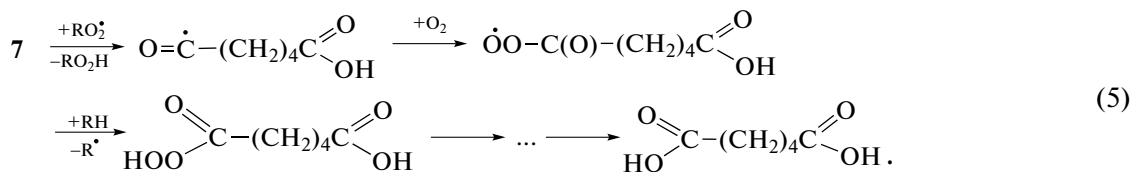
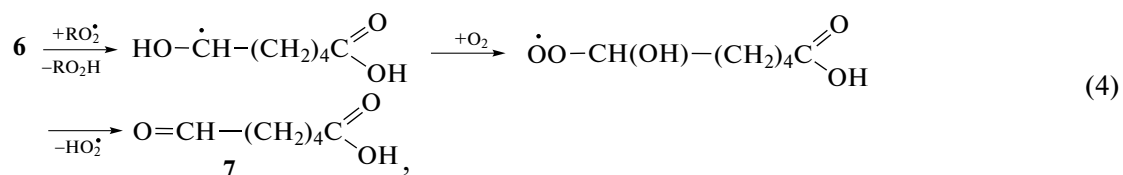
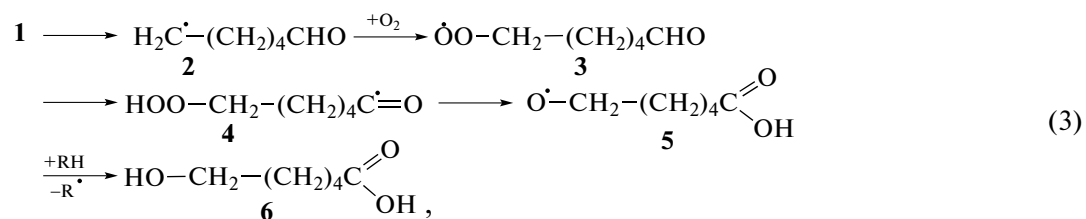
The cyclohexyloxy radical (**1**) is generated in the case of thermal, catalytic, and free radical-induced decomposition of cyclohexyl hydroperoxide [1, 4, 5, 17]. The homolytic decomposition of the latter is accelerated by oxygen-containing compounds (alcohols, ketones, carboxylic acids, etc.) [1, 5, 17]. The

main pathway of the transformation of **1** in the medium of cyclohexane under oxidation is the dehydrogenation of the substrate yielding cyclohexanol [1, 4, 5]:



To a substantially lesser extent **1** is subjected to the destructive decomposition with the opening of the cyclohexane ring which leads to 6-oxohexyl radical (**2**) [4, 5]. In the case of thermal decomposition of *tert*-butylcyclohexyl peroxide in cyclohexane at 140°C, 56% cyclohexyloxy radicals are transformed to cyclohexanol [4].

It is supposed in [6–8] that in the case of oxidation of cyclohexane (145°C, conversion of up to 7.5%), the side products are predominantly formed as a result of radical chain transformations of radical **2**. According to [6], in a medium of cyclohexane under oxidation, **2** is successively transformed to 6-hydroxyhexanoic (reactions (3)), 6-oxohexanoic (reactions (4)), and adipic (reactions (5)) acids:



The feasibility of transforming primary hydroxy and aldehyde groups into carboxyl groups during cyclohexane oxidation cannot be denied. However, the likelihood of a number of transformation steps (3)–(5) appears to be low. The conversion of **3** to **4** and **4** to **5** should occur through nine- and seven-membered transition states. It is known [10] that in the case of formation of large cycles, the formation of a cyclic transition state becomes progressively more unlikely

with an increase in the number of units. This limitation is associated with an increase in the entropic barrier for the formation of a folded conformation of an alicyclic molecule [10]. In the case of cyclization of ω-bromocarboxylic acids to lactones

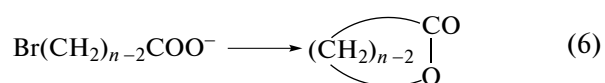


Table 1. Influence of the size of the cyclic transition state on the directionality of the abstraction of hydrogen atoms by an ω -formyl radical ($\cdot(\text{CH}_2)_n\text{CHO}$) (160°C, dodecane, N_2) [23]

	Number of atoms in transition state N	Directions of H atom abstraction, %		
		intramolecular from $-\text{CHO}$	from solvent	other $\text{CH}-$ bonds of the radical
$n = 4$	$N = 6$	74	12	14
$n = 5$	$N = 7$	29	19	52
$n = 6$	$N = 8$	38	8	54

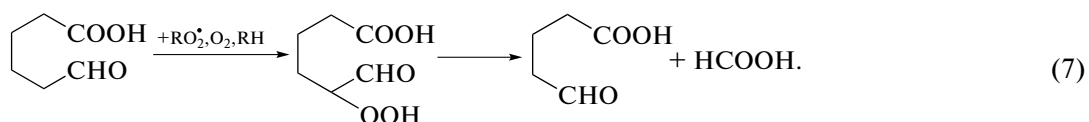
the relative rate of reaction (6) at 150°C is as follows [10]:

Number of atoms in the cycle	5	6	7	8	9	10	11
Relative rate	1.5×10^6	1.7×10^4	97.3	1.00	1.12	3.35	8.51

The fact that the intramolecular transformations of **3** to **4** and **4** to **5** are little competitive with the corresponding intermolecular interactions is also confirmed by the published data [23] obtained in a study

of the directions of abstraction of hydrogen atoms by ω -formyl radicals (Table 1).

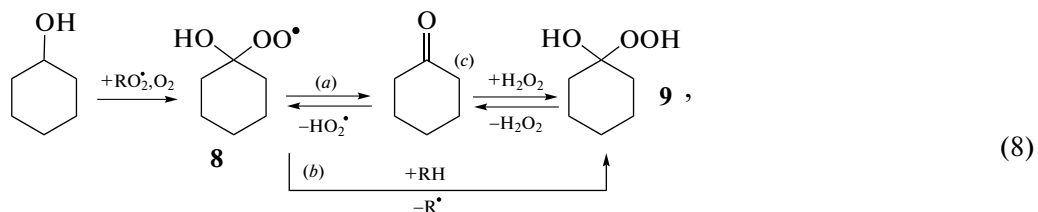
The selectivity of the transformation of **2** to 6-hydroxyhexanoic, 6-oxohexanoic, and adipic acids should also be decreased by the side reactions of decarbonylation (e.g., of radical **2** [5]) and decarboxylation [5], the probability of the occurrence of which under the conditions of oxidation of cyclohexane is quite high. The oxidation of 6-oxohexanoic acid by the $\text{CH}-$ bonds in position 5 leads to formic and 5-oxohexanoic acids identified in the composition of the cyclohexane oxidation products [24]:



Formation of Bifunctional C_6 Acids from Cyclohexanol and Cyclohexanone

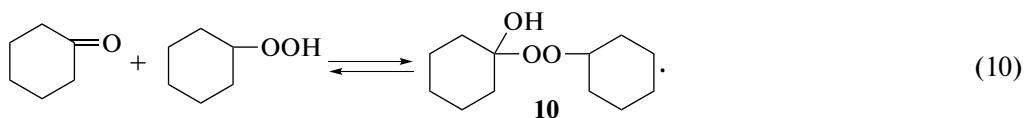
Under the conditions of a radical chain process, cyclohexanol is predominantly oxidized at the α -CH bonds (reaction (8)) [1, 5]. The chain propagating spe-

cies are predominantly HO_2^{\cdot} radicals (reaction (9)), and there are mobile equilibria between cyclohexanone and α -hydroxycyclohexylperoxyl radical (**8**) (reaction (8a)) [25] and between cyclohexanone and α -hydroxycyclohexyl hydroperoxide (**9**) [5, 17, 26].



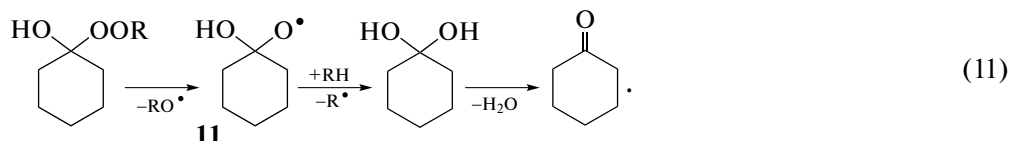
In the presence of hydroperoxides, e.g., cyclohexyl hydroperoxide or 2-hydroperoxycyclohexanone, in

the reaction mixture, they reversibly add to cyclohexanone to give semiperketal (**10**) [1, 4, 5, 17]:



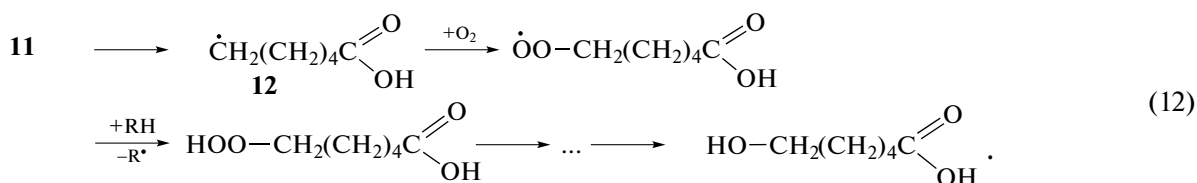
In addition to the dissociation to cyclohexanone and the corresponding peroxide compound,

compounds **9** and **10** undergo homolysis [4, 5, 17]:



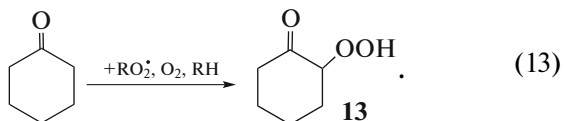
At temperatures below 80°C, 1-hydroxycyclohexyloxy radical (**11**) predominantly abstracts a hydrogen atom from the substrate with the regeneration of

cyclohexanone (reaction (11)). At higher temperatures, the ring-opening degradation of **11** leading to ω-carboxyalkyl radical **12** is possible [4, 5]:

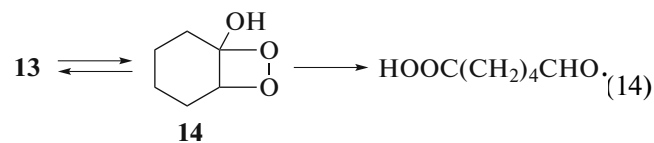


Radical **12** can either dehydrate the substrate to give hexanoic acid or add oxygen to be transformed into ω-carboxyhydroperoxide and then to 6-hydroxyhexanoic acid (reaction (12)) [4, 5].

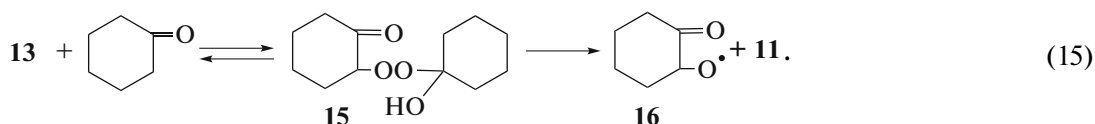
Cyclohexanone undergoes oxidation according to the free-radical mechanism predominantly at the α-CH bonds, the reactivity of which is substantially higher than that of the C–H bonds in cyclohexanone [27], to form 2-hydroperoxycyclohexanone (**13**):



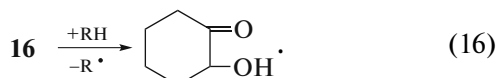
The transformation of **13** to 6-oxohexanoic acid can occur through dioxetane intermediate (**14**) [5]:



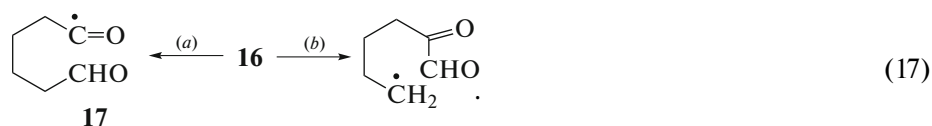
Like cyclohexyl hydroperoxide, **13** can enter intermolecular interactions with oxygen-containing compounds which will accelerate its homolytic decomposition. In cyclohexanone under oxidation, the reaction with the substrate yielding semiperketal (**15**) which degrades to form **11** and 2-oxocyclohexyloxy radical (**16**) is preferable [1, 4, 5, 17]:



Radical **16** is transformed to 2-hydroxycyclohexanone [5, 19, 20, 22, 28, 29]:



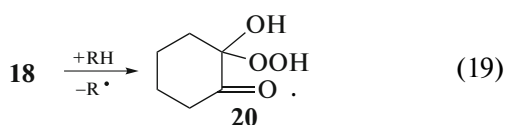
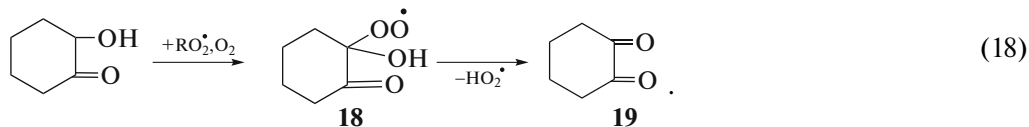
There are two possible routes of the transformation of 2-oxocyclohexyloxy radical **16** with the degradation of the carbon chain. Route 17a explains the formation of 6-oxohexanoic, monoperadipic, and adipic acids in the cyclohexanone oxidation process [1, 4, 5]:



Formation of Bifunctional C₆ Acids During Oxidation of 2-Hydroxycyclohexanone

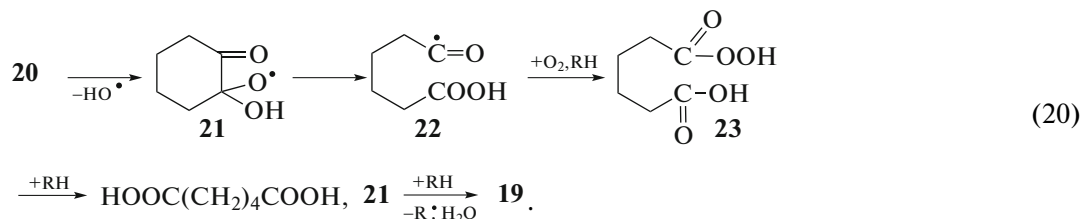
The oxidation of 2-hydroxycyclohexanone occurs according to the radical chain mechanism by the most reactive α -C-H bond [5, 19, 20, 28]. Peroxyl radical

(18) either eliminates the HO₂[•] radical to be transformed into 1,2-cyclohexanedione (19) [5] (reaction (18)) or abstracts hydrogen from the substrate to form 2-hydroxy-2-hydroperoxycyclohexanone (20) (reaction (19)):



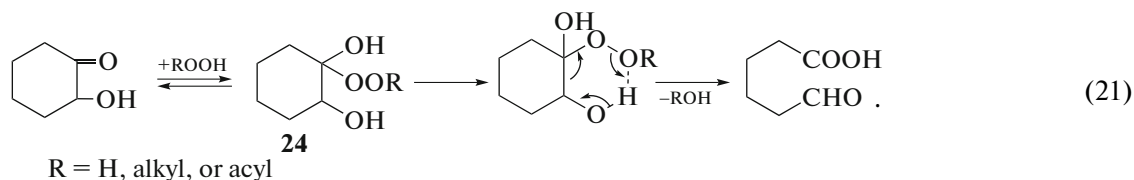
Compound 20 reversibly dissociates to 1,2-cyclohexanedione and H₂O₂ or undergoes degradation via homo-

lytic and nonhomolytic mechanisms [5, 28]. The homolytic decomposition of 20 predominantly involves the degradation of the carbon chain and leads to adipic acid in the presence of oxygen (through the adipic monoperoxyacid (23) step) [5, 28], with 19 being formed as well, although in smaller amounts (reaction (20)):



By comparing the potential yield of the peroxyacid with the yield of adipic acid in the case of oxidation of 2-hydroxycyclohexanone at 50°C, it was found that about 50% of adipic acid was formed according to reaction (20) [5, 28]. The other half amount of adipic acid was formed in parallel with adipic anhydride as a result of the pericyclic rearrangement of 20 through dioxetane and oxirane intermediates, respectively [5, 28]. 2-Hydroxycyclohexanone not only participates in radical chain oxi-

dation, but also interacts with peroxide compounds. The effective rate constants of decomposition of *tert*-butyl hydroperoxide at 150°C in the presence of equimolar additions of cyclohexanol, cyclohexanone, and 2-hydroxycyclohexanone $k_{\text{ef}} \times 10^4$ are 0.17, 0.20, and 10.0 s⁻¹, respectively [5, 22]. The interaction can include the addition of the peroxide compound to the carbonyl group of 2-hydroxycyclohexanone and lead to 6-oxohexanoic acid [5, 22, 28]:



In the case of introduction of methyl ethyl ketone to 2-hydroxycyclohexanone subjected to oxidation at

123°C, almost complete inhibition of the oxidation of the latter was observed [22]; the oxidation was

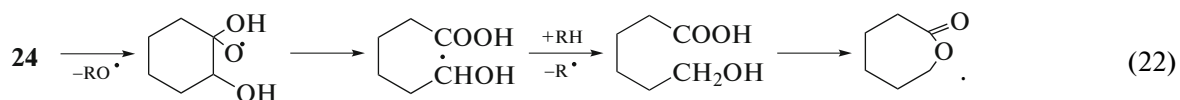
Table 2. Effect of conversion and catalysts on the relative concentration of 6-hydroxyhexanoic (HHA), 6-oxohexanoic (OHA), and adipic (AA) acids (mol % of their total amount (ΣRCOOH)) in the case of oxidation of cyclohexane, cyclohexanone, and 2-hydroxycyclohexanone

Object and conditions of oxidation	$\Sigma\text{RCOOH} = 0.05 \text{ mol/L}$			$\Sigma\text{RCOOH} = 0.1 \text{ mol/L}$		
	HHA	OHA	AA	HHA	OHA	AA
Cyclohexane, 150°C	35.0	23.3	41.7	30.3	27.4	42.3
Cyclohexane + cobalt(II) naphthenate, 150°C	41.1	21.0	37.9	29.3	20.9	49.8
Cyclohexanone, 120°C, chlorobenzene [21]	1.7	40.0	58.3	3.9	28.8	67.3
Cyclohexanone + cobalt(II) naphthenate, 120°C, chlorobenzene [20]	23.8	4.8	71.4	20.0	8.0	72.0
Cyclohexanone + chromium(III) naphthenate, 120°C, chlorobenzene [21]	2.0	25.5	72.5	4.1	24.5	71.4
2-Hydroxycyclohexanone, 123°C, methyl ethyl ketone [22]	9.4	13.6	77.0			
	21.2 ^a	7.3 ^a	71.5 ^a			

^a Taking into account ϵ -caprolactone formed according to reaction (22).

resumed after the quantitative conversion of 2-hydroxycyclohexanone to adipic anhydride and adipic acid (apparently, through **20**), 6-oxohexanoic acid

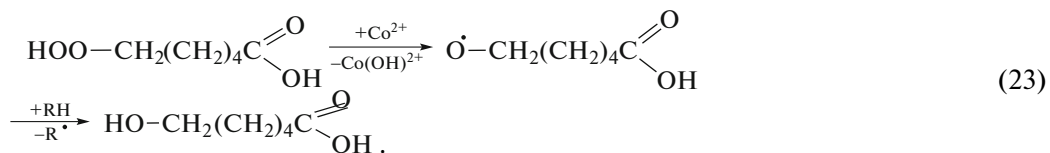
(reactions of type (21)), 6-hydroxyhexanoic acid, and ϵ -caprolactone. The formation of the latter is most likely due to the homolytic decomposition of (**24**):



Therefore, there are several parallel and consecutive—parallel routes of the formation of 6-hydroxyhexanoic, 6-oxohexanoic, and adipic acids, which are not always distinguishable. On the basis of the results shown in Figs. 1 and 2 and published data, Table 2 was composed to present information about the influence of the conversion and catalysis nature on relative concentrations of the acids under consideration.

It is seen from Table 2 that the relative concentration of 6-hydroxyhexanoic acid substantially decreases on passing from the cyclohexane oxidation to the cyclohexanone oxidation experiments. This finding can support the idea that a significant part of this compound is produced from the cyclohexyloxy radical and/or upon the oxidation of cyclohexanol. The second option is preferable, since **11** decomposes with the

destruction of the C—C bond more readily than **1** [4, 5] and the formation of 6-hydroxyhexanoic acid from it requires smaller number of stages. The increase in the concentration of 6-hydroxyhexanoic acid in the case of oxidation of cyclohexanone in the presence of a cobalt (not chromium) catalyst (Table 2) also deserves attention. Since the yield of 6-oxohexanoic acid in the presence of the cobalt catalyst decreases simultaneously with the growth in the concentration of 6-hydroxyhexanoic acid, it can be supposed that cobalt naphthenate not only stimulates the homolytic decomposition of **10** to give **11** (reaction (12)), but also promotes the transformation of 6-hydroperoxyhexanoic acid to 6-hydroxyhexanoic rather than 6-oxohexanoic acid:



Transformations of type (23) provide a higher yield of cyclohexanol in comparison with cyclohexanone in the industrial cyclohexane oxidation process [1, 5, 17].

In the case of uncatalyzed and cobalt salt-catalyzed oxidation of cyclohexane a decrease in the relative concentration of 6-hydroxyhexanoic acid and a simul-

Table 3. Calculated values for the relative rates of reactions of the products of oxidized cyclohexane (150°C, $\Delta RH = 0.6$ mol/L) with a cumyl peroxy radical at 85°C

Product	k_p^{br} , L mol ⁻¹ s ⁻¹	Without a catalyst		With Co(II) naphthenate	
		C_i , mol/L	k_p^{br} ,	C_i , mol/L	W_i/W_{ch}
Cyclohexane	0.21 [31]	7.40	1.00	7.40	1.00
Cyclohexanol	6.5 [31]	0.21	0.88	0.30	1.25
Cyclohexanone	0.58 [31]	0.34	0.13	0.24	0.09
2-Hydroxycyclohexanone	41.7 [32]	0.011	0.30	0.010	0.27

Table 4. Calculated values for the relative rates of reactions of the products of oxidized cyclohexane (150°C, $\Delta RH = 0.6$ mol/L) with a *tert*-butyl peroxy radical

Product	T , °C	k_p^{br} , L mol ⁻¹ s ⁻¹	Without a catalyst		With Co(II) naphthenate	
			C_i , mol/L	W_i/W_{ch}	C_i , mol/L	W_i/W_{ch}
Cyclohexane	60	0.046 ^a	7.4	1	7.4	1
	150	2.2 ^a [33]		1		1
Cyclohexanol	60	0.43 [27]	0.21	0.26	0.30	0.38
Cyclohexanone	60	0.22 [27]	0.34	0.22	0.24	0.16
6-Hydroxyhexanoic acid	60	0.63	0.014	0.026	0.016	0.029
6-Oxohexanoic acid	60	2.19 ^b	0.01	0.064	0.007	0.046
	150	69.2 ^b		0.043		0.030

^a Calculated from the data $\log A = 10.4$ and $E = 81.5$ kJ/mol [33]. ^b Calculated from the data $\log A = 3.7$ and $E = 15.05$ kJ/mol for butanal [34].

taneous increase in the relative concentration of adipic acid are observed with the increase in the depth of oxidation (Figs. 1 and 2, Table 2). This does not imply that the successive transformation of 6-hydroxyhexanoic acid to 6-oxohexanoic and adipic acids is of substantial importance. Oxidized cyclohexane contains adipic anhydride and monocyclohexyl adipate (Figs. 1 and 2). The formation of the latter is associated exceptionally with the alcoholysis of adipic anhydride by cyclohexanol [29, 30]. Because of this, the concentration of the ester reflects the amount of adipic anhydride formed. The latter is produced in parallel with adipic acid during the radical chain oxidation of 2-hydroxycyclohexanone, with adipic acid being formed in a larger amount than the anhydride [5, 19, 22, 28]. The buildup kinetics of adipic acid and monocyclohexyl adipate (Figs. 1, 2) suggest that a significant amount of adipic acid is produced from 2-hydroxycyclohexanone even at a low conversion of cyclohexane.

This assumption is also confirmed by evaluation calculation of the relative rates for the reaction of the cyclohexane oxidation products with cumyl peroxy radicals and *tert*-butyl peroxy radicals (Tables 3 and 4).

The rate of oxidation of an organic compound is defined by the equation $W_i = k_{pi}^{br}[C_i][RO_2^{\cdot}]$ and the rate normalized to the rate of oxidation of cyclohexane, by the equation $W_i/W_{ch} = k_{pi}^{br}[C_i]/k_{pch}^{br}[C_{ich}]$,

where k_{pi}^{br} and k_{pch}^{br} are the rate constants of the chain propagation reaction of the i th compound and cyclohexane, L mol⁻¹ s⁻¹, and C_i and C_{ch} are the concentrations of the product and cyclohexane, mol/L, respectively.

There is information on k_{pi}^{br} for cyclohexane and some of its oxidation products in reactions with cumyl and *tert*-butyl peroxy radicals (Tables 3 and 4). For 6-oxohexanoic acid, k_{pi}^{br} for butanal has been adopted [34]. For 6-hydroxyhexanoic acid, there are no data with these radicals [33]. It is known that partial rate constants of the reaction of a secondary hexadecyl peroxy radical with the α -CH bonds of 2-octanol and 1-decanol at 130°C are 20.7 and 15.1 L mol⁻¹ s⁻¹, respectively [33]. From these data, the ratio of the overall rate constants for primary and secondary alcohols will be $2 \times 15.1/1 \times 20.7 = 1.46$. To evaluate the rate of oxidation of 6-hydroxyhexanoic acid, k_{pi}^{br} equal to $1.46k_{pi}^{br}$ for cyclohexanol was used.

The consideration of the data of Tables 3 and 4 shows that in the case of uncatalyzed and cobalt naphthenate-catalyzed oxidation of cyclohexane ($\Delta RH = 0.6$ mol/L (~6 mol %)), 2-hydroxycyclohexanone present in the reaction medium is oxidized at a rate that is by an order of magnitude higher than that for 6-

hydroxyhexanoic and 6-oxohexanoic acids (Tables 3 and 4). Therefore, in the case of cyclohexane oxidation, the major amount of adipic acid is formed from 2-hydroxycyclohexanone.

The contribution from the radical chain oxidation reactions of 6-hydroxyhexanoic and 6-oxohexanoic acids to the formation of adipic acid in the case of oxidation of cyclohexane remains insufficiently clear. These acids accumulate in parallel in the cases of oxidation of cyclohexanone [20, 21] and 2-hydroxycyclohexanone [21] like in the case of oxidation of cyclohexane (Figs. 1, 2). Based on the investigation of the liquid-phase oxidation of 6-oxohexanoic acid, Agabekov et al. [35] arrived at the conclusion that this compound in the case of oxidation of cyclohexanone is a final product, not an intermediate.

REFERENCES

- I. V. Berezin, E. T. Denisov, and N. M. Emanuel, *The Oxidation of Cyclohexane* (Elsevier, Oxford, 2013).
- R. A. Sheldon and G. Franz, in *Ullmann's Encyclopedia of Industrial Chemistry* (Wiley-VCH, Weinheim, 2012), Vol. 25, p. 543.
- E. F. J. Duynstee and J. Hennekens, *Rec. Trav. Chim. Pays-Bas* **89**, 769 (1970).
- D. G. Hendry, C. W. Gould, D. Schuetzle, et al., *J. Org. Chem.* **41**, 1 (1976).
- A. L. Perkel', S. G. Voronina, and B. G. Freidin, *Russ. Chem. Rev.* **63**, 751 (1994).
- I. Hermans, J. Peeters, and P. A. Jacobs, *J. Phys. Chem. A* **112**, 1747 (2008).
- I. Hermans, P. Jacobs, and J. Peeters, *Chem. A Eur. J.* **13**, 754 (2007).
- I. Hermans, J. Peeters, and P. A. Jacobs, *Top. Catal.* **50**, 124 (2008).
- S. V. Puchkov, Yu. V. Nepomnyashchikh, E. S. Kozlova, and A. L. Perkel', *Polzunov. Vestn.*, No. 1, 190 (2013).
- W. A. Smit, A. F. Bochkov, and R. Caple, *Organic Synthesis: The Science behind the Art* (The Royal Society of Chemistry, Cambridge, 1998).
- Organic Solvents: Physical Properties and Methods of Purification*, Ed. by A. Weissberger (Interscience, New York, 1955).
- A. L. Perkel' and S. G. Voronina, *J. Anal. Chem.* **53**, 299 (1998).
- A. L. Perkel' and S. G. Voronina, *Vestn. KuzGTU*, No. 6, 80 (2014).
- A. L. Perkel', B. G. Freidin, and S. G. Voronina, *Zh. Anal. Khim.* **48**, 1697 (1993).
- A. L. Perkel', B. G. Freidin, S. G. Voronina, and R. L. Perkel', *Zh. Anal. Khim.* **48**, 1399 (1993).
- A. L. Perkel' and B. G. Freidin, *Zh. Anal. Khim.* **48**, 353 (1993).
- E. T. Denisov and I. B. Afanas'ev, *Oxidation and Anti-oxidants in Organic Chemistry and Biology* (CRC, Boca Raton, FL, 2005).
- S. V. Puchkov, E. G. Moskvitina, Yu. V. Nepomnyashchikh, and A. L. Perkel', *Russ. J. Phys. Chem.* **87**, 737 (2013).
- A. A. Akimov, S. V. Puchkov, Yu. V. Nepomnyashchikh, and A. L. Perkel', *Kinet. Catal.* **54**, 270 (2013).
- B. G. Freidin and A. L. Perkel', *J. Appl. Chem. USSR* **53**, 1257 (1980).
- A. L. Perkel', B. G. Freidin, and O. V. Borodina, *J. Appl. Chem. USSR* **58**, 2483 (1985).
- A. L. Perkel', G. M. Bogomol'nyi, R. V. Neginskaya, and B. G. Freidin, *J. Appl. Chem. USSR* **60**, 1493 (1987).
- J. D. Druliner, F. G. Kitson, M. A. Rudat, and C. A. Tolman, *J. Org. Chem.* **48**, 4951 (1983).
- T. S. Kotel'nikova, S. G. Voronina, and A. L. Perkel', *Russ. J. Appl. Chem.* **79**, 416 (2006).
- E. G. Moskvitina, S. V. Puchkov, I. M. Borisov, and A. L. Perkel', *Kinet. Catal.* **54**, 538 (2013).
- S. V. Puchkov, E. I. Buneeva, and A. L. Perkel', *Russ. J. Appl. Chem.* **75**, 248 (2002).
- S. V. Puchkov, Yu. V. Nepomnyashchikh, E. S. Kozlova, and A. L. Perkel', *Kinet. Catal.* **54**, 139 (2013).
- A. L. Perkel', *J. Appl. Chem. USSR* **62**, 1038 (1989).
- T. S. Kotel'nikova, O. A. Revkov, S. G. Voronina, and A. L. Perkel', *Russ. J. Appl. Chem.* **82**, 287 (2009).
- T. S. Kotel'nikova, O. A. Revkov, S. G. Voronina, and A. L. Perkel', *Russ. J. Appl. Chem.* **82**, 466 (2009).
- V. I. Timokhin, Extended Abstract of Doctoral Dissertation (Lvov, 1991).
- A. A. Akimov and A. L. Perkel', *Polzunov. Vest.*, No. 3, 63 (2009).
- Landolt-Börnstein, *Numerical Data and Functional Relationships in Science and Technology. New Series, Group II: Atomic and Molecular Physics*, vol. 13: *Radical Reaction Rates in Liquids* (Springer, Berlin, 1984), Subvol. D.
- L. A. Tavadyan, V. A. Mardoyan, and M. V. Musaelyan, *Int. J. Chem. Kinet.* **28**, 555 (1996).
- I. I. Korsak, V. E. Agabekov, and N. N. Mitskevich, *Izv. Akad. Nauk BSSR, Ser. Khim.*, No. 6, 28 (1974).

Translated by E. Boltukhina