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Stabilization of long-chain intermediates in solution. Octyl radicals and cations

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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- ► Rearrangements products distribution study of the long-chain radicals and cations.
- stabilization processes of 1-octyl radical.
- determined by Monte Carlo simulation

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- ▶ Monte Carlo simulation of the
- Ratio of homolitical rearrangements

ABSTRACT

The rearrangements of 1-octyl, 1-decyl and 1-tridecyl intermediates obtained from thermal lead(IV) acetate (LTA) decarboxylation of nonanoic, undecanoic and tetradecanoic acid were investigated experimentally through analysis and distribution of the products. The relationships between 1,5-, 1,6- and possibly existing 1,7-homolytic hydrogen transfer in 1-octyl-radical, as well as successive 1,2-hydride shift in corresponding cation have been computed via Monte-Carlo method. Taking into account that ratios of 1,5-/ 1,6-homolytic rearrangements in 1-octyl- and 1-tridecyl radical are approximately the same, the simulation shows very low involvement of 1,7-hydrogen rearrangement (1,5-/1,6-/1,7-hydrogen rearrangement = 85:31:1) in 1-octyl radical.

1,5-H[•](p=2, q=3)

1.6-H[•](p=1, q=4)

1,7-H[•](p=0, q=5)

benzene, 81 °C

1,5/1,6/1,7-H[•]=85:31:1

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1. Introduction

The 1,5- and 1,6-intramolecular hydrogen abstractions are the important stabilization pathways of primary flexible alkyl radical chain [1]. 1,5-Transposition of the radical center from carbon to the δ -carbon atom involves 1,5-hydrogen transfer, passing through a chair-like six-membered cyclic transition state I (Scheme 1), and seven-membered cyclic transition state in the case of 1,6-hydrogen atom abstraction [2].

1,4-Hydrogen migration, involving a five-membered cyclic transition state, is rare [1,3] but it was theoretically considered [1,4]. 1,7-Hydrogen atom abstraction by silvlmethyl radicals in aryl sulfones substrate is one stage of Fuchs' synthesis of alkenes [5]. Beside the most common 1,5- and 1,6-intramolecular homolytical rearrangements of long-chain primary alkyl radical, higher distance transfer of 1,10- and 1,11-type were proposed in mechanism for thermal peroxy-alkanoic acids decarboxylation [6]. The oxidative decarboxylations of saturated carboxylic acids, RCOOH, with lead(IV) acetate (LTA) (under thermal or UV-photolytic conditions, in different solvents) have been the subject of numerous studies which have shown that the major fragmentation products obtained in these oxidations were, usually, esters (i.e. acetoxyalkanes, ROAc, and carboxylates, ROCOR) and alkenes, R(-H), in addition to saturated hydrocarbons, RH, and phenylalkanes, RPh (when benzene was used as a solvent) [7,8]. Moreover, it was established that all these decarboxylation products are derived from the initial carbon centered radical fragment R[•] (which is generated in a free-radical chain process [8]) and the corresponding, subsequently formed (by one-electron oxidation), carbocation (R^+) , whereby the relative product distribution is dependent on structural features of the starting acid and reaction conditions.





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Scheme 1. 1,5-Hydrogen atom abstraction.

The formation of rearranged products can also be explained via 1,2-hydride shifts, known as successive rearrangement in the alkyl cations. Higher order rearrangements are not excluded (particularly 1,3-hydride shift) [9]. However, their possible participations do not influence significantly the product distribution.

Monte Carlo (MC) simulation is powerful method for determination of many parameters and for study of complicated processes, such as chain dimension evaluation [10], calculation of low-energy structures [11], simulation of consecutive metastable fragmentations [12], carbonium ion rearrangements [13] and optimization in the refinement of molecular structure parameters from gasphase electron diffraction data [14]. In order to better model magnetic field effects on radical pairs in homogenous solutions Monte Carlo approaches have recently been employed [15–18]. This paper deals with transfer of hydrogen and hydride in long chain alkyl intermediates such as 1-octyl, 1-decyl and 1-tridecyl radicals, obtained by LTA reaction of corresponding alkanoic acids [19]. The pathways of 1-octyl radical stabilization were analyzed by Monte Carlo simulation method. The yields of the products obtained experimentally were used as input data for Monte Carlo simulation.

2. Experimental

2.1. General remarks

The benzene, 1-phenyloctane, 1-phenyldecane, 1-phenyltridecane, 7-tridecanone, 1-, 2-, 3-, 4-octanol, 1-, 2-, 3-, 4-, 5-decanol, 1-, 2-, 3-, 4-, 5-, 6-tridecanol, nonanoic, undecanoic and tetradecanoic acid were commercial *p.a.* reagents (Sigma Aldrich, Fluka), dried and distilled just before use by conventional techniques. Purity of carboxylic acids was checked by GC analysis of their methyl esters, which were obtained by reaction of these acids with methanol in the presence of sulfuric acid as a catalyst.

The synthesis of 7-tridecanol was performed by reduction of 7-tridecanone with LiAlH₄ in dry Et₂O.

All acetoxyoctanes, acetoxydecanes and acetoxytridecanes were prepared from corresponding alcohols by the reaction with acetic anhydride in pyridine (the yields were 90–97%). Acetox-yalkanes were purified by preparative GC and their purity was checked by analytical GC and characterized by IR, ¹H and ¹³C NMR spectra.

Lead(IV) acetate (Sigma Aldrich) was recrystallized twice from glacial acetic acid containing 3% acetic anhydride, sucked dry in a Büchner funnel, and dried in a vacuum desiccators over potassium hydroxide.

Preparative GC: Varian Aerograph 920 gas chromatograph; the column consisted of CW20M; hydrogen was used as a carrier gas at inlet pressure of 0.18 MPa. Analytical gas chromatography (GC): Varian Model 3400 gas chromatograph and Perkin–Elmer F-11 gas chromatograph equipped with a flame ionization detector was used to measure the retention characteristics. Hydrogen was used as a carrier gas at different inlet pressure. The conditions for the separation of octenes and octane: 200 m long capillary glass column packed with Squalane (SQ), at 42 °C under 0.18 MPa H₂;

acetoxyoctanes: 100 m long capillary glass column packed with CW20M, at 130 °C under 0.25 MPa H₂ and 100 m long capillary glass column packed with CW20M, at 100 °C under 0.25 MPa H₂; phenyloctanes: 60 m long capillary glass column packed with CW20M, at 120 °C under 0.18 MPa H₂; acetoxydecanes: 100 m long capillary glass column packed with Carbowax 20M (CW20M), at 140 °C under 0.25 MPa H₂; decenes and decane: 100 m long capillary glass column packed with *O*-4-*n*-pentyloxybenzoyl oxime (PBO) liquid crystal in chloroform [20]; phenyldecane: capillary glass column packed with 4-methoxy-4'-ethoxyazoxybenzene (MEAB), at 130 °C under 0.18 MPa H₂, 20 m long; tridecene and tridecane: 100 m long capillary glass column packed with Cure on the decane: 100 m long capillary glass column packed with PBO liquid crystal, at 82 °C under 0.18 MPa H₂ [16]; acetoxytridecanes: 100 m long capillary glass column packed with CW20M, at 57 °C under 0.25 MPa H₂.

IR spectra: Perkin–Elmer FTIR spectrophotometer model Spectrum One.

NMR spectra: Varian Gemini 2000 NMR spectrometer at 200 MHz. Samples was analyzed as CDCl₃ solutions using tetramethylsilane (TMS) as internal standard.

GCMS analysis: the gas chromatograph (Varian Gas-Chromatograph Model 340, column packed with CW20M) was connected via an open split interface and a fused silica capillary (at 250 °C) to the ion source of a Finnigan MAT 8230 spectrometer; EIMS: ion source, 170 °C, 70 eV.

Reaction mixtures were first fractionated by preparative gas chromatography. Every fraction was analyzed by analytical gas chromatography and GCMS analysis. Reaction product (acetates, alkenes, phenylalkanes, etc.) were known compounds and were characterized and identified on the basis of the spectral data and/ or by comparison with authentic samples synthesized by independent routes.

2.2. Oxidative lead(IV) acetate decarboxylation of alkanoic acids

The thermal LTA decarboxylation in benzene was performed as described previously [21]. Mixture of 10 mmol of LTA and 10 mmol of alkanoic acids (nonanoic, undecanoic or tetradecanoic acid) was dissolved in 60 cm³ of benzene. Before starting the oxidative decomposition slow stream of purified Ar was introduced into stirred mixture of acid and LTA in benzene for 30 min at room temperature and in the absence of light. The oxygen-free mixture resulting from the above described procedure [21] was stirred and heated under reflux (without light protection) until completion (i.e. until disappearance of tetravalent lead which was monitored by potassium iodide/strach paper tracks) and then worked up.

After completion of the LTA oxidation, the mixture was cooled, treated with 50 cm^3 of diethyl ether and filtered off. The filtrate was washed with water, diluted HCl (1:1), aqueous Na₂CO₃ (5%) and water. After drying (CaSO₄), the solvents were removed under reduced pressure and the products in the residue were analyzed by analytical gas chromatography and separated by preparative gas chromatography. The results of all runs are given in Tables 1, 3 and 4.

Table 1

Product distribution (%) in LTA reaction with nonanoic (n = 8), undecanoic (n = 10) and tetradecanoic (n = 13) acid.^{a,b,c,d}

$C_nH_{2n+1}COOH \rightarrow C_nH_{2n+1}X + C_nH_{2n}$ Yield %				
	X = H	X = Ph	X = OAc	C_nH_{2n}
<i>n</i> = 8	17.33	39.80	16.90	15.84
<i>n</i> = 10	7.91	55.53	21.72	4.44
<i>n</i> = 13	12.70	50.67	12.37	11.61

^a Acid:LTA molar ratio = 1:1.

^b Solvent: benzene; temperature: 81 °C.

^c Yields calculated from analytical liquid-gas chromatograms.

^d For isomers see Tables 3 and 4.

Table 2

Homolytical rearrangement of long-chain 1-alkyl radicals

Radicals	Type of hydrogen atom abstraction		
	1,5-	1,6-	1,7-
1-tridecyl	<i>p</i> = 7	<i>p</i> = 6	<i>p</i> = 5
	<i>q</i> = 3	<i>q</i> = 4	<i>q</i> = 5
1-decyl ^a	<i>p</i> = 4	<i>p</i> = 3	p = 2
	<i>q</i> = 3	<i>q</i> = 4	<i>q</i> = 5
1-octyl	<i>p</i> = 2	<i>p</i> = 1	<i>p</i> = 0
	q = 3	q = 4	q = 5

^a 5-Decyl radical is formed by 1,5- and also by 1,6-hydrogen rearrangements of 1decyl radical.

Table 3

Relative yields (%) of acetoxy alkane products obtained by oxidative thermal LTA decarboxylation of nonanoic (n = 8), undecanoic (n = 10) and tetradecanoic (n = 13) acid.

$C_n H_{2n+1} OAc^a$			
	<i>n</i> = 8	<i>n</i> = 10	<i>n</i> = 13
1- 2- 3- 4- 5-	17.40 9.00 19.70 53.90	7.83 1.11 0.41 1.10 89.55	6.00 0.60 0.70 1.80 65.60
6-+7-			25.30

^a These numbers represent normalized values to 100%, overall yields of isomers are given in Table 1.

Table 4	
Relative yields (%) of alkene products obtained by oxidative thermal LTA deca	rbox-
vlation of nonanoic $(n = 8)$, undecanoic $(n = 10)$ and tetradecanoic $(n = 13)$ acid	

$C_n H_{2n}^a$			
	<i>n</i> = 8	<i>n</i> = 10	<i>n</i> = 13
1-	2.80	8.90	16.74
(Z)-2-	4.83	0.83	0.26
(E)-2-	18.59	1.39	0.51
(Z)-3- ^b	44.42	0.17	0.43
(E)-3- ^b		0.29	0.86
(Z)-4-	6.51	11.40	7.21
(E)-4-	22.86	33.37	22.40
(Z)-5-	-	10.01	9.45
(E)-5-	-	33.65	31.16
(Z)-6-	-	-	2.49
(<i>E</i>)-6-	-	-	8.50

^a These numbers represent normalized values to 100%, overall yields of isomers are given in Table 1.

^b (Z)- and (E)-3-octenes are partially separated. Roughly calculated ratio: 1:3.

2.3. Monte Carlo simulation

Fortran 90 generated the numbers uniformly distributed between 0 and 1 by using an intrinsic function called *RANDOM_NUM-BER* (*gamma*). The optional name "gamma" is defined by the user. It works according to the next algorithm:

- 1. Assume the transition probability p_{ij} for all intermediates. They have values between 0 and 1.
- 2. Then generate a start element **1a**.
- 3. By using intrinsic function RANDOM_NUMBER (gamma), the probability of formation any element is given.
- 4. It was assumed that the element *i* was created if the condition was satisfied $\sum_{k=1}^{i} p_k \leq \gamma$.
- 5. Points 3 and 4 are repeated until the final product is created.
- 6. The reaction is monitored with the probability assignment scheme.
- 7. The final outcome is the occurrence of any of the final products, A_{i} .
- 8. When it comes to the final product, element **1a** is generated again and so on with N replications, and the final product is counted, $A_i = A_i + 1$.

After N repetitions valid response is $\Sigma A_i = N$. Fractions of the final products of $f_i = A_i/N$ are compared with our experimental data (Experimental Section 2.2) and thus for all possible sets of probabilities p_{ij} . Finally, the probability p_{ij} is chosen so that the best fractions obtained agree with experimental data.

3. Results and discussion

Oxidative degradation of alkanoic acids by means of LTA under thermal conditions ($81 \,^{\circ}$ C) in benzene gives products as shown in Table 1. Beside these products, in this reaction carboxylates are also obtained. However, they are not analyzed by gas chromatography because of their long retention time. Distribution of the obtained alkanes, as well as acetoxyalkanes and alkenes, indicates the significance of homolytical rearrangements of 1-alkyl radical (Table 2).

Tetradecanoic acid gives 1-tridecyl radical as intermediate. Primary 1-trydecyl radical isomerizes by 1,5- and 1,6-homolytical rearrangement to more stable secondary 5- and 6-tridecyl radicals. 1-Tridecyl radical can be oxidized to 1-tridecyl cation, which can undergo 1,2-hydride shift isomerisation [22]. Beside oxidation of 1-tridecyl radical, there is a possibility that the rearranged tridecyl radicals can undergo oxidation and hydride shift isomerisation. One stabilization pathway of unrearranged tridecyl radical, used here as example, is shown in Scheme 2.

In this paper, particular attention was paid to the product distribution of isomeric alkenes and acetoxy alkanes in order to determine the involvements of 1,5- and 1,6-homolytic rearrangement of hydrogen in 1-tridecyl, 1-decyl and specially 1-octyl radical (Tables 3 and 4). Besides, it was interesting to estimate also the involvement of 1,7-rearrangement in these 1-alkyl radicals.

It has been considered that formation of acetoxy alkanes (Table 3) goes through acetylation of rearranged and unrearranged alkyl cations [22]. The formation of 7-tridecyl cation goes mainly through 6,7-hydride shift in 6-tridecyl cation. An interesting question here is if 7-tridecyl radical obtained by 1,7-homolytical rearrangement of 1-tridecyl radical is also a precursor of 7-tridecyl-cation. It has to be pointed out that formation of the 7-radical happens with less probability due to enthropic factor, in comparison with 1,5- and 1,6-hydrogen atom abstraction processes.

In Table 3 yields of 6- and 7-acetoxytridecane are given overall because chromatographic conditions for the separation of 6- and 7- isomers unfortunately have not been found.



Scheme 2. One stabilization pathway: oxidation of unrearranged and 1,5-rearranged tridecyl radical to corresponding cation and its hydride shift isomerisation.

Accordingly, 1-decyl radical undergoes the similar way of stabilization, giving isomeric acetoxydecanes (Table 3) and isomeric decenes (Table 4). The positions 5 and 6 are equivalent in unlabeled decyl system. Consequently, 1,5- and 1,6-rearrangement of primary decyl radical are not distinguishable. Therefore, the percentage yield of 5-acetoxydecane is comparable to the sum of percentage yield of 5-, 6- (and possibly existing 7-acetoxytridecane). The formation of 4-acetoxydecane is interesting, concerning the possibility of 1,7-homolytical rearrangement of 1-decyl radical, beside the process of hydride-type rearrangement (from 5-decyl cation mainly, and to a less extent from 1-decyl cation by successive 1,2-, 2,3-, 3,4-H⁻ transfers).

Decarboxylation of nonanoic acid gives 1-octyl radical **1a** (Scheme 3) which partially undergoes to corresponding cation **1b**. The radical isomerizes to form more stable secondary 5- and 6-octyl radicals **5a** and **6a** by 1,5- and 1,6-hydrogen atom abstraction, respectively (**5a**=**4a** and **6a**=**3a** in our system which is unlabeled).

The estimation of involvement of 1,7-hydrogen rearrangement in unlabeled substrate is complicated because the product of this process is 7-octyl radical **7a** which may be easily oxidized to 7-octyl cation **7b** (**7b**=**2b**), but also could be formed via 1,2-hydride shift of **1b** which is analog with process shown in Scheme 2. All octyl radicals are also subjected to oxidation to give isomeric octyl cations (Table 2).

Octyl radicals react also with benzene resulting in formation of phenyloctanes. The formation of 1-phenyloctane might be explained by oxidation of free radical intermediate II [8] (Scheme 4). From other phenyloctanes only 2-phenyloctane is detected ($\sim 2\%$ compared to 1-phenyloctane).

It is interesting that the percentage yield of 2-acetoxyoctane **2e** as well as 2-octenes **2f**, formed under thermolysis of lead(IV) nonanoate, is notably higher in comparison with analogous products obtained from undecanoic and tetradecanoic substrates. At first sight, it seems that 1,7-hydrogen atom abstraction in **1a** has significant contribution to product distribution. More acceptable explanation is as follows: 6-octyl radical **6a** (**6a**=**3a**), obtained by 1,6-hydrogen rearrangement, is primarily oxidized to 6-octyl cation **6b** (**6b**=**3b**), following with 3,2-hydride shift and resulting in formation of more stable **7b** (**7b**=**2b**) (Scheme 3). This mechanistic proposal is supported by higher expected ratio of 4-acetoxy/3acetoxyoctane than the one of 5-acetoxy/6-acetoxytridecane.

The stabilization pathway of **1a** is shown in Scheme 3. Intermediates and stable products nomenclature were taken in such way that numbering of carbon chain is started from the primary carbon atom previously carrying radical center. Unfortunately, the system is not labeled. Identical products from different pathways of stabilization are hardly distinguished, e.g. 5-octyl cation **5b** gives 4-acetoxyoctane **4e** in an unlabeled system.

Since in all LTA reactions toluene is present in reaction mixtures as a result of decarboxylation of acetic acid itself, methyl radical might contribute ratio of octyl radicals. Although, its contribution is expected to be in less extent, still it was taking into account (see Scheme 3, path presented by interrupted line).

Monte Carlo method is useful for quantitative estimation of the products and intermediates which is not distinguishable by an experiment (e.g. **2e** and **7e**, **3e** and **6e**, **4e** and **5e**).

Algorithm and program in this paper are easily adaptable for different carbon chain lengths, thus including all the processes in the given reaction. Using MC simulation it is possible to efficiently and quickly (much faster than the time needed for isotopic marked substrates preparation and analyze more complex mixture of the products) investigate the impact of some factors on the concentration of intermediates and final products, as well as to evaluate the stability and relationship between all the products.

To estimate relative rates of 1,5-, 1,6- and possibly existing 1,7homolytic transfer of hydrogen in **1a**, the product analysis and product distribution were performed by MC simulation method. The final yields of the stable products or their fractions were determined experimentally. As the carbon skeleton was not labeled, some intermediates and products are the same, such as **2b** and **7b**, **3b** and **6b**, **4b** and **5b**.

Scheme 3 presents **1a** stabilization processes. All intermediates branch to the next, previous one (except to **1a**) or end product. These branches of intermediates have fractions. The condition that the sum of all fractions from an intermediate equals to 1 must be satisfied.

Therefore, these fractions can be treated as probability of forming an intermediate from another one, or some final product.

Let us separate and analyze "element **3b**" and present it in Scheme 5. From Schemes 3 and 5 it can be seen that element **3b** arises from elements **2b**, **4b** and **3a**, while the considered element forms elements **2f**, **3f**, **4b**, **3e** and **2b**.

Input arrows show forming of "element **3b**", while output arrows show forming of its products. Corresponding forming probabilities are presented with p_{ii} .

If element **3b** was occurred, then elements **2f**, **3f**, **4b**, **3e** and **2b** are formed with corresponding probabilities. The probability that



^aExperimentally obtained yields (%)

^bCalculated yields (%)

a-radicals; b-cations; c-phenylalkane; d-alkane; e-acetates; f-alkenes

The numbers along interrupted line reflex the probability of formation of secondary octyl radicals from octane and methyl radical

Scheme 3. Monte Carlo (MC) simulation of octyl radical stabilization processes.



Scheme 4. Formation of 1-phenyloctane.

element **2f** arises from element **3b** is p_{3b2f} . All probabilities which describe element **3b** were presented in Scheme 5, where following expression is valid $p_{3b2f} + p_{3b3f} + p_{3b2b} + p_{3b3e} + p_{3b4b} = 1$.

Thus, the idea of applying MC method for simulation the reaction of octyl radical or octyl cation isomerization was clear. For that reason, a program code was written to simulate the given transfer probabilities of all "intermediates" in the proposed simple model reaction.

Considering the values obtained by MC simulation, it is important to point out that ever experimental value has to be equal to the sum of MC simulated values concerning the pseudoisomeric products (e.g. **2e** plus **7e** = 2.39 what is in very good agreement with experimental value of 2.32 for **2e**, but not in the case of **2f**; **2f** plus **7f** = 3.33 while experimental value is only 1.93).

First, 1,5- and 1,6-homolytic rearrangements appeared to be the most interesting process. 5- and 6-Octyl radicals, **5a** and **6a**, generated in this way undergo further oxidation, giving 5- and 6-octyl cations **5b** and **6b**. 5- and 6-Acetoxyoctanes (**5e** and **6e**), as well as (Z/E)-4-, 5- and 6-octenes **4f**, **5f** and **6f** are the products of their final stabilization (appeared as **4f**, **3f** and **2f**). It is supposed that the ratio of 1,5- and 1,6-transposition in **1a** is very similar to corresponding rearrangement in 1-tridecyl radical.



Scheme 5. Element 3b.

Octane **1d** is also a product of LTA oxidative decarboxylation of nonanoic acid, rationalized in terms of intermolecular hydrogen abstraction. This scheme is simplified and does not include the process of **1a** disproportionation because of the restriction imposed by the nature of MC simulation applied in this experiment in order to distinguish different pathways in obtaining the above mentioned products.

Primary **1a** is also the subject of oxidative transformation to obtain the **1b**, which is partially decomposed by 1,2-successive hydride shift. Besides, **1e** and **1f** which belong to non-rearranged products, there are also additional acetoxy alkanes (**2e** and **3e**) and alkenes ((Z/E)-**2f**, (Z/E)-**3f**) as rearranged products.

It is very interesting to analyze the existing "7-octyl radical" **7a** resulting from 1,7-homolytical rearrangement of **1a**. Unfortunately, 1,2-hydride shift in the 1-octyl cation is probably the main contributor for its formations. Therefore, determination of contribution of 1,7-homolytic rearrangement is difficult task in this length of the carbon chain. However, MC simulation of stabilization of the 1-octyl radical enables estimation of relative ratios of 1,5-, 1,6- and 1,7-hydrogen abstraction (1,5-/1,6-/1,7-hydrogen abstraction = 85:31:1).

4. Conclusions

By using one simple scheme of stabilization of 1-octyl radical obtained by LTA decarboxylation of nonanic acid, and MC method, it was possible to determine the relative ratios of different type of its stabilization. This methodology differentiates isomeric products in this unlabeled system where some intermediates as well as products are the same even they were obtained from different stabilization pathways. Input data for MC simulation were based on the relative ratios of the specific products obtained experimentally. The 1-octyl radical represents an interesting intermediate, particularly due to the increased possibility for its transformation into relative stable 2-octyl systems, in comparison with corresponding 1-decyl and 1-tridecyl system. The relationships between 1,5-, 1,6and possibly existing 1,7-homolytic hydrogen transfer in 1-octylradical, as well as successive 1,2-hydride shift in corresponding cation have been computed via Monte-Carlo method. Taking into account that ratios of 1,5-/1,6-homolytic rearrangements in 1-octyl- and 1-tridecyl radical are approximately the same, the simulation shows very low involvement of 1,7-hydrogen rearrangement (1,5-/1,6-/1,7-hydrogen rearrangement = 85:31:1) in 1-octyl radical.

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