ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 6, pp. 1047–1059. © Pleiades Publishing, Ltd., 2013.
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Oxidation of Alkylarene C–H Bonds by *tert*-Butyl Hydroperoxide in the Presence of Cobalt, Chromium, and Vanadium Acetylacetonates

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Received May 14, 2012

Abstract—Cobalt, chromium, and vanadium acetylacetonates catalyze efficient hydroperoxide oxidation of alkylarenes under mild conditions (20°C). The process takes place with either conservation, or destruction of carbon backbone of the hydrocarbon. Oxidizing agents are oxygen generated in the system, as well as *tert*-butylperoxy radicals. In the formation of end products alkylperoxy radicals originating in the substrates, *tert*-butylperoxy radicals, as well as metal-containing peroxides are involved. For the oxidative degradation processes a recombination reaction of the alkylperoxy radicals is suggested with the intermediate formation of 1,2-dioxetanes.

DOI: 10.1134/S1070363213060078

The main products of reactions of *tert*-butyl hydroperoxide (**I**) with cobalt, chromium, or vanadium acetylacetonate [$(acac)_2Co$ (**II**), $(acac)_3Cr$ (**III**) and $(acac)_2VO$ (**IV**)] in C_6H_6 at 20°C are *tert*-butanol and oxygen [1–3]. It was shown by the examples of the oxidation of anthracene, 9,10-dimethylanthracene, and phenylethenes that the acting agents were oxygen generated in the system, metal-containing trioxides, and peroxy radicals. Oxidative intermediates of different nature may be involved in parallel reactions with the same reagent [4].

Acetylacetonates of transition metals are known to catalyze the processes of hydroperoxide functionalization of organic compounds. Chromium acetylacetonate is a catalyst of stereoselective epoxidation under mild conditions, but at higher temperature allyl methylene group is oxidized to the hydroxy and keto groups [5]. Hydrogen peroxide or *tert*-butyl hydroperoxide oxidize secondary and allyl alcohols [6, 7] and epoxidized alkenes in the presence of vanadyl acetylacetonate [8].

Acetylacetonates **II**–**IV** in combination with hydroperoxides oxidize or catalyze oxidation of hydrocarbons. Hydroperoxide **I** converts alkanes to ketones at the catalysis by cobalt, chromium, or vanadium acetylacetonates (50–80°C) [9]. The products of functionalization of cycloalkanes (90°C) are alcohols, *tert*-butylperoxycycloalkanes and, to a lesser extent, ketones [1]. The research on the use of derivatives of these metals in the process of oxidation with peroxides continues [10, 11]. However, the data on the oxidation of C–H bonds are insufficient. The schemes of formation of products are either absent or include the step of homolytic and molecular transformations. According to [12], in the decay of cumyl hydroperoxyde in ethylbenzene (45°C) in the presence of **II** the proportion of molecular pathway reaches 40%. The main product of transformation of hydroperoxide is $PhCMe_2OH$, the corresponding alcohol from ethylbenzene is not found, and the unidentified substance (~30%) was assumed to be an ether, although in no way confirmed. Based on this scheme, it should be the ether of the composition $PhC(Me)_2OCH(Me)Ph$.

In this paper we investigated the reactions in the systems of *tert*-butyl hydroperoxide-acetylacetonate **II**–**IV** with alkylarenes containing methylene and methine C–H bonds, in order to reveal the nature of oxidizers, transformation of intermediates to final products, and the effect of the metal nature. As starting compounds ethyl-, isobutyl-, and *sec*-butylbenzenes were selected. Reactions were carried out in the environment of the corresponding alkylarene at room temperature, at the 15:1 molar ratio of hydroperoxide **I**

Table 1. The products of alkylarene (PhR) oxidation by *tert*-butyl hydroperoxide in the presence of acetylacetonates of cobalt (**II**), chromium (**III**), and vanadyl (**IV**) (molar ratio of 15:1, 20°C, in moles per 1 mole of hydroperoxide)

Reaction products[a]	R = CH_2CH_3			R = $CH_2CH(CH_3)_2$		R = $CH(CH_3)C_2H_5$		
	II	**III**	**IV**	**II**	**III**	**II**	**III**	**IV**
PhCHO	0.01	0.05	Traces	0.20[b]	0.10[b]	–	–	–
Ketone	PhCOMe			PhCOPr-*i*		PhCOMe		
	0.31	0.47	0.27	0.27	0.24	0.35	0.21	0.15
Alcohol	PhCH(OH)Me			PhCH(OH)Pr-*i*		PhC(OH)(Me)Et		
	0.20	0.22	0.16	0.08	0.04	0.14	0.25	0.13
Hydroperoxide	PhCH(OOH)Me			PhCH(OOH)Pr-*i*		PhC(OOH)(Me)Et		
	0.04	0.05	–	–	–	0.03	0.17	0.07
Peroxide	PhCH(Me)OOBu-*t*			PhCH(Pr-*i*)OOBu-*t*		PhC(Me)(Et)OOBu-*t*		
	0.35	0.10	0.08	Not identified		0.22	0.06	0.09
Products	HCOOH		[c]	Me_2CO		CH_3COOH		[c]
of oxidation of R	0.04	0.05		0.09	0.10	0.16	0.18	
t-BuOH[d]	0.69	0.77	0.64[e]	0.70	0.78	0.75	0.83	0.46[e]
H_2O	0.15	0.21		0.24	0.22		0.29	

[a] The averaged results. [b] Found 0.06 and 0.02 mol of benzoic acid, respectively. [c] Up to 3 moles of acetic acid and 1.47 moles of CO_2 were identified, pyruvic acid and *tert*-butyl acetate, formed by oxidation of the acetylacetonate ligand [3] were determined qualitatively. [d] In addition, 0.01 to 0.04 mol of *tert*-butyl peroxide and 0.03 to 0.13 mol of starting hydroperoxide were identified. [e] Also 0.12 and 0.21 moles of acetone in the case of ethylbenzene, and *sec*-butylbenzene were defined, respectively.

to the metal acetylacetonate. The reactions in the presence of **IV** are exothermic, the appearance of the wine-red color during the first 10–15 min indicates the intermediate formation of vanadium peroxy compounds [3]. The results are shown in Table 1.

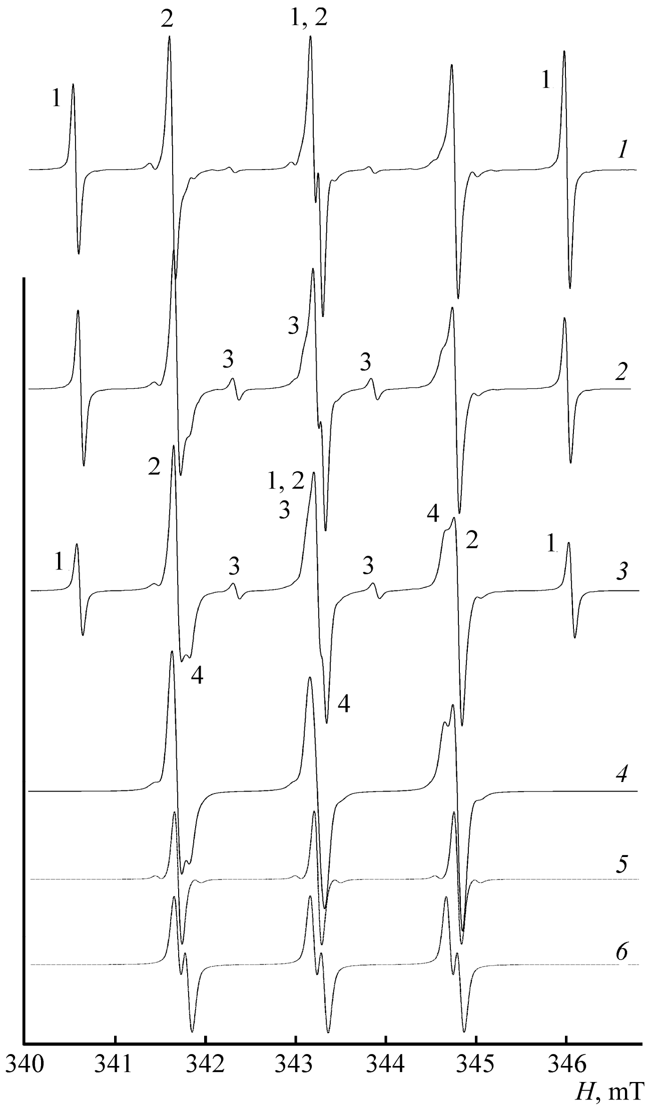
As seen from Table 1, the preferential oxidation occur at the α-C–H bonds. The composition of products suggests that the processes taking place include both conservation and destruction of the alkylarene. The first trend prevails in the hydrocarbons containing benzyl fragment, the second, in the case of *sec*-butylbenzene. The maximum product yield (0.69–0.90 mol with respect to the original hydroperoxide) was registered in the case of acetylacetonates **II** and **III**. The highest rate of accumulation of the products of ethylbenzene oxidation in the case of alkoxide **II** is observed within 1 h, with a maximum decrease in the concentration of organic peroxide, within 2 h. The reaction of ethylbenzene catalyzed by compound **IV** proceeds to 70–80% in the first 40–50 min. In the case of the chromium derivative **III** the process is completed within few days. The hydroperoxide is reduced to *tert*-butanol.

The reactions of the system of alkoxides **II-IV** - hydroperoxide **I** in alkylarenes in the presence of spin traps 2-methyl-2-nitrozopropane and C-phenyl-N-*tert*-butylnitrone were studied by the ESR method. All spectra were recorded at room temperature. The ESR spectrum of *sec*-butylbenzene after the addition of 2-methyl-2-nitrosopropane in 5 min after mixing the reagents contained two triplets (Fig. 1). A triplet (1:1:1) with $g_i = 2.0056$ and $a_N = 2.72$ mT belongs to 2-methyl-2-nitrosopropane adduct with the *tert*-butoxy radical *t*-BuON($O^•$)Bu-*t* (1) [13]. A triplet with g_i = 2.0060 and hyperfine coupling constant $a_N = 1.54$ mT and $a(^{13}C) = 0.43$ mT belongs to the spin-trap adduct with tertiary 2-phenylbutyl radical PhC(Me)(Et)N($O^•$) Bu-*t* (2). The intensity of signal (1) falls with time. After 30 minutes, along with the peaks of the adducts 1 and 2 a minor triplet (3), $g_i = 2.0068$, $a_N = 0.78$ mT was fixed corresponding to to an unidentified acyl-*tert*-butylnitroxyl radical, and a poorly resolved signal 4 appears of an adduct, whose structure was established by simulating the spectra of spin-adducts 2 and 4 (see figure, curves *3*–*6*). The triplet of doublets 4 with the g_i = 2.0060 and hyperfine coupling constants a_N =

1.50 mT and a_H = 0.12 mT belongs to an adduct of the spin trap with a secondary radical. We suggest that here is fixed the PhCN(Me)(HC$^{\bullet}$Me) radical. However, the signal intensity of the [PhCH(Me)CH(Me)· N(O$^{\bullet}$)Bu-*t*] (4) is much weaker than that of 2.

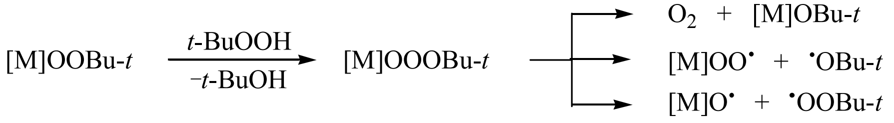
In 20 min after mixing vanadyl **IV** with hydroperoxide **I** (molar ratio 1:2) in ethylbenzene in the presence of 2-methyl-2-nitrosopropane two signals of the eight lines were recorded, characteristic of V^{+4}: g_i = 1.9721, a_V = 10.83 mT and g_i = 1.9741, a_V = 9.63 mT, and a triplet of di-*tert*-butylnitroxyl (g_i = 2.0061, a_N = 1.54 mT). At increasing the amount of the hydroperoxide to 10 moles all the signals disappear. Adding *C*-phenyl-*N*-*tert*-butylnitron to the system under study (15:1), followed by degassing of the solution leads to the ESR spectrum of two separate signals: a triplet of doublets and a triplet. The main triplet of doublets with g_i = 2.0062 and hyperfine coupling constants a_N = 1.330 mT and a_H = 0.108 mT, corresponds to the spin-adduct of α-phenylethylperoxy radical PhCH[OOCH(Me)Ph][N(O$^{\bullet}$)Bu-*t*] [13]. The triplet signal (1:1:1), according to the values of its isotropic parameters [g_i = 2.0071 and a_N = 0.79 mT] refers to the benzoyl-*tert*-butylnitroxy radical PhC(O)· N(O$^{\bullet}$)Bu-*t*, which is formed by oxidation of the spin trap by either singlet oxygen or peroxy radicals. The signals of V^{4+} are absent.

An identical ESR spectrum was recorded at the oxidation of ethylbenzene with the system hydroperoxide **I**–alkoxide **II** in the presence of *C*-phenyl-*N*-*tert*-butylnitrone. This observation confirms the presence of α-phenylethyl radical in the systems and its interaction with oxygen. In the latter case, the shape of the spectrum and intensity of the signal does not change during 2 h, indicating the generation of the PhCH(OO$^{\bullet}$)Me radical in the course of time. The data of ESR spectroscopy indicate homolytic nature of the processes of oxidation. In addition, in the reaction products of ethyl- and *sec*-butylbenzene dimers were detected of α-alkylbenzyl radicals, 2,3-diphenylbutane and 3,4-dimethyl-3,4-diphenylhexane, obtained, probably in the late stages of interaction, after consumption of the most of oxygen.



ESR spectrum, recorded in the course of oxidation of *sec*-butylbenzene by *tert*-butyl hydroperoxide in the presence of cobalt acetylacetonate (15:1, 20°C), the spin trap is 2-methyl-2-nitrosopropane: (*1*) 5 min after mixing the reagents, (*2*) after 30 min (*3*) after 65 minutes, (*4*) superposition of simulated spectra 2 and 4, (*5*) simulated spectrum 2 (*6*) simulated spectrum 4. Degassed sample. The numbers in the figure correspond to the numbers of the adducts.

The oxidizer for the C–H bonds is oxygen generated by the studied systems through the stages of formation of the metal peroxides and trioxides [3, 4]. We suggest that the process is initiated by the oxygen-containing radicals formed at the decomposition of the trioxide, by analogy with the reactions of hydroperoxide **I** with aluminum, titanium, and vanadium *tert*-butoxides [13–15] [scheme (1)].



$$\text{[M]OOBu-}t \xrightarrow[-t\text{-BuOH}]{t\text{-BuOOH}} \text{[M]OOOBu-}t \longrightarrow \begin{cases} O_2 + \text{[M]OBu-}t \\ \text{[M]OO}^{\bullet} + {}^{\bullet}\text{OBu-}t \\ \text{[M]O}^{\bullet} + {}^{\bullet}\text{OOBu-}t \end{cases} \quad (1)$$

M = (acac)$_2$Co, (acac)$_2$Cr, (acac)V(O).

$$\mathrm{PhCH(R)R' + XO^{\bullet} \longrightarrow Ph\dot{C}(R)R' \xrightarrow{O_2} PhC(OO^{\bullet})(R)R'} \qquad (2)$$

R = H, R' = Me; R = H, R' = *i*-Pr; R = Me, R' = Et. X = *t*-Bu, *t*-BuO, $(acac)_2M$, $(acac)_2MO$; M = Co, Cr, V.

The carbon centered radicals are converted into peroxy radicals [Eq. (2)].

Peroxy radicals split off hydrogen and transformed into hydroperoxides, which were identified by reaction with triphenylphosphine by the increase in the yield of alcohol. However, the amount of hydroperoxide is small (Table 1). The main direction of transformation of α-benzylperoxy radicals is disproportionation along the scheme of Russell [16] [Eq. (3)].

$$\mathrm{2PhCH(OO^{\cdot})R \rightarrow PhCH(OH)R + PhCOR + O_2}, \qquad (3)$$

R = Me, *i*-Pr.

The yield of ketones in the oxidation of ethyl- and isobutylbenzene 1.5–3 times exceeds the yield of alcohol. It is shown that a possible way of increase in the amount of ketone due to further oxidation of alcohol, at least in the systems of alkoxide (**II, III**)-hydroperoxide **I**, is unlikely because of the low rate of this process.

A recently published paper [17] on the thermal (150°C) oxidation of ethylbenzene experimentally and by theoretical calculations revealed the mechanism explaining the predominant formation of ketone. It was shown that the source of both acetophenone and 1-phenylethanol is 1-hydroperoxy-1-phenylethane. The α-phenylethylperoxy radical reacts with the α-hydrogen of hydroperoxide 10 times faster than with the parent alkylarene. In the reaction cage both ketone and hydroxy radical are formed. The interaction of the latter with alkylarene leads to release of water. Similar processes may occur in the studied reactions [scheme (4)].

$$\begin{aligned}&\mathrm{PhCH(OO^{\cdot})R + PhCH(OOH)R \rightarrow PhCH(R)OOH}\\ &\qquad\qquad\mathrm{+\ PhC^{\cdot}(OOH)R},\\ &\qquad\mathrm{PhC^{\cdot}(OOH)R \rightarrow PhCOR + HO^{\cdot}}, \qquad (4)\\ &\qquad\mathrm{SH + HO^{\cdot} \rightarrow H_2O + S^{\cdot}}\end{aligned}$$

The ethers predicted in [12] were not detected. Since to the moment of formation of hydroperoxides from alkylarene all cobalt is transformed in Co^{3+} state [4], the ternary complexes $[Co(acac)_2{\cdot}ROOH{\cdot}EtPh$; R = *t*-Bu, PhCH (Me)], responsible for the molecular pathway of formation of the 1-phenyletan-1-ol and ethers, are absent. However, among the reaction products unsymmetrical dialkylperoxides were found, formed either in the reaction of alkylaryl radicals with the *tert*-butylperoxyl, or as a result of dimerization of two alkylperoxy radicals [Eqs. (5), (6)]. For example:

$$\mathrm{PhC^{\cdot}H(Me) + \mathit{t}\text{-}BuOO^{\cdot} \rightarrow PhCH(Me)OOBu\text{-}\mathit{t}}, \qquad (5)$$

$$\begin{aligned}&\mathrm{PhCH(OO^{\cdot})Me + \mathit{t}\text{-}BuOO^{\cdot}}\\ &\mathrm{\rightarrow PhCH(Me)OOBu\text{-}\mathit{t} + O_2}. \qquad (6)\end{aligned}$$

The oxidation of isobutyl- and *sec*-butylbenzene by the systems alkoxide **II–IV**–hydroperoxide **I**, leading to the formation of products with the conservation of the carbon skeleton, can be described by the above equations. However, in the case of *sec*-butylbenzene, the tertiary alkylperoxy radical **A** is not able to disproportionation by the Russell scheme. According to generally accepted views, its dimerization through a tetraoxide should lead to the alkoxy radical, which is further converted into alcohol [scheme (7)].

$$\begin{aligned}&\mathrm{2PhC(Me)(Et)OO^{\cdot} \rightarrow \underset{\mathbf{A}}{[PhC(Me)(Et)OO]_2}}\\ &\xrightarrow[-\mathrm{O_2}]{} \underset{\mathbf{B}}{\mathrm{2PhC(Me)(Et)O^{\cdot}}} \xrightarrow[-2\mathrm{S^{\cdot}}]{\mathrm{SH}} \mathrm{2PhC(Me)(Et)OH}. \qquad (7)\end{aligned}$$

Along with the expected tertiary alcohol and the corresponding hydroperoxide acetophenone was detected formed in the yield close or significantly higher than the yield of the alcohol (Table 1). Besides these compounds acetaldehyde and acetic acid were found. The products of splitting backbone were identified also at the oxdidation of isobutylbenzene (benzaldehyde, acetone) and in small quantities in the reaction with ethylbenzene (benzaldehyde, formic acid). Their formation can be explained by β-decay of alkoxy radicals [Eq. (8)] followed by oxidation of alkyl radicals, or by their interaction with the arene.

$$\mathrm{PhCH(O^{\cdot})R \rightarrow PhCHO + R^{\cdot}}, \qquad (8)$$

R = Me, *i*-Pr.

In trace amounts methylethylbenzene and *sec*-butylethylbenzene, the latter in the reaction with *sec*-butylbenzene, were identified by gas chromatography-mass spectrometry.

The decomposition of tertiary alkoxy radical **B** according to Eq. (8) should lead to acetophenone. The second possible ketone, ethylphenylketone, was

Table 2. The products of 1,1-diphenylalkanes Ph_2CHR oxidation by *tert*-butyl hydroperoxide in the presence of cobalt (**II**), chromium (**III**), and vanadyl (**IV**) acetylacetonates (molar ratio of 10:30:1, benzene, 20°C, in moles per 1 mole of unreacted hydrocarbon)

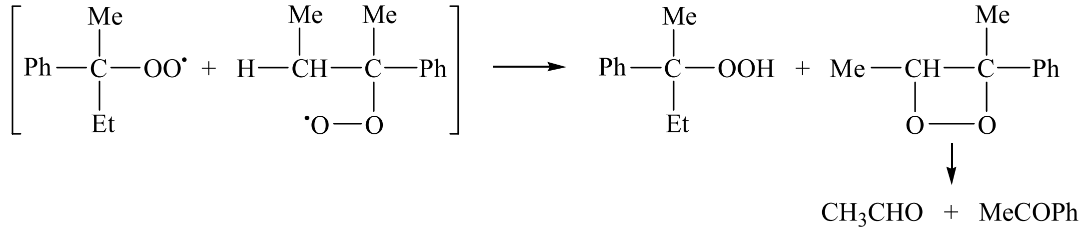
Reaction products[a]	R = Me			R = Et		
	II[b]	**III**[b]	**IV**[b]	**II**[c]	**III**[c]	**IV**[c]
$Ph_2C(OOH)R$	0.18	0.25	0.13	0.26	0.24	0.28
$Ph_2C(OH)R$	0.51	0.47	0.47	–	–	0.01
Ph_2CO	0.05	0.08	0.01	0.60	0.63	0.05
PhCOR	0.12	0.16	0.10	0.06	0.07	0.05
R'COOH	0.07[d]	0.09[d]	[f]	0.50[д]	0.62[e]	[f]

[a] The averaged results. [b] The degree of conversion for Ph_2CHMe for **II** and **III** 70%, for **IV** 30%. [c] The degree of conversion of Ph_2CHEt in the reactions with alkoxylates **II–IV** is 30, 40, and 42% respectively. [d] R' = H, also was identified formaldehyde. [e] R' = Me, also was identified acetaldehyde. [f] A mixture of acids due to the oxidation of the radical R and the acetylacetonate ligand [3].

detected in amounts less than 0.01 mol. However, it is know that the processes of degradation of alkoxy radicals usually occur at an elevated temperature. According to [17], 1-phenylethoxy radical at 150°C is converted to 90% into alcohol and only to 10% it undergoes β-decay. The studied reaction takes place at 20°C, so the decay of the radicals is hardly probable.

It can be assumed that the presence of the compounds of transition metal with variable valence will contribute to the latter pathway. In particular, the decomposition of tertiary butoxy radical to acetone in the reaction of vanadyl acetylacetonate with *tert*-butyl hydroperoxide in benzene was noted [3], as well as at the oxidation of ethylbenzene by the system of vanadium tetra-*tert*-butoxide–*tert*-butyl hydroperoxide [15]. Further studies showed that this process is caused by inorganic vanadium derivatives produced in the reactions with hydroperoxide **I**. In the reactions of this hydroperoxide with cobalt or chromium acetylacetonates in an unoxidizable solvent, benzene, acetone either was not detected or was found in trace amounts.

Based on the foregoing, we suggest that carbonyl compound is formed not due to β-decay of alkoxyl radical, but as a result of intracage recombination of the alkylperoxy radical. Attack of the latter on the β-CH bond of another radical should lead to hydroperoxide and dioxetane. Hydroperoxide then reacts with the metal alcoxylate, while dioxetane decomposes to carbonyl compound. By an example of the tertiary peroxy radical **A** the process can be represented by Eq. (9).



(9)

Acetaldehyde was identified as 2,4-dinitrophenylhydrazone, but it is mostly oxidized to acid.

Equation (9) explains the virtual absence of phenyl ethyl ketone in the products of oxidation of *sec*-butylbenzene. Of the two possible C–H bonds (methylene and methyl), the peroxy radical should attack the CH_2 group, owing to the lower binding energy and the greater stability of the secondary radical. The recombination of the peroxy radicals derived from isobutylbenzene, according to Eq. (9), explains the formation of benzaldehyde and acetone. The extremely small amounts of benzaldehyde and formic acid in the case of ethylbenzene are also consistent with this equation.

In order to prove the assumed recombination of alkylperoxy radicals, we performed the oxidation of alkylarenes containing a tertiary carbon atom (1,1-diphenylethane and 1,1-diphenylpropane) by the hydroperoxide **I**–acetylacetonate **II–IV** systems. The reactions were carried out in benzene at room temperature. Molar ratio of metal alkoxide–alkylarene was 1:10, alkylarene-hydroperoxide, 1:3. The results are shown in Table 2.

The composition of products suggests that the oxidation of diphenylalkanes also takes place both with preservation and with the destruction of the carbon backbone. The first direction results in the formation of hydroperoxides and alcohols. The formation of the latter is represented by Eqs. (2) and (7). Splitting off of hydrogen by peroxide and alkoxy radicals can take place from the solvent and hydroperoxie [Eq. (10)].

$$Ph_2C(Me)O^{\bullet} + \begin{cases} \xrightarrow{SH} Ph_2C(Me)OH + S^{\bullet} \\ \xrightarrow{t\text{-}BuOOH} Ph_2C(Me)OH + t\text{-}BuOO^{\bullet} \end{cases} \qquad (10)$$

However, the formation of the tertiary alcohol in a high yield (up to 0.5 mole per 1 mole of reacted alkylarene) was found only in the transformation of 1,1-diphenylethane.

It should be noted that the second direction at the oxidation of phenylalkanes is predominant in the case of 1,1-diphenylpropane. The main identified products of splitting the alkylarene backbone are benzophenone, phenyl alkyl ketone and aldehydes (formaldehyde, acetaldehyde), as well as the corresponding carboxylic acids. The formation of benzophenone and aldehydes can be explained by the decomposition of alkoxy radicals $Ph_2C(O^{\bullet})R$ according to Eq. (8). It is known [18] that at the decay of the alkoxy radicals the most stable radical, ethyl in these reactions, is split off. But in the case of 1,1-diphenylpropane the tertiary alcohol is absent, hence the alkoxy radicals $Ph_2C(O^{\bullet})Et$ have not been formed. The benzophenone yield reaches up to 0.60 mole per 1 mole of reacted alkylarene. That is, the processes described by Eqs. (7) and (8) have no place in the case of 1,1-diphenylpropane. The formation of carbonyl compounds is due to the recombination of alkylperoxy radicals according to Eq. (9). Dioxetane is decomposed to benzophenone and acetaldehyde, the oxidation of the latter resulted in acetic acid. Nearly equimolar amounts of benzophenone and acetic acid were obtained. The hydroperoxide enters into a subsequent reaction with the metal alkoxylate.

The probability of reaction (9) of the peroxy radical formed from 1,1-diphenylmethane is obviously much lower, since the CH binding energy is greater in the methyl than in the methylene group (104.8 and 96.9 kcal mol^{-1}, respectively [19]). Therefore, the degree of recombination of peroxy radicals $Ph_2C(Me)OO^{\bullet}$ is low. The main direction is their transformation into the alkoxy radicals responsible for the formation of tertiary alcohol [Eqs. (7), (10)].

Besides the benzophenone other phenyl alkyl ketones, acetophenone and ethyl phenyl ketone were found (Table 2). The presence of the ketones in the oxidation products of 1,1-diphenylalkanes can be explained by the rearrangement and the subsequent decomposition of the alkylperoxy radicals or the metal peroxides, at least in the case of cobalt and vanadium acetylacetonates [Eqs. (11), (12)] by an example of Ph_2CHMe].

$$Ph_2C(Me)OO \longrightarrow [PhC^{\cdot}(Me)OOPh] \\ \rightarrow PhCOMe + [PhO^{\cdot}], \qquad (11)$$

$$(acac)_2CoOOCPh_2(Me) \\ \longrightarrow (acac)_2CoOC(Me)(Ph)OPh \\ \rightarrow (acac)_2CoOPh + PhCOMe. \qquad (12)$$

In all cases, phenol was detected in an amount not exceeding 0.01 mol, perhaps, due to the oxidation during the reaction. An indirect confirmation may be the yellow color of the organic phase of the reaction product hydrolyzate, regardless of the used metal derivative.

The degree of conversion of 1,1-diphenylethane under identical conditions is from 1.5 to 2 times higher than in the case of 1,1-diphenylpropane. This is consistent with the relative reactivity of tertiary C–H bonds of these hydrocarbons in the oxidation reactions (1.37 and 0.63, respectively) [20].

In order to clarify the role and a degree of involvement of hydroperoxides and peroxy radicals in

Table 3. The products of induced and catalytic decomposition of $Ph_2C(R)OOH$ (R = Me, Et) under the action of di-*tert*-butyl peroxalate and cobalt acetylacetonate in benzene (in mol per 1 mol of hydroperoxide)

Reaction products	$Ph_2C(R)OOH + [C(O)OOBu\text{-}t]_2$[a]		$Ph_2C(R)OOH + (acac)_2Co$[b]	
	R = Me	R = Et	R = Me	R = Et
$Ph_2C(OH)R$	0.54	0.39	0.33	0.42
Ph_2CO	0.06	0.26	0.09	0.40
PhC(O)R	0.13	0.07	0.13	0.02
R'COOH	0.06[c]	0.04[d, e]	0.08[c]	0.25[d]
$Ph_2C(OOH)f$[e]	0.26	0.19	0.36	0.11

[a] Molar ratio 4:1, 45°C, 3 h. [b] Molar ratio 10:1, 20°C, 24 h. [c] R' = H, identified as formaldehyde 2,4-dinitrophenylhydrazone. [d] R' = Me, identified acetaldehyde. [e] Found 0.12 mol of MeCHO. [f] Also identdfied 0.005 to 0.04 mol of phenol.

the formation of the final products of oxidation of 1,1-diphenylalkanes, we studied the reaction of the hydroperoxide with the cobalt acetylacetonate and di-*tert*-butylperoxalate (Table 3).

The main products of reactions of hydroperoxides are the same as in the oxidation of 1,1-diphenylalkanes: a tertiary alcohol, benzophenone, and an alkyl aryl ketone. It is known that di-*tert*-butyl peroxalate decomposes affording *tert*-butoxy radical that abstracts hydrogen from the hydroperoxy group and turns the hydroperoxide to the respective peroxy radical. The interaction of a hydroperoxide with the alkoxylate **II** should also lead to the formation of alkoxy and peroxy radicals [Eqs. (13), (14)] [4, 12].

$$ROOH + (acac)_2Co \rightarrow (acac)_2CoOH + RO^{\bullet}, \qquad (13)$$

$$ROOH + RO^{\bullet} \rightarrow ROH + ROO^{\bullet}, \qquad (14)$$

$$R = Ph_2CMe,\ Ph_2CEt.$$

The subsequent transformation of the peroxy radical is described by Eqs. (7), (9), and (11). The data in Table 3 confirm the involvement of the alkylperoxy radicals in the formation of all the products of alkylarene oxidation.

Thus, oxidation of the alkylarenes containing benzyl or benzylidene group by *tert*-butyl hydroperoxide in the presence of transition metal acetylacetonates proceeds with both preservation and destruction of the carbon backbone. In the presence of methylene or methine C–H bond in the β-position of the alkyl radical (with respect to the benzene ring), the process proceeds with the formation of 1,2-dioxetanes.

The proposed scheme of oxidation of C–H bonds is typical as well of the systems based on *tert*-butyl hydroperoxide and *tert*-butoxides of aluminum, titanium, vanadium [13, 15, 21]. We performed the previously unstudied reactions of *sec*-butylbenzene with these systems (Table 4). The ratio of initial reagents corresponded to that published in the literature. Table 4 shows that the composition of the products is identical to that determined for the oxidation of the *sec*-butylbenzene with hydroperoxide **I** in the presence of acetylacetonates **II**–**IV** (Table 1). In addition to the tertiary hydroperoxide the corresponding alcohol, 2-phenyl-2-*tert*-butylperoxybutane, and acetophenone were found. The formation of these products can also be described by Eqs. (2), (5), (7), and (9).

Evidence of the homolytic nature of oxidation is the detection, in the case of aluminum *tert*-butoxide–*tert*-butyl hydroperoxide system, of the product of dimerization of the radical formed from the solvent, 3,4-dimethyl-3,4-diphenylhexane (0.015 mol).

As follows from the above the oxidizers in the systems of *tert*-butyl hydroperoxide–metal acetylacetonate are oxygen and *tert*-butylperoxy radical. However, we cannot exclude the participation of the metal peroxides in these processes, at least in the case of vanadium derivative. The initial stage of the interaction of vanadium alkoxide **IV** with hydroperoxide **I** (C_6H_6, 20°C) is the ligand displacement and the formation of the vanadium peroxy compound. Acetylacetone is then subjected to destructive oxidation. The oxygen release occurs at a ratio of reactants at least 1:8–1:10 [3].

By the example of ethylbenzene we showed that its oxidation (20°C) occurs at the ratio of vanadium derivative **IV**–hydroperoxide **I** equal to 1:3. There are

Table 4. The products of oxidation of *sec*-butylbenzene by the sysyems of a metal alkoxide–*tert*-butyl hydroperoxide, 20°C, 20 h (in mol per 1 mole of hydroperoxide)

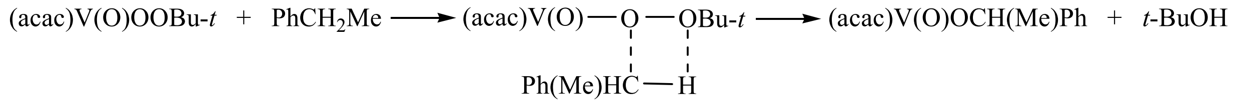
Reaction products[a]	Al(OBu-*t*)$_3$		Ti(OBu-*t*)$_4$	V(OBu-*t*)$_4$
	1:3[b, c]	1:5[b]	1:2[b, d]	1:3[b]
PhCOMe	0.15	0.20	0.10	0.10
PhC(OH)(Me)Et	0.10	0.19	0.11	0.20
PhC(OOH)(Me)Et	0.11	0.16	0.17	0.15
PhC(Me)(Et)OOBu-*t*	0.11	0.08	–	
CH_3COOH[e]	0.03	0.03	0.07	Traces
t-BuOOH	0.20	0.19	–	–

[a] *sec*-Butylbenzene as a solvent. [b] Molar ratio. [c] 3 h. [d] Oxygen release found. [e] Also identified as acetaldehyde 2,4-dinitrophenylhydrazone. In the case of Al(OBu-*t*)$_3$ were found the products of aldehyde condensation.

two processes: the oxidation of the ligand and of the alkylarene. Among the products were found (in moles per 1 mole of hydroperoxide): CO_2 (0.21), *t*-butyl peracetate (0.01), *tert*-butyl acetate (0.09), acetic acid (0.36), acetophenone (0.16), 1-phenylethan-1-ol (0.22) 1-hyderperoxy-1-phenylethane (0.03). Alcohol in the products prevails over ketone.

The vanadium-containing product of reaction of vanadyl **IV** with hydroperoxide **I** (1:3) in benzene after removal of the solvent and volatile products is a dark brown mass, which, according to IR spectroscopy, contains the acetylacetonate ligand. Ethyl benzene and 5 mol of hydroperoxide per 1 mol of the parent vanadium compound was added to it. After 2 h in the reaction mixture 0.04 mol of acetophenone and 0.24 mol of 1-phenylethan-1-ol (per 1 mole of initial *t*-BuOOH) were detected. Therewith the vanadium-containing product of $HOVO_2{\cdot}H_2O$ composition without containing organic groups pecipitated [3].

The lack of oxygen evolution at a ratio of the vanadium compound **IV**: *t*-BuOOH below 1:8, 1:10 in benzene, and of any radical in ethylbenzene formed from the latter (α-phenylethyl or the corresponding peroxyl), and the prevalence of alcohol yield over ketone allows a suggestion of a molecular interaction of the vanadium peroxy compound with the substrate [Eq. (15)].

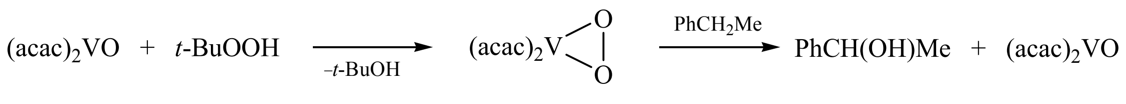


$$\text{(acac)V(O)OOBu-}t + \text{PhCH}_2\text{Me} \longrightarrow \begin{array}{c}\text{(acac)V(O)}-\text{O}-\text{OBu-}t\\ \text{Ph(Me)HC}-\text{H}\end{array} \longrightarrow \text{(acac)V(O)OCH(Me)Ph} + t\text{-BuOH} \quad (15)$$

It is presumable that the hydroxylation of ethylbenzene by the vanadium peroxo complex proceeds along the scheme (16) [22].

However, according to [22], peroxo complex not only oxidizes hydrocarbons to alcohols, but also hydroxylates the benzene ring. The arene hydroxy derivatives were not detected, which allows to give preference to Eq. (15). The lack of effect of oxygen on the yield of PhCH(OOH)Me at the carrying out the process $(acac)_2VO$–*t*-BuOOH (1:3) in ethylbenzene in a stream of oxygen also confirms the process to occur along Eq. (15). Further oxidation of vanadium alkoxy compound to acetophenone is possible at the action of both hydroperoxide **I** and vanadium-containing peroxide. Thus, if the metal complex contains at least one acetylacetonate ligand the preferential oxidation of ethylbenzene to alcohol occurs. As the oxidizing agents may act the vanadium-containing peroxy compounds.

When the vanadyl acetylacetonate **IV**: *t*-BuOOH ratio raises to 1:15, the oxidation of alkylarene performs the oxygen generated in the system by the homolytic path. This leads to complete destruction of



(16)

the structure **IV** and the formation of inorganic residue of the above composition.

The $HOVO_2 \cdot H_2O$ residue, despite its extremely limited solubility in arenes, decomposes *tert*-butyl hydroperoxide with evolution of oxygen [3] and catalyzes the ethylbenzene oxidation (20°C). The ESR spectrum of the reaction mixture containing the residue and *t*-BuOOH in 1:15 ratio in ethylbenzene after adding C-phenyl-N-*tert*-butylnitrone is a triplet of doublets with $g_i = 2.0064$, and hyperfine coupling constants $a_N = 1.345$ mT, $a_H = 0.13$ mT, which corresponds to the spin-adduct of *tert*-butylperoxy radical [13]. Ethylbenzene is mostly oxidized to acetophenone and to a lesser extent, to the alcohol. The process at room temperature is rather slow, and it is accompanied by the formation of significant amounts of acetone, which indicates the formation of *tert*-butoxy radicals.

As to the effect of the nature of metal in the acetylacetonate on the oxidation of the hydroperoxide alkylarene, we can draw the following conclusions.

(1) The composition of products for each of the hydrocarbons is independent of the metal alkoxide.

(2) The degree of the alkylarene conversion and the product yields at using either cobalt or chromium acetylacetonates are close. However, the rate is much lower in the latter case compared to the former, and up to 40–50% of chromium acetylacetonate remains unused.

(3) Due to the high rate of the oxygen generation, ligand removal and oxidation [3], vanadyl acetylacetonate is less effective in the reactions of oxidation.

EXPERIMENTAL

Reaction products were analyzed by GLC and TLC, as well as ESR and IR spectroscopy. The IR spectra were recorded on the IR Prestige-21 spectrophotometer (KBr tablets or thin layer). Chromatography-mass spectrometry analysis (GC-MS) was performed on an Agilent-6890 instrument equipped with a Net Work-5973 mass detector, and HP-5-MS column. The samples were injected at 90°, then the temperature was raised to 300°C for 15 min. The ESR spectra were recorded on a Bruker EMX instrument (operating frequency ~9.75 GHz). In determining the *g*-factor, diphenylpicrylhydrazyl (DPPH) was used as the reference. The analysis was carried out in the probe of the ESR spectrometer. To improve the resolution of the lines in the ESR spectrum and to remove the oxygen liberated during the reaction, the reaction solutions were degassed. The concentration of metal acetylacetonates was 0.005 M.

Chromatographic analysis of reaction products in the liquid phase was performed on a Tsvet-2-160 instrument equipped with a flame ionization detector, carrier gas argon. Analysis of benzaldehyde, acetophenone, phenyl ethyl ketone, isopropyl phenyl ketone, 1-phenylethane-1-ol, 1-phenyl-2-methylpropane-1-ol, 2-phenylbutane-2-ol, and methyl benzoate was performed on a column 2400×3 mm, carrier Chromaton N-AW-DMCS, stationary phase 15% Reoplex-400, temperature 150-170°C. For the analysis of 2,3-diphenylbutane, 3,4-dimethyl-3,4-diphenylhexane, and chromium acetylacetonate was used a column 2400×3 mm, stationary phase 5% SE-30, carrier Inerton-AW, 200-260°C. Analysis of acetylacetone, methyl *tert*-butyl peroxide was carried out on the same column, temperature 45°C. The compounds: Ph_2CHMe, Ph_2CHEt, $Ph_2C(OH)Me$, $Ph_2C(OH)Et$, Ph_2CO, PhCH(Me)OOBu-*t*, and PhC(Me)(Et)OOBu-*t* were analyzed on a GC-2010a unit (Shimadzu) with a flame ionization detector, carrier gas nitrogen, capillary column Equity-5, 30000×0.32 mm, temperature 180°C. Analysis of volatile components of the liquid phase was performed on a LHM-80 instrument with a thermal conductivity detector, column 2400×3 mm, carrier gas helium, stationary phase 15% dinonyl phthalate, adsorbent Chromaton N-AW-DMCS, 90–100°C. The calculation was performed using external references, using appropriate reference compounds in each case. At the separation of the products by column chromatography silica gel 60 (0.06–0.2 mm) as the adsorbent was used.

The qualitative and quantitative identification of carboxylic acids was carried out using the methyl esters formed at the treatment with diazomethane. Quantitative analysis of hydroperoxides was performed by iodometric titration. Carbonyl compounds were identified as 2,4-dinitrophenylhydrazones by the melting point determination and by TLC comparing the R_f values of spots of the sample and the reference substance. Sorbent Silpearl, the large porous silica gel on aluminum foil (Silufol UV-254), eluent carbon tetrachloride-diethyl ether,9:1. Quantitative determination of CO_2 in the reaction products was performed by the method of [23].

Vanadyl acetylacetonate was prepared from V_2O_5 by sequntial processing with freshly distilled acetylacetone and sodium carbonate [24], mp 252°C [25]. Synthesis of chromium acetylacetonate was carried out by the reaction of chromium triacetate, acetyl acetone, and acetic acid. Bright violet crystals, mp 217°C ($CHCl_3$ + C_6H_6) [26]. Di-*tert*-butyl peroxalate was obtained by treatment of oxalyl chloride with *tert*-butyl hydroperoxide in the presence of pyridine, mp 50°C [27]. 1,1-Diphenylethane was obtained by the Friedel-Crafts reaction of benzene with PhCH(OH)Me in the presence of $AlCl_3$, bp 114–115°C (4 mm Hg), n_D^{21} 1.5740 [28]. 1,1-Diphenylpropane was synthesized similarly, using PhCH(OH)Et, bp 130–132°C (4 mm Hg), n_D^{20} 1.5620 [28]. 1,1-Diphenylethan-1-ol was synthesized by treatment of ethyl acetate with phenylmagnesium bromide, mp 61°C [28]. 1,1-Diphenylpropan-1-ol was synthesized from ethylmagnesium bromide and benzophenone, mp 94°C (from alcohol) [29]. 1-Hydroperoxy-1,1-diphenylethane and 1-hydroperoxy-1,1-diphenylpropane were obtained by treating the corresponding alcohols by the 88% solution of hydrogen peroxide in the medium of diethyl ether in the presence of conc. H_2SO_4 at a temperature of 0–5°C. $Ph_2C(OOH)Me$ was purified by precipitation with petroleum ether from concentrated solution in ether, $Ph_2C(OOH)Et$ was recrystallized twice from hexane, mp 84 and 80°C, respectively [30]. The concentration of the synthesized hydroperoxides was at least 98%. 1-*tert*-Butylperoxy-1-phenylethane was synthesized by the method [31] by the reaction of α-phenylethyl bromide with the potassium *tert*-butyl peroxidate, bp 56°C (1 mm Hg), n_D^{20} 1.4810. 2-*tert*-Butyl peroxy-2-phenylbutane was obtained by reacting 2-phenylbutane-2-ol with *tert*-butyl hydroperoxide in glacial acetic acid containing conc. H_2SO_4 as catalyst [32], bp 60–62°C (1 mmHg), n_D^{20} 1.4780. Synthesis of 3,4-dimethyl-3,4-diphenylhexane was carried out by the decomposition of *tert*-butyl peroxide in a medium of*sec*-butylbenzene [33], mp 43°C.

2,3-Diphenylbutane was synthesized by Wuertz reaction, using α-chloroethylbenzene, mp 125°C [28]. The concentration of *tert*-butyl hydroperoxide was at least 99.6–99.8%. We used the following commercial reagents from Acros Organics: *sec*-butylbenzene, 99%; isobutylbenzene, 99.5%, cobalt acetylacetonate, 99%.

Reaction of *tert*-butyl hydroperoxide with chromium acetylacetonate in ethylbenzene (15:1, 20°C). To a solution of 0.11 g of chromium acetylacetonate in 15 ml of ethylbenzene was added 0.43 g of *tert*-butyl hydroperoxyde. The reaction solution immediately took the color of the initial chromium acetylacetonate, but after a few minutes the color changed to violet-red. On the next day the solution had a cherry-red color. On the wall of the flask appeared droplets of a liquid immiscible with the solvent. The ethylbenzene solution was decanted. The residue was treated with excess methylmagnesium iodide, and from the volume of released methane the amount of water was calculated (0.025 g). In the decanted solution was identified 0.037 g of unreacted chromium acetylacetonate and 0.014 g of 2,3-diphenylbutane. Volatile products and solvent were condensed in a trap cooled with liquid nitrogen. In the condensate was identified 0.25 g of *tert*-butyl alcohol, 0.093 g of 1-*tert*-butylperoxy-1-phenylethane, 0.01 g of HCOOH, 0.01 g of unreacted *tert*-butyl hydroperoxide, and 0.006 g of *tert*-butyl peroxide. The dark violet residue was hydrolyzed by 10% H_2SO_4, extracted with ether, and dried over Na_2SO_4. In the condensate and the hydrolyzate was identified 0.09 g of 1-hydroperoxy-1-phenylethane, 0.23 g of acetophenone, and 0.13 g of 1-phenylethan-1-ol. In aqueous-acidic hydrolyzate was identified 0.02 g of *tert*-butyl alcohol by the method of Deniges [34].

The formation of these products is confirmed by gas chromatography-mass spectrometric analysis. In addition to these compounds were also found in trace amounts styrene and methylethylbenzene. To identify the 1-hydroperoxy-1-phenylethane an aliquot of the reaction solution was treated with an excess of triphenylphosphine. By comparing the data of determination of 1-phenylethan-1-ol in the mixture before and after treatment with PPh_3 the content of the hydroperoxide was revealed.

Oxidation of *sec*-butylbenzene by *tert*-butyl hydroperoxide in the presence of cobalt acetylacetonate (15:1, 20°C). In a flask were placed 0.08 g of cobalt acetylacetonate, 10 ml of *sec*-butylbenzene, and 0.42 g of *tert*-butyl hydroperoxide. The solution immediately became dark green. On the next day at the bottom of the flask a light-brown precipitate and drops of an immiscible liquid were observed.

In the reaction solution were identified: 0.25 g of *tert*-butyl alcohol, 0.20 g of 2-*tert*-butylperoxy-2-phenylbutane, 0.22 g of acetophenone, 0.10 g of 2-phenylbutan-2-ol, 0.003 g of *tert*-butyl hydroperoxide, 0.01 g of *tert*-butyl peroxide, and 0.015 g of 3,4-dimethyl-3,4-diphenylhexane. Acetophenone was identified by melting point and by the melting point of the mixed sample of its 2,4-dinitrophenylhydrazone with the authentic substance, mp 249°C. An aliquot of the reaction solution was treated with diazomethane. About 0.047 g of methyl acetate was identified, which corresponds to 0.036 g of acetic acid. The titration of the liquid insoluble in *sec*-butylbenzene by 0.1 N $KMnO_4$ showed the presence of 0.0034 g of hydrogen peroxide. The method of gas chromatography-mass spectroscopy showed the presence in the reaction mixture of ethyl-*sec*-butylbenzene and phenyl ethyl ketone in trace amounts.

Oxidation of isobutylbenzene by *tert*-butyl hydroperoxide in the presence of cobalt acetylacetonate (15:1, 20°C). To 0.03 g of cobalt complex was added 5 ml of isobutylbenzene and 0.17 g of *tert*-butyl hydroperoxide. After 20 h in the reaction solution 0.08 g of isopropyl phenyl ketone, 0.05 g of benzaldehyde, 0.03 g of 1-phenyl-2-methylpropan-2-ol, and 0.01 g of acetone were identified. After treatment of the reaction solution with 2,4-dinitrophenylhydrazine were isolated by column chromatography (eluent chloroform) 2,4-dinitrophenylhydrazones of the following ketones (mp, °C): isopropyl phenyl ketone (153), benzaldehyde (234), and acetone (127). The melting points of mixed samples with authentic compounds showed no depression.

Oxidation of ethylbenzene by the system of *t*-BuOOH-VO(acac)$_2$. To a suspension of 0.34 g of VO(acac)$_2$ in 25 ml of benzene was added 0.34 g of *t*-butyl hydroperoxide (1:3). Vanadyl dissolves, the solution acquires an intense cherry-red color that quickly turned to a greenish-brown. After 14 h (20°C) the volatile substances and the solvent were condensed in a trap cooled with liquid nitrogen. To the black-brown residue was added 20 ml of ethyl benzene and 0.57 g of *t*-BuOOH. The reaction is strongly exothermic, the wine-red color of the solution gradually turned to brown, and a precipitate separated. After 3 h it was filtered off and dried in air. A powder of dark green color was isolated, consisting of $HOVO_2 \cdot H_2O$. In the pale brown filtrate was identified 0.33 g of *t*-BuOH, 0.030 g of acetophenone, and 0.18 g of PhCH(OH)Me. The filtered off and dried vanadium-containing precipitate was placed in a flask, and 15 ml of ethyl benzene and 0.46 g of *tert*-butyl hydroperoxide was added to it. The dissolution of the precipitate does not occur, the solution remained clear and almost colorless. After 5 days the test for peroxide compounds was negative. After removal of vanadium compounds, in the filtrate was identified 0.11 g of acetone, 0.19 g of *t*-BuOH, 0.14 g of PhC(O)Me, and 0.06 g of PhCH(OH)Me.

Oxidation of *sec*-butylbenzene by the system of *t*-BuOOH-(*t*-BuO)$_4$V (3:1). In a round-bottom flask was placed 10 ml of *sec*-butylbenzene and 0.44 g of vanadium tetra-*tert*-butoxide. To the formed solution of intense blue color was added 0.35 g of *t*-BuOOH. Instantly the color became wine-red, but after a few minutes the solution became yellow. The mixture was heated, the oxygen evolution was observed. After 20 h, the solvent and volatile reaction products were condensed in a trap cooled with liquid nitrogen. In the condensate was identified 0.55 g of *t*-BuOH, 0.03 g of acetone, 0.04 g of acetophenone, and 0.04 g of 2-phenylbutan-2-ol The dark brown mobile liquid residue was treated with distilled ether and hydrolyzed with 10% sulfuric acid solution. The ether layer was separated, the aqueous acidic solution was extracted several times with ether. The ether extract was dried over Na_2SO_4 and analyzed. In it was identified 0.12 g of *tert*-butyl alcohol, 0.01 g of acetophenone, 0.06 g of $PhC(OH)(CH_3)C_2H_5$, and, by iodometric titration, 0.10 g of 2-hydroperoxy-2-phenylbutane. *tert*-Butyl hydroperoxide was not found among the volatile products or in the hydrolyzate. Condensates of several experiments were combined and the first fraction was distilled into a solution of 2,4-dinitrophenylhydrazine to obtain acetone 2,4-dinitrophenylgidrazone, mp 126°C. By treatment of the remaining solution with 2,4-dinitrophenylhydrazine the acetophenone derivative was isolated, mp 250°C.

Decomposition of 1-hyderperoxy-1,1-diphenylethane in the presence of di-*tert*-butylperoxalate (4:1, benzene, 45°C, 3 h). A reaction mixture containing 0.10 g peroxalate and 0.37 g of $Ph_2C(OOH)Me$ in 10 ml of benzene was heated to reflux at 45°C for 3 h. The solution became bright yellow. In the reaction solution was identified 0.19 g of $Ph_2C(OH)Me$, 0.02 g of Ph_2CO, 0.03 g of PhC(O)Me, and 0.005 g of HCOOH. An aliquot of the reaction solution was treated with an excess of triphenylphosphine and reanalyzed for the tertiary alcohol. 0.27 g of $Ph_2C(OH)Me$ was determined. Increase in the content of alcohol (0.09 g) indicates the presence in the solution of unreacted starting hydroperoxide (0.09 g).

Oxidation of 1,1-diphenylethane by the system of *t*-BuOOH-(acac)$_2$**Co (10:30:1, benzene, 20°C)**. A mixture of 0.03 g of (acac)$_2$Co, 0.35 g of *tert*-butyl hydroperoxide, and 0.24 g of Ph_2CHMe in 10 ml of benzene was left at room temperature for 20 h The solution was dark green, with brown precipitate on the bottom. In the reaction solution was found 0.07 g of unreacted alkylarene, 0.01 g of benzophenone, 0.01 g of acetophenone, 0.09 g of $Ph_2C(OH)Me$, and 0.03 g of $Ph_2C(OOH)Me$. As 2,4-dinitrophenylhydrazones were identified formaldehyde, acetophenone, and benzophenone. Content of formic acid (0.003 g) was determined by the method of [35].

The oxidation of Ph_2CHEt by the system of *t*-BuOOH-$(acac)_3Cr$ (1:3:0.1, benzene, 20°C). A mixture of 0.05 g of $(acac)_3Cr$, 0.36 g of *t*-BuOOH and 0.26 g of alkylarene in 10 ml of benzene was kept at room temperature for 20 h. In the formed wine-red solution were identified benzophenone, phenyl ethyl ketone, and acetaldehyde. After the reaction in the solution were identified: 0.03 g of Ph_2C (OOH)Et, 0.01 g of $(t\text{-}BuO)_2$, 0.06 g of Ph_2CO, 0.004 g of PhC(O)Et, 0.17 g of unreacted alkylarene, while $Ph_2C(OH)Et$ was not found. After treatment an aliquot of the reaction solution with diazomethane was revealed 0.018 g of methyl acetate, which corresponds to 0.015 g of CH_3COOH.

The experiments and analysis of products not listed in the experimental part were carried out similarly.

ACKNOWLEDGMENTS

The authors thank A.I. Poddelskii for the help in recording and interpreting the ESR spectra.

REFERENCES

1. Sheldon, R.A. and van Doorn, J.A., *J. Catal.*, 1973, vol. 31, no. 3, p. 427.
2. Johnson, N.A. and Gould, E.S., *J. Am. Chem. Soc.*, 1973, vol. 95, no. 8, p. 5198.
3. Stepovik, L.P. and Gulenova, M.V., *Zh. Obshch. Khim.*, 2009, vol. 79, no. 8, p. 1304.
4. Stepovik, L.P., Potkina, A.Yu., and Poddel'skii, A.I., *Zh. Obshch. Khim.*, 2012, vol. 82, no. 9, p. 1473.
5. Muzart, J., *Chem. Rev.*, 1992, vol. 92, no. 1, p. 113.
6. Kaneda, K., Kawanishi, Y., Jitsukawa, K., and Teranishi, S., *Tetrahedron Lett.*, 1983, vol. 24, no. 45, p. 5009.
7. Itoh, T., Jitsukawa, K., Kaneda, K., and Teranishi, S., *J. Am. Chem. Soc.*, 1979, vol. 101, no. 1, p. 159.
8. Adam, W., Braun, E., Griesbeck, A., Luccini, V., Staab, E., and Will, B., *J. Am. Chem. Soc.*, 1989, vol. 111, no. 1, p. 203.
9. Glushakova, V.N., Skorodumova, N.A., Gryzina, O.Yu., and Razuvaev, G.A., *Izv. Akad. Nauk, Ser. Khim.*, 1983, no. 5, p. 1193.
10. Adam, W., Haira, S., Herderich, M., and Saha-Möller, C.R., *Org. Lett.*, 2000, vol. 2, no. 18, p. 2773.
11. Pokucca, A.P., Le Bra, Zh., Myuzar Zh., *Izv. Akad. Nauk, Ser. Khim.*, 2005, no. 2, p. 307.
12. Matienko, L.I., Skibida, I.P., and Maizus, Z.K., *Izv. Akad. Nauk, Ser. Khim.*, 1975, no. 6, p. 1322.
13. Stepovik, L.P., Martynova, I.M., Dodonov, V.A., and Cherkasov, V.K., *Izv. Akad. Nauk, Ser. Khim.*, 2002, no. 4, p. 590.
14. Stepovik, L.P., Gulenova, M.V., Martynova, I.M., Mar'yasin, B.A., and Cherkasov, V.K., *Zh. Obshch. Khim.*, 2008, vol. 78, no. 2, p. 288.
15. Stepovik, L.P., Gulenova, M.V., Tishkina, A.N., and Cherkasov, V.K., *Zh. Obshch. Khim.*, 2007, vol. 77, no. 7, p. 1173.
16. Russell, G.A., *J. Am. Chem. Soc.*, 1957, vol. 79, no. 14, p. 3871.
17. Hermans, I., Peeters, J., and Yacobs, P.A., *J. Org. Chem.*, 2007, vol. 72, no. 8, p. 3057.
18. Traylor, T.G., Russell, C.A., *J. Am. Chem. Soc.*, 1965, vol. 87, no. 16, p. 3698.
19. Timergazin, K.K. and Khursan, S.L., *Izv. Akad. Nauk, Ser. Khim.*, 1996, no. 12, p. 2858.
20. Pritskov, V.V. and Suprun, V.Ya., *Usp. Khim.*, 1996, vol. 65, no. 6, p. 538.
21. Stepovik, L.P., Gulenova, M.V., and Martynova, I.M., *Zh. Obshch. Khim.*, 2005, vol. 75, no. 4, p. 545.
22. Mimoun, H., Saussine, L., Daire, E., Postel, M., Fisher, J., and Weiss, R., *J. Am. Chem. Soc.*, 1983, vol. 105, no. 10, p. 3101.
23. Stepovik, L.P., Gulenova, M.V., Kalacheva, I.A., and Potkina, A.Yu., *Zh. Obshch. Khim.*, 2011, vol. 81, no. 3, p. 454.
24. Kolkhaun, H.M., Kholton, D., Tompson, D., and Tvigg, P., *Novye puti organicheskogo sinteza. Prakticheskoe ispol'zovanie perekhodnyh metallov* (New Ways of Organic Synthesis. The Practical Use of Transition Metals), Moscow: Khimiya, 1989, p. 365.
25. Korneev, N.N., Popov, A.F., and Krentsel', B.A., *Kompleksnye metallorganicheskie katalizatory* (Complex Organometallic Catalysts), Leningrad: Khimiya, 1969, p. 84.
26. Brauer, G., *Rukovodstvo po neorganicheskomu sintezu* (A Guide to Inorganic Synthesis), Moscow: Mir, 1986, vol. 5, p. 1622.
27. Bartlett, P.D., Benzing, E.P., and Pincock, R.E., *J. Am. Chem. Soc.*, 1960, vol. 82, no. 7, p. 1762.

28. *Slovar' organicheskikh soedinenii* (Dictionary of Organic Compounds), Moscow: Inostrannaya Literatura, 1949, vol. 1.
29. *Preparativnaya organicheskaya khimiya* (Preparative Organic Chemistry), Moscow: Goshimizdat, 1959, p. 647.
30. Davies, A.G., *Organic Peroxides*, London: Butterworths, 1961, p. 17.
31. Kornblum, N. and DeLaMare, H.E., *J. Am. Chem. Soc.*, 1952, vol. 74, no. 12, p. 3079.
32. Davies, A.G., Foster, R.V., and White, A.M., *J. Chem. Soc.*, 1954, no. 7, p. 2200.
33. Huang, R.L. and Kum-Tatt, L., *J. Chem. Soc.*, 1954, no. 7, p. 2570.
34. Polyanskii, N.G. and Safronenko, E.D., *Zh. Prikl. Khim.*, 1961, vol. 34, no. 6, p. 1376.
35. Baujer, K., *Analiz organicheskih soedinenii* (Analysis of Organic Compounds), Moscow: Inostrannaya Literatura, 1953, p. 234.