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System Vanadium Alkoxy Compound–*tert*-Butyl Hydroperoxide–Oxidant of Hydrocarbon C–H Bonds

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Abstract—Vanadium alkoxy compounds [$(t\text{-BuO})_4V$, $(t\text{-BuO})_3VO$] react with *tert*-butyl hydroperoxide (C_6H_6, 20°C) to liberate oxygen, partly in the singlet form, and to form alkoxyl and peroxyl radicals via the intermediacy of vanadium peroxides and trioxide. These systems are capable of oxidizing hydrocarbon C–H bonds. The process is radical in nature and involves formation of carbon-centered radicals and their reaction with oxygen generated in the systems. Vanadium-containing peroxides, too, take part in the oxidation reaction.

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Vanadium compounds catalyze peroxide oxidation of hydrocarbons. The decomposition of H_2O_2 is acetic acid in the presence of V(V) complexes is accompanied by liberation of singlet oxygen [1]. The oxidation of anthracene gives rise to anthraquinone in a nearly quantitative yield. Acyclic and alkylaromatic alkenes udergo oxidative cleavage into carbonyl compounds under the action of the H_2O_2–V(V)–CH_3COOH system [2].

Systems on the basis of vanadium alkoxides and *tert*-butyl hydroperoxide oxidize organic substrates in aprotic solvents. In the presence of $(t\text{-BuO})_3VO$, $(t\text{-BuO})_4V$, and $V(O)(acac)_2$, *tert*-butyl hydroperoxide converts alkanes to isomeric ketones [3–5]. The yield of the oxidation products depends on temperature, as well as initial concentrations and ratio of hydroperoxide and vanadate [4, 5]. The function of oxidants was initially believed to belong to vanadium-containing peroxides, but, in view of the fact that the decomposition of *t*-BuOOH in the presence of V(O)(acac)2 is a homolytic process [6], a mechanism was proposed involving a V(O)(acac)2 · 2*t*-BuOOH intermediate complex and V(V) peroxides.

The reactions of aluminum [7, 8] and titanium *tert*-butoxides [9] with *t*-BuOOH in benzene and chlorobenzene at a 1 : 2 reactant ratio liberate 0.80–0.90 mol of oxygen which oxidizes hydrocarbons to carbonyl compounds, alcohols, and hydroperoxides, which the participation of free radicals [7–9]. It should be noted that Al and Ti in these reactions do not change their oxidation degree, whereas the reactions of vanadium alkoxides $(RO)_4V$ with *t*-BuOOH involve formation of alkoxyvanates in which the oxidation degree of vanadium is +5 [10].

The aim of the present work was to study reactions of vanadium alcoholates [$(t\text{-BuO})_4V$ (**I**), $(t\text{-BuO})_3VO$ (**II**)] with *tert*-butyl hydroperoxide (**III**) in an inert solvent (C_6H_6) and also the oxidative ability of these systems toward hydrocarbon C–H bonds.

The reactions of vanadium alcoholates **II** and **I** with *t*-BuOOH in benzene were performed in benzene at room temperature and $(t\text{-BuO})_3VO$–*t*-BuOOH and $(t\text{-BuO})_4V$–*t*-BuOOH ratios of 1 : 2 and 1 : 3, respectively. In the latter case, 1 mol of *t*-BuOOH is consumed to oxidize V(IV) to vanadyl V(V) by scheme (1).

$$\underset{\mathbf{I}}{(t\text{-BuO})_4V} + \underset{\mathbf{III}}{t\text{-BuOOH}} \xrightarrow[-t\text{-BuOH}]{} (t\text{-BuO})_3VOOBu\text{-}t$$

$$\longrightarrow \underset{\mathbf{II}}{(t\text{-BuO})_3V{=}O} + t\text{-BuO}^{\cdot}. \tag{1}$$

Vanadyl **II** was isolated individual (up to 0.50 mol), and *t*-BuO$^{\cdot}$ radicals were detected by ESR as spin adducts with 2-methyl-2-nitrosopropane (**IV**). The yield of *t*-BuOH attains 1.4 mol, which is greater than expected by reaction (1). Probably, *tert*-butoxyl radicals abstract hydrogen from alcoholate alkoxy groups and also partially disproportionate to form alcohol and isobutylene oxide. The latter was identified as 2-methylpropanal after treatment with $BF_3 \cdot Et_2O$.

The reactions of vanadium compounds **I** and **II** with *t*-BuOOH in benzene involve liberation of oxygen (Table 1). The first stage is substitution of the alkoxy group by the hydroperoxide *tert*-butylperoxy group to give vanadyl peroxide **A** [3, 4] [scheme (2)].

$$(t\text{-BuO})_3\text{VO} + t\text{-BuOOH} \rightleftarrows t\text{-BuOH} + \underset{\mathbf{A}}{(t\text{-BuO})_2\text{V(O)OOBu-}t}. \tag{2}$$

By analogy with the reactions of aluminum [7] and titanium alcoholates [8], further reaction of peroxide **A** with the second mole of hydroperoxide **III** provides an unstable vanadium-containing trioxide **B** [scheme (3)].

$$(t\text{-BuO})_2\text{V(O)OOBu-}t + t\text{-BuOOH} \longrightarrow t\text{-BuOH} + \underset{\mathbf{B}}{(t\text{-BuO})_2\text{V(O)OOOBu-}t}. \tag{3}$$

The latter predominantly decomposes, liberating singlet oxygen and concurrently generating alkoxyl and peroxyl radicals [scheme (4)].

$$\mathbf{B} \begin{cases} \longrightarrow (t\text{-BuO})_3\text{V=O} + {}^1\text{O}_2, \\ \longrightarrow (t\text{-BuO})_3\text{V(O)OO}^\bullet + {}^\bullet\text{OBu-}t, \\ \longrightarrow (t\text{-BuO})_2\text{V(O)O}^\bullet + {}^\bullet\text{OOBu-}t. \end{cases} \tag{4}$$

To fix and quantify ${}^1O_2$, we reacted compounds **I** and **II** with *t*-BuOOH in the presence of typical acceptors of singlet oxygen: anthracene and 9,10-dimethylanthracene. The reactions of the systems **I**–*t*-BuOOH and **II**–*t*-BuOOH with anthracene gave 0.80–0.50 mol of anthraquinone. The reaction in the system **I**–*t*-BuOOH–9,10-dimethylanthracene (1 : 3:1) gave up to 0.45–0.50 mol of 9,10-dimethylepidioxyanthracene which was isolated and characterized by ^1H NMR spectroscopy [$CDCl_3$, δ, ppm: 1.48 s (3H), 7.2 and 7.4 (both m, *AA'BB'*, 2H)] [11].

Evidence for the homolytic nature of the decomposition of trioxide **B** was obtained by ESR spectroscopy. No addition of *t*-BuOOH to a benzene solution of V(OBu-*t*)$_4$ (20°C) in the absence of spin traps, the signal characteristic of V(IV) disappears, and a very broad singlet appears. A more clear picture was obtained at reduced temperature in toluene. Five minutes after the reagents had been mixed at –70°C, the ESR signal looked like a singlet assigned, based of g_i 2.015, to a peroxyl radical [12, 13] (Fig. 1a). A singlet with the same g factor was also detected in the system $(t\text{-BuO})_3\text{VO}^\bullet$–*t*-BuOOH ($C_6H_6$, 20°C) (Fig. 1b). Most probably, this signal belongs to a vanadium-containing peroxyl radical $(t\text{-BuO})_2\text{V(O)}\cdot\text{OO}^\bullet$ [7, 9], since $t\text{-BuOO}^\bullet$ is not detected by ESR in the absence of spin traps.

Table 1. Products of the reaction of vanadium *tert*-butoxy derivatives with *t*-BuOOH, (C_6H_6, 20°C, mol/mol vanadium alcoholate)[a]

Reaction products	$(t\text{-BuO})_4V$		$(t\text{-BuO})_3V{=}O$
	1 : 3	1 : 10	1 : 2
Volatile reaction products[b]			
O_2	0.85	2.33	0.95
t-BuOH	3.36	8.80	2.36
$(t\text{-BuO})_2$	0.11	0.48	0.07
$(CH_3)_2C{=}O$[c]	0.01	0.13	0.01
Hydrolysis products of nonvolatile residue[d]			
t-BuOH	2.56	2.24	2.17
H_2O_2	0.16	0.12	0.09

[a] Averaged results. [b] Traces of PhOBu-*t* were also detected by TLC. [c] 4-Methylpen-3-en-2-one was qualitatively identified by TLC. [d] One mol of vanadium was used in all experiments.

In the presence of a spin trap, *C*-phenyl-*N*-*tert*-butylnitrone (**V**), the ESR spectra of the systems alcoholate **I**, **II**–*t*-BuOOH in benzene (Fig. 2) are a superposition of a triplet signal and a triplet of doublets with asymmetric lines. The triplet signal (1 : 1 : 1) is assignable, by its isotropic parameters [g_i 2.0069 and $a_i(^{15}N)$ 0.790 mT], to benzoyl-*tert*-butylnitroxyl

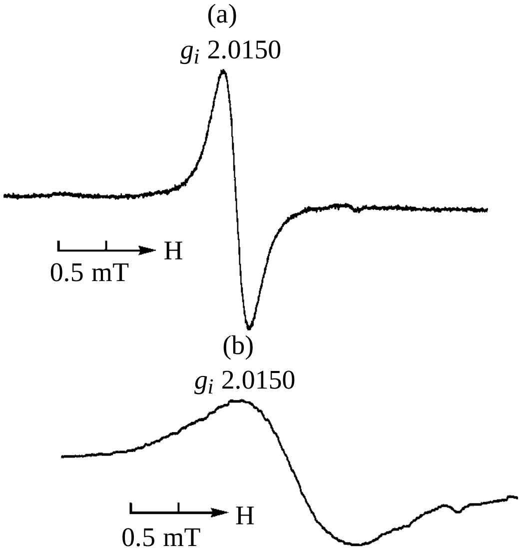


Fig. 1. ESR spectrum in the absence of spin traps. (a) $(t\text{-BuO})_4V$–*t*-BuOOH (1 : 3), 5 min after reagent mixing {toluene, –70°C, *c* [V(OBu-*t*)$_4$] 0.15 M}. (b) $(t\text{-BuO})_3\text{VO}^\bullet$–*t*-BuOOH (1 : 2) 5 min after reagent mixing [benzene, 20°C, *c* $(t\text{-BuO})_3$VO 0.20 M].

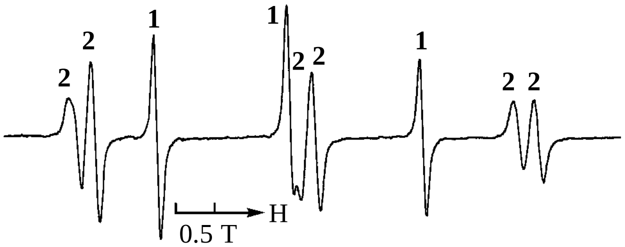
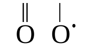
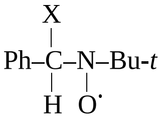


Fig. 2. ESR spectrum of the system $(t\text{-BuO})_3\text{VO}^{\bullet}t\text{-BuOOH}$ (1 : 2) in benzene in the presence of *C*-phenyl-*N*-*tert*-butylnitrone (**V**), 20°C, measured 10 min after reagent mixing and degassing. Figures over the lines relate to the numbers of radical species.

radical **1** by oxidation of the spin trap with either singlet oxygen or peroxyl radicals [7, 14]. Nitroxyl **2** [g_i 2.0059, $a_i(^{15}\text{N})$ 1.325 mT, $a_i(\text{H})$ 0.120 mT] cab be an adduct of spin trap **V** with $t\text{-BuOO}^{\bullet}$ or $(t\text{-BuO})_2\cdot\text{V(O)OO}^{\bullet}$, or their superposition [7, 15].


$\mathrm{Ph{-}\underset{O}{\underset{\|}{C}}{-}\underset{O^{\bullet}}{\underset{|}{N}}{-}Bu\text{-}}t$

1


$\mathrm{Ph{-}\overset{X}{\overset{|}{\underset{H}{\underset{|}{C}}}}{-}\underset{O^{\bullet}}{\underset{|}{N}}{-}Bu\text{-}}t$

2

X = $(t\text{-BuO})_2\text{V(O)OO}$, t-BuOO.

The intensity of the peroxyl signal (Fig. 1b) does not decrease over the course of 1.5–2 h, implying that the species is generated with time. After degassing of the reaction solutions, the signal did not get narrower. This is accounted for by an effect of the liberated oxygen [2]. *tert*-Butoxyl radical was registered as spin adduct **3** with 2-methyl-2-nitrosopropane (**IV**) [$t\text{-BuN(O}^{\bullet}\text{)OBu-}t$ (**3**), g_i 2.0055, $a_i(^{15}\text{N})$ 2.715 mT] [7].

Table 2. Products of the reaction of ethylbenzene with the systems vanadium alkoxy compound–*tert*-butyl hydroperoxide, 20°C (moles per mole metal alcoholate)[a]

Reaction products	$(t\text{-BuO})_4\text{V}$			$(t\text{-BuO})_3\text{V=O}$	
	1	**1'**	**2**	**1**	**2**
t-BuOH[b]	3.49	3.15	5.02	2.31	3.71
Me_2CO[b]	–	–	0.80	0.20	0.65
PhC(O)Me[b]	0.50	0.74	1.85	0.27	1.09
PhCH(OH)Me[c]	0.07	traces	0.53	0.11	0.33
PhCH(OOH)Me[c]	0.30	0.16	1.40	0.02	1.01

[a] Averaged results. (**1**) Under argon; (**1**') in the presence of powdered molecular sieves (4 Å, calcined at 300°C in a vacuum for 8 h); (**2**) under oxygen. [b] In the volatile fraction. Acetaldehyde was quantitatively identified. [c] Among products of hydrolysis of the nonvolatile residue.

Thus, the systems $\text{V(OBu-}t)_4$–t-BuOOH and $(t\text{-BuO})_3\text{VO}^{\bullet}t\text{-BuOOH}$ generate oxygen during decomposition of the vanadium-containing trioxide and are similar in this respect to systems on the basis of aluminum and titanium *tert*-butoxides.

Razuvaev and co-workers [4, 5] suggested molecular reactions of hydrocarbons with vanadium compounds containing a VOOR group for performing conversions of alkanes under the action vanadium alcoholate–hydroperoxide systems. However, the schemes of C–H oxidation were not detalized. It was shown that the oxidation in $\text{M(OBu-}t)_n$–t-BuOOH systems (M = Al, $n = 3$; M = Ti, $n = 4$) is homolytic in nature, which was evidenced by the identification of carbon-centered and their corresponding peroxyl radicals.

We studied the reactions of $(t\text{-BuO})_4\text{V}$–t-BuOOH and $(t\text{-BuO})_3\text{VO}^{\bullet}t\text{-BuOOH}$ with hydrocarbons containing primary, secondary, and tertiary C–H bonds (hexane, toluene, ethylbenzene, triphenylmethane). The standard was ethylbenzene. The working concentrations of vanadium alcoholates were 0.1–0.3 M. The principal oxidation products were 1-phenylethyl hydroperoxide (**VI**), acetophenone, and 1-phenylethan-1-ol (Table 2).

The oxidation of ethylbenzene was studied by ESR spectroscopy. 2-Methyl-2-nitrosopropane was added to a solution of alcoholate **II**–hydroperoxide **III** in PhEt (20°C), and an ESR spectrum was measured immediately after mixing. The spectrum contained a triplet of doublets with the following HFC constants: $a_i(^{15}\text{N})$ 1.496 mT, $a_i(\text{H}_\alpha)$ 0.378 mT, $a_i[\text{H(CH}_3)]$ 0.048 mT, and g_i 2.0062. The spectrum was assigned to an adduct of the α-phenylethyl radical with spin trap **IV**: $\text{PhCH(Me)N(O}^{\bullet}\text{)Bu-}t$ (4) [16]. A signal with the same parameters is also observed in the spectrum of the system $(t\text{-BuO})_4\text{V}$–t-BuOOH. Additionally, an adduct of the *tert*-butoxyl radical was found [g_i 2.0055, $a_i(^{15}\text{N})$ 2.720 mT] (Fig. 3). It should be noted that consecutive measurements of spectra within ~10 min showed an increasing signal of the *tert*-butoxyl radical, whose intensity reached that of the α-phenylethyl radical and remained unchanged for at least 40 min (Fig. 4). These findings provide evidence for a radical mechanism of the reaction of the system with substrates and for release of carbon-centered radicals from the solvent cage.

Let us consider the possible ways of formation of the compounds listed in Table 2. Oxygencentered radicals [scheme (4)] can abstract hydrogen from the methylene group and initiate oxidation of the hydrocarbon. The radicals that form react with oxygen generated by the systems to give the peroxyl radicals $PhCH(Me)OO^{\cdot}$ which undergo further transformations [scheme (5)].

$$PhCH_2Me + RO^{\cdot} \xrightarrow[-ROH]{} Ph\dot{C}HMe$$

$$\xrightarrow{O_2} PhCH(OO^{\cdot})Me, \qquad (5)$$

$$R = t\text{-Bu},\ t\text{-BuO},\ (t\text{-BuO})_3V,\ (t\text{-BuO})_2VO.$$

As follows from Table 2, the product yields in the reaction in the system $(t\text{-BuO})_3VO^{\cdot}t\text{-BuOOH}$ (1:2) is less than half that in the reaction in the system $(t\text{-BuO})_4V$–*t*-BuOOH (1:3). The strongest difference is in the yield of hydroperoxide **VI**. In our opinion, this can be explained by the fact that in the latter case the quantity of alkoxyl radicals, specifically *tert*-butoxyl, capable of abstracting hydrogen from ethylbenzene is much greater than in the system $(t\text{-BuO})_3\cdot VO^{\cdot}t\text{-BuOOH}$ [scheme (1)].

Evidence for scheme (5) was obtained from the results of the oxidation of ethylbenzene with oxygen, initiated by di-*tert*-butyl peroxalate (50°C, 2 h). We isolated (per 1 mol of peroxalate): 1.15 mol of hydroperoxide **VI**, 0.8 mol of acetophenone, 0.94 mol of 1-phenylethan-1-ol, 2 mol of CO_2, and 1.50 mol of *t*-BuOH. The close quantities of ketone and alcohol suggest formation of the alkylperoxyl radicals $PhCH(Me)OO^{\cdot}$ and their disproportionation to alcohol and ketone by the Russell scheme (6) [17].

$$2PhCH(Me)OO^{\cdot} \longrightarrow PhC(O)Me$$

$$+\ PhCH(OH)Me + O_2. \qquad (6)$$

The yield of products of the oxidation of ethylbenzene with the systems $(t\text{-BuO})_4V$–*t*-BuOOH and $(t\text{-BuO})_3V$–*t*-BuOOH under oxygen after 3–4 h at room temperature (Table 2, exp. no. 2) reaches 3–4 mol [per 1 mol of $(t\text{-BuO})_4V$] in the first case and is no more than 2.5 mol in the second, and then remains almost invariable with time. We found 0.50–0.70 mol of $PhCH(OH)CH_3$, 1.40–1.90 mol of $PhC(O)CH_3$, and 1–2 mol of hydroperoxide **VI**. The latter was identified by its reaction with triphenylphosphine: The reaction gave triphenylphosphine oxide, and the gain in the quantity of *t*-BuOH corresponded to the quantity of the hydroperoxide. In the reactions in an oxygen atmosphere, the content of *t*-BuOH in the volatile fraction was as high as 5.0–5.5 mol, which implies decomposition of vanadium alcoholates. The latter fact is probably responsible for the termination of the oxidation of ethylbenzene with the systems in hand.

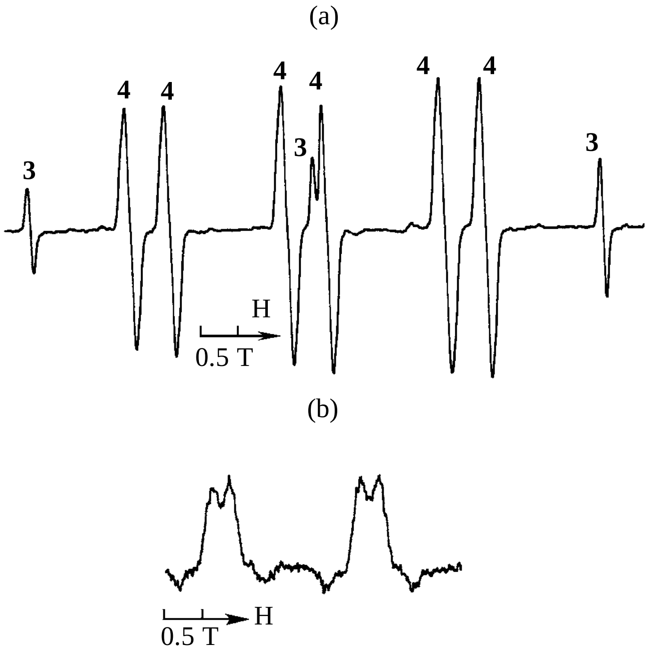


Fig. 3. (a) ESR spectrum of the system $(t\text{-BuO})_4V$–*t*-BuOOH (1:3) in ethylbenzene, measured immediately after reagent mixing [in the presence of 2-methyl-2-nitrosopropane (**IV**), 20°C]; (**3**) signals of the adduct with the *tert*-butoxyl radical, (**4**) signal of the adduct with the α-phenylethyl radical. (b) Methyl hydrogen splitiing.

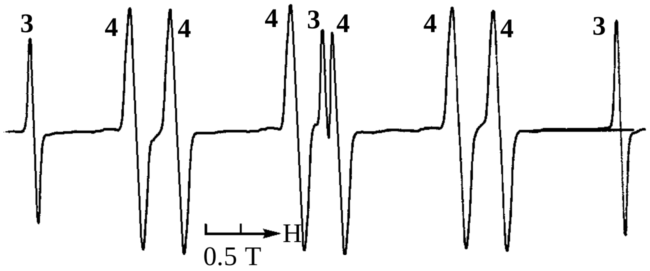
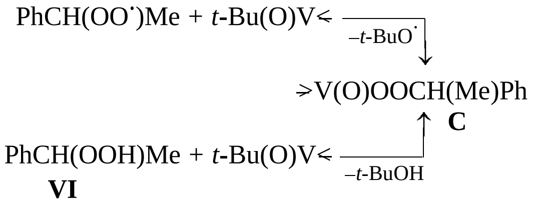


Fig. 4. ESR spectrum of the system $(t\text{-BuO})_4V$–*t*-BuOOH (1:3) in ethylbenzene, 30 min after reagent mixing [in the presence of 2-methyl-2-nitrosopropane (**IV**), 20°C].

The above experiments provide evidence to show that the oxidation is initiated by radicals generated by decomposition of peroxytrioxide **B**. It should be noted that the gain in the quantity of ketones on the oxidation of alkanes with vanadium alcoholate–hydroperoxide systems in the presence of oxygen was reported earlier by Spirina et al. [4]. However, the referees gave no explanation for this phenomenon.

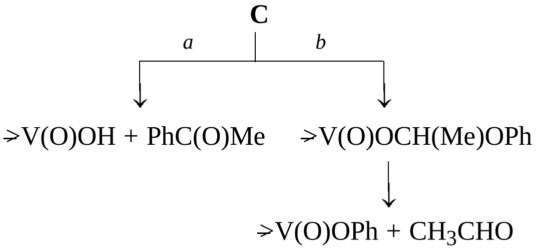
Along with disproportionation and hydrogen abstraction reactions, alkylperoxyl radicals can undergo homolytic *S*R2 substitution to form peroxide **C**. This compound can also be formed by an exchange reaction between hydroperoxide **VI** and the *tert*-butoxy group on metal [scheme (7)].



(7)

Peroxide **C** is involved in the formation of the final products of the oxidation of ethylbenzene. The quantities of hydroperoxide after hydrolysis of the reaction mixtures or nonvolatile residues (Table 2) correspond to its quantities in the postreaction mixtures. However, if the reaction solution is kept for 10–12 h at room temperature, peroxide **C** decomposes. A dark green precipitate forms, whose IR spectrum contains the following bands, ν, cm^{-1}: 1631 (carboxylate ion), 1004 (V=O), and 762 (V–O) [18], as well as a very strong broad at 3418 cm^{-1}, assigned to stretching vibrations of the hydroxyl group (V–OH). The spectrum shows no bands characteristic of *t*-BuO groups.

Peroxide **C** decomposes along two routes [scheme (8)].



(8)

The first route *a* leads to ketone and the second *b* involves rearrangement with subsequent decomposition of alkoxy compound to acetaldehyde and phenoxyvanadium. Acetaldehyde was identified as 2,4-dinitrophenylhydrazone and phenol, as 2,4,6-tribromophenol. Acetaldehyde is partially oxidized to acetic acid. The formation of phenol and acetaldehyde, along with acetophenone and $PhCH(OH)CH_3$, was earlier observed [19] in the nickel acetylacetonate-catalyzed oxidation of ethylbenzene with oxygen at 120°C. The largest quantities of PhOH and CH_3CHO were found in the decomposition of hydroperoxide **VI** at the same temperature but in an inert atmosphere. A radical mechanism of this process was suggested [19].

It is seen from of the results of the oxidation of ethylbenzene in the presence of di-*tert*-butyl peroxalate and vanadium alkoxy compound–*t*-BuOOH systems that in the latter case the quantity of acetophenone is always greater compared to alcohol, and in certain cases alcohol was not detected at all. This can be explained by the fact that ketone is formed by several routes [schemes (6) and (8)], and also by partial oxidation of alcohol. The systems alcoholate **I**, **II**–hydroperoxide **III** oxidize 1-phenylethan-1-ol (C_6H_6, 20°C). Successive treatment of $V(OBu\text{-}t)_4$ with alcohol and hydroperoxide **III** (1 : 1 : 1) gives 0.50–0.60 mol of acetophenone and 2.46–2.60 mol of *t*-BuOH. The conversion of 1-phenylethan-1-ol is 50–65%. No radicals were detected by ESR. We suppose that the prevailing reaction route is formation and decomposition of V(IV) peroxide rather than oxidation of alcoholate **I** to vanadyl [Scheme (9)].

$$\begin{gathered}(t\text{-BuO})_4V + PhCH(OH)Me + t\text{-BuOOH}\\ \longrightarrow 2t\text{-BuOH} + \{(t\text{-BuO})_2V[OCH(Ph)Me]OOBu\text{-}t\}\\ \longrightarrow t\text{-BuOH} + PhCOMe + (t\text{-BuO})_2VO. \qquad (9)\end{gathered}$$

Along with the above routes of the reactions of the alcoholate **I**, **II**–hydroperoxide **III** oxidative systems with alkylarene C–H bonds, the possibility exists of formation of carbon-centered and hydroperoxyl radicals under the action of oxygen on C–H bonds. These radicals can react with each other to form hydroperoxide or, via oxidation of the α-phenylethyl radical, acetophenone and water which can hydrolyze V–OBu-*t* bonds [scheme (10)].

$$\begin{gathered}PhCH_2Me + O_2 \longrightarrow [Ph\dot{C}HMe + \dot{O}OH]\\ \begin{cases}\xrightarrow{a} PhCH(OOH)Me,\\ \xrightarrow{b} PhCOMe + H_2O.\end{cases} \qquad (10)\end{gathered}$$

However, as known, the oxidation of hydrocarbons with oxygen to hydroperoxide by scheme (10a) predominantly occurs in the gas phase [20]. The reaction of *t*-BuOOH with $(t\text{-BuO})_4V$ in the presence of water acceptor (molecular sieves) gives the same quantitative yield of oxidation products (Table 2, exp. no. 1'). Consequently, reaction (10) in the systems in hand is unlikely.

Other hydrocarbons containing primary, secondary, or tertiary C–H bonds can follow the same transformation routes as ethylbenzene. Methyl oxidation was observed in toluene only. Benzaldehyde, 0.26 mol, was found in the volatile fraction and 0.53 mol of benzoic acid and traces of benzyl alcohol in products of hydrolysis of the nonvolatile residue. Upon the oxidation of hexane by the system $(t\text{-BuO})_4V$–*t*-BuOOH (1 : 3), in the volatile fraction we found *t*-BuOH (3.11 mol per 1 mol of vanadium alcoholate), hexan-2-one (0.10), and hexan-3-one (0.10), and hydrolysis of the nonvolatile residue gave *t*-BuOH (1.72), hexan-2-one (0.02), hexan-3-one (0.11), hexan-2-ol (0.04), and hexan-3-ol (0.06). In addition, a small quantity of a mixture of carboxylic acids was found, implying destructive oxidation of hexanones, as well as ketone condensation products.

Upon the reaction of the system with triphenylmethane (1 : 3:1) we found 3.39 mol of *t*-BuOH, 0.20 mol of Ph_3COOH and its conversion products: 0.13 mol of Ph_2CO and 0.03 mol of PhOH. The latter undergoes oxidation under the reaction conditions. The starting triphenylmethane, 0.55 mol, was also isolated.

Consequently, the yield of oxidation products and the conversion of substrates depend on the structure of the latter. The highest values are characteristic of ethylbenzene and the lowest with triphenylmethane. This is explained both by the reactivity of C–H bonds in alkylarenes and their corresponding peroxyl radicals and by steric factors [21].

EXPERIMENTAL

The IR spectra were measured on a Specord IR-75 instrument (liquid film between KBr windows). The ESR spectra were taken on a Bruker ER-200D-SRC instrument equipped with an ER 4105DR double resonator (working frequency ~9.5 GHz) and an ER 4111VT temperature control unit. The g factors were determined using diphenyl picryl hydrazyl (DPPH) as reference. Analysis was performed in an ESR cell. Reaction solutions were degassed for better resolution and removal of oxygen released on reactions of **I**, **II**, and **III**. Spin traps **IV** and **V** were added at the initial reaction stages.

Chromatographic analysis of reaction products in the liquid phase was performed on a Tsvet-2-65 instrument with FID, carrier gas argon, adsorbent Chromaton N-AW-DMCS. Volatile components (acetone, *tert*-butanol, *tert*-butyl hydroperoxide) were analyzed on a 2400 × 3-mm column packed with 10% PEGA on a TZKM brick, temperature 55–80°C. High-boiling products (benzaldehyde, acetophenone, benzophenone, phenol, 1-phenylethan-1-ol, styrene, etc.) were analyzed on a 3000 × 3-mm column packed with 5% SE-30 on Inerton-AW, 100–190°C. *tert*-Butyl peroxide in benzene was analyzed on a 3000 × 3-mm column packed with 5% SP-2401 on Chromaton N-AW-DMCS, 50°C. Anthracene, 9,10-dimethylanthracene, and anthraquinone were analyzed on a 3000 × 3-mm column packed with 5% OV-15 on Inerton Super, 180–210°C. Hexan-2- and -3-ones and hexan-2- and -3-ols were determined on a 1200 × 3-mm column packed with 15% Reoplex-400, 90–180°C. The chromatograms were treated by the external reference technique.

All operations with vanadium-containing alkoxy compounds were performed under dry oxygen-free argon.

The number of *tert*-butoxy groups was determined by the Deniges method [22] and aliphatic acids in nonvolatile residues were determined by the procedure in [23]. Carboxylic acids were identified as methyl esters after treatment with diazomethane [24]. Carbonyl compounds were determined as 2,4-dinitrophenylhydrazones by TCL on Silufol UV-254 plates (eluent benzene or benzene–diethyl ether, 9 : 1). Certain hydrazones were isolated individual and characterized by melting points. The quantity of released oxygen was determined by the weight of benzoic acid formed by the reaction of O_2 with benzaldehyde [25]. Analysis for vanadium was performed by oxidimetry [26].

Vanadium tetra-*tert*-butoxide (I) was synthesized by an exchange reaction of vanadium trichloride and lithium *tert*-butoxide (1 : 2) in hexane, followed by refluxing for 2 h. After removal of the solvent and distillation, $V(OBu\text{-}t)_4$ was isolated as a dark blue liquid highly sensitive to oxygen and moisture, bp 89–90°C (1 mm Hg) [27].

Tri-*tert*-butoxyvanadyl (II) was prepared by the reaction of lithium *tert*-butoxide with $VOCl_3$, mp 97–98°C (2 mm Hg); colorless crystals, mp 47–48°C [28]. The concentration of *tert*-butyl hydroperoxide used in the work was no less than 99.6–99.8%.

Reaction of vanadium tetra-*tert*-butoxide with *tert*-butyl hydroperoxide (1:1) in benzene, 20°C. To 0.32 g of $(t\text{-BuO})_4V$ in 5 ml of benzene, 0.08 g of *t*-BuOOH was added. Immediately after the reagents had been mixed, the reaction solution got bright red and then yellow. Benzene and volatile products were removed into a trap cooled with liquid nitrogen. In the volatile fraction we found 0.09 g of *tert*-butanol. The condensate gave positive reactions on the oxirane ring (with iodonic acid [29] and with pyridine under heating [30]).

Tri-*tert*-butoxyvanadyl was isolated using a device constructed of two ampules sealed together (H-shaped device). One of the ampules was preliminarily sealed. The residue after removal of the solvent and volatile reaction products (colorless crystals in a yellow terry material) was dissolved in 3 ml of benzene, and the solution was placed to the second ampule of the device. The device was degassed. Benzene was removed at 20°C at reduced pressure, and the knee of the ampule with its content was sealed. When the residue was heated, tri-*tert*-butoxyvanadyl sublimed in the first ampule, yield 0.12 g, mp 47°C [28].

In a parallel experiment, the residue after removal of volatile components was dissoled in diethyl ether, treated with 10% sulfuric acid, extracted with small portions of diethyl ether, and dried over Na_2SO_4. According to chromatography, the ether extract contained 0.16 g of *t*-BuOH. The aqueous acid hydrolysate contained 0.05 g of *t*-BuOH.

Reaction of vanadium tetra-*tert*-butylate with *tert*-butyl hydroperoxide (1 : 3) in benzene, 20°C. To 0.62 g of V(OBu-*t*)$_4$ in 10 ml of benzene, 0.49 g of *t*-BuOOH was added (room temperature), hydrogen evolution was observed. The reaction solution got intensively yellow. A day after, benzene and volatile reaction products were removed at 20°C at reduced pressure. On treatment of part of the condensate with 2,4-dinitrophenylhydrazine hydrazones of acetone and 4-methylpent-3-en-2-one precipitated (TLC). In the volatile fraction, 0.45 g of *t*-BuOH, 0.001 g of acetone, 0.029 g of (*t*-BuO)$_2$, and traces of PhOBu-*t* were found, and isobutylene oxide was qualitatively detected [30, 31]. The latter was identified as 2-methylpropanal 2,4-dinitrophenylhydrazone after treatment with the benzene solution with BF_3 etherate [31]. 2-Methylpropanal hydrazone was isolated by column chromatography (adsorbent Silicagel-60, 0.060–0.20 mm, eluent benzene–diethyl ether, 18 : 1), mp 182°C.

The residue, a dark yellow tarry material was hydrolyzed with 10% H_2SO_4 and extracted with ether. In the ether extract, 0.30 g of *t*-BuOH was found. In the aqueous acid layer, 0.04 g of *tert*-butanol [22] and 0.01 g of hydrogen peroxide were found; the latter was identified by the procedure in [32].

For quantitative determination of the released oxygen, the parallel reaction was performed in an evacuated H-shaped ampule. Benzaldehyde, 0.35 g, was placed in one knee of the ampule (the starting reagent ratio is the same as above). Benzoic acid, 0.35 g [1.60 mol per 1 mol of V(OBu-*t*)$_4$] was found, which corresponds to 0.046 g of O_2 (0.80 mol per 1 mol of the starting vanadium alcoholate).

Oxidation of ethylbenzene with the system V(OBu-*t*)$_4$–*t*-BuOOH (1:1 : 3). A mixture of 0.63 g of V(OBu-*t*)$_4$ in 10 ml of benzene with 0.50 g of *t*-BuOOH in 5 ml of ethylbenzene was prepared. No oxygen liberation was observed. After 20 h (20°C) the solvent and volatile compounds were condensed in a trap cooled with liquid nitrogen. The condensate contained 0.34 g of *t*-BuOH, 0.05 g of acetophenone, and 0.01 g of 1-phenylethan-1-ol. Part of the distilled solvent was treated with 2,4-dinitrophenylhydrazine. The precipitate of 2,4-dinitrophenylhydrazones (acetophenone, acetone, and acetaldehyde) was analyzed by TLC, eluent petroleum ether–ethanol, 18 : 1. The residue, a dark orange mobile liquid, was dissolved in diethyl ether and treated with 10% H_2SO_4. The ether extract contained 0.36 g of *t*-BuOH, 0.02 g of PhCH(OH)Me, 0.05 g of PhC(O)Me, and 0.007 g of PhCH=CH_2. Phenol and *tert*-butyl hydroperoxide were not found in the reaction products. By iodometric titration, 0.09 g of PhCH(Me)OOH was found. To identify the latter, the residue of hydrolysis products was dissolved in benzene and heated in the presence of a catalytic amount of *p*-toluenesulfonic acid at 60°C for 3 h [24]. Phenol, 0.04 g, was found by chromatography. The formation of this product suggests presence of PhCH(Me)OOH. The aqueous layer was analyzed for *t*-BuO groups (0.06 g) by the Deniges method.

Reaction of ethylbenzene with the system V(OBu-*t*)$_4$–*t*-BuOOH under oxygen. A solution of 1.38 g of V(OBu-*t*)$_4$ in 40 ml of ethylbenzene saturated with oxygen. The solution remained blue-colored. When 1.08 g of *t*-BuOOH was added, the solution first got orange and then yellow. Dry oxygen was slowly bubbled through the solution for 4 h and then it was divided into halves. The first half was hydrolyzed with 10% H_2SO_4 and extracted with benzene. The extract contained 0.82 g of acetophenone and 0.25 g of 1-phenylethan-1-ol. The solution was then heated at 45°C in the presence of a catalytic amount of *p*-toluenesulfonic acid. Acetaldehyde was simultaneously distilled into a trap with 2,4-dintrophenylhydrazine (2,4-dintrophenylhydrazone, mp 167°C). The residue contained 0.56 g of phenol.

Triphenylphosphine, 0.50 g, was added to the second half. Heat release was observed. After hydrolysis, chromatographic monitoring showed an increasing content of *tert*-butanol (up to 0.63 g) at invariable content of acetophenone. Ethylbenzene was removed, the residue was dissolved in methanol, and the solution was poured into water to isolate 0.53 g of Ph_3PO, mp 154°C. Mixed sample gave no melting point depression.

The reactions with of *p*-toluenesulfonic acid and Ph_3P showed that the oxidation of ethylbenzene gave, along with *tert*-butanol and acetophenone, no less than 0.72 g of 1-phenylethyl hydroperoxide.

In a separate experiment, the reaction solution was let to stand until peroxy compounds disappeared completely (12 h, 20°C); therewith, a dark green precipitate formed. The solvent and volatile components were removed at reduced pressure at room temperature. The volatile fraction contained *t*-BuOH and acetophenone. After hydrolysis of the residue, phenol and 1-phenylethan-1-ol were found.

Oxidation of 1-phenylethan-1-ol with the system $(t\text{-BuO})_4V$–*t*-BuOOH (1 : 1 : 1), C_6H_6. 1-Phenylethan-1-ol, 0.22 g, was added to 0.63 g of $(t\text{-BuO})_4V$ in 10 ml of benzene. The solution changed from bright blue to dark blue. Hydroperoxide **III**, 0.16 g, was added. Heat release was observed, and the solution got yellowish orange.

The condensed solvent contained 0.34 g of *t*-BuOH and 0.11 g of acetophenone. The condensate was treated with a solution of 2,4-dinitrophenylhydrazine to isolate acetophenone 2,4-dinitrophenylhydrazone, mp 246–247°C. Mixed sample gave no melting point depression. The residue, a thick brownish-green material, was dissolved in ether, hydrolyzed with 10% H_2SO_4, and extracted with ether. The extract contained 0.15 g of *tert*-butanol, 0.03 g of acetophenone, and 0.08 g of the starting alcohol. The aqueous acid hydrolysate contained 0.10 g of *tert*-butanol.

The reactions of the other hydrocarbons with the systems vanadium alcoholate **I**, **II**–*tert*-butyl hydroperoxide and analysis of the reaction products were performed in a similar way.

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