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Specific Features of the Reaction of Vanadyl Acetylacetonate with *tert*-Butyl Hydroperoxide

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Abstract—Reaction of vanadyl acetylacetonate with *tert*-butyl hydroperoxide (benzene, 20ºC) at any molar ratio leads to the elimination of ligand and its oxidation mainly to CO_2 and acetic acid. At the $(acac)_2$VO: *t*-BuOOH ratio above 1:10 liberation of oxygen partially in the singlet state takes place.

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Vanadyl acetylacetonate **I** is a catalyst of oxidation of various classes of organic compounds such as secondary alcohols [1], amines [2], sulfides [3], of epoxydation of alkenes [4, 5] and allyl alcohols [6], etc. with hydrogen peroxide or *tert*-butyl hydroperoxide **II**. In many cases amount of hydroperoxide essentially exceeds the amount of the substrate oxidized, but no reasons of such situation are presented. Different reaction schemes explaining the formation of final products are offered.

On the other side it is known that vanadyl acetylacetonate catalyses the decomposition of secondary [7] and tertiary [8, 9] hydroperoxides. Alkoxydioxovanadate is suggested as a catalytically active particle [7]. It is shown that about 20–30% of hydroperoxide decomposes to form free radicals. In the products of decomposition of cumyl hydroperoxide CO_2 was found [8]. Batyrshin et al. [9] have described decomposition of hydroperoxide **II** according to the suggested mechanism including the formation of the intermediate complex OV$(acac)_2$–2*t*-BuOOH. Activation of catalyst and its regeneration proceed by means of reorganizing the ligand surrounding of V^{+5}. At the same time it was marked that at the [*t*-BuOOH]: [catalyst] ratio above 7 black precipitate was formed what indicated the decomposition of the latter. It was shown that 1 mole of decomposed hydroperoxide **I** gave 0.33 mol of *tert*-butanol by a nonradical process. No data on the possible reaction of acetylacetonate ligands with hydroperoxides and on the pathways of formation of carbon dioxide was published.

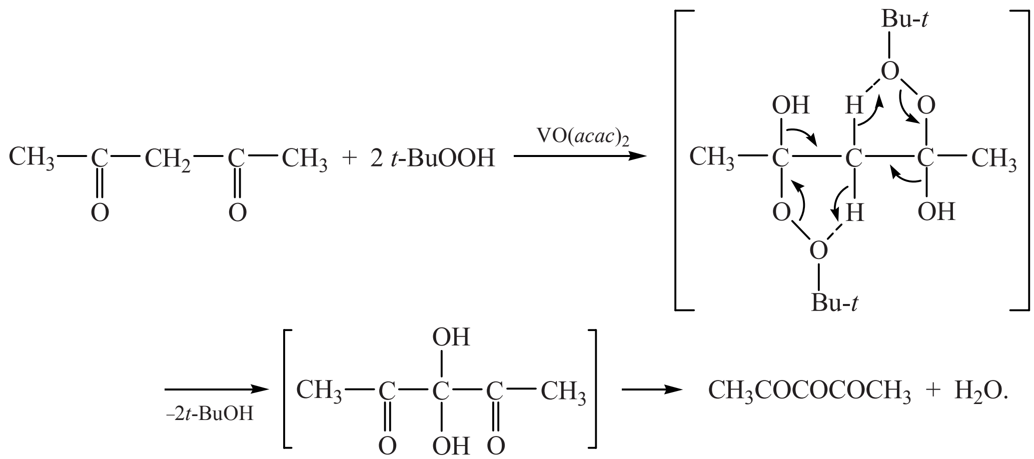
The present work deals with the investigation of the reaction of acetylacetonate **I** with hydroperoxide **II** at various reagents ratio. The process was carried out in benzene at 20ºC because no reaction with solvent was observed at this temperature.

Due to the limited solubility of OV$(acac)_2$ in aromatic hydrocarbons its concentration was no more than 0.01 mol l^{-1}. When higher concentrations of vanadyl were used addition of hydroperoxide caused fast and complete dissolution of the precipitate. The reaction is exothermic at any reagent ratio. The process is accompanied by alteration in the coloration of solutions from blue to dark green and light brown at the vanadyl **I**:hydroperoxide **II** ratio varying from 1:2 to 1:4 and 1:15 respectively. In all the cases the intermediate claret color was observed showing either the formation of vanadyl(I) complexes with *t*-BuOOH or the vanadium peroxocompounds [7, 10].

The results obtained are listed in the table. The presence of CO_2, acetic and pyruvic acids, *tert*-butylacetate, and *tert*-butylperacetate shows that the destruction of acetylacetonate ligand takes place. In spite of the significant difference in pK_a between acetylacetone and *t*-BuOOH, it can be probably replaced by hydroperoxide [Eq. (1)].

$$(acac)_2\text{VO} + t\text{-BuOOH} \rightleftarrows [(acac)_2\text{VO}\cdot t\text{-BuOOH}] \rightleftarrows \underset{\text{A}}{acac\text{V(O)OOBu-}t} + \text{MeCOCH}_2\text{COMe}, \quad (1)$$

Acetylacetone in the concentration equal to the concentration of starting catalyst was found recently



(2)

while treating vanadyl **I** with cyclohexyl peroxide at 10ºC [7]. No acetylacetone in free state was found by us by means of GLC and the IR spectroscopy. It was subjected to further oxidation to pentanetrione [11]. One of the possible pathways including the nucleophilic addition of *t*-BuOOH to the carbonyl group of diketone is presented in the scheme (2).

Peroxide **A** may also play the part of an oxidant of acetylacetone. Then formation of vanadyl oxide *acac*V(O)OV(O)*acac* must be expected together with pentanetrione.

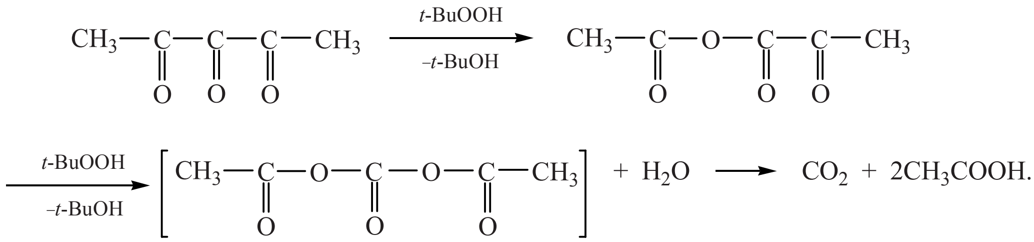
Products of the reaction of OV$(acac)_2$ with *t*-BuOOH in benzene at 20ºC (mol per mol of metal compound)

Reaction products[a]	OV$(acac)_2$:*t*-BuOOH			
	1:2	1:4	1:10	1:15
Volatile reaction products				
O_2	–	–	0.58	3.78
CO_2	0.42	0.82	1.82	1.99
t-BuOH	1.47	2.10	6.90	11.20
MeCO	0.05	0.10	Traces	0.18
$(t\text{-BuO})_2$	–	0.03	0.38	0.36
t-BuOOH	–	–	0.53	0.94
MeC(O)OBu-*t*	0.15	0.12	0.28	0.32
MeC(O)OOBu-*t*	0.05	0.12	0.24	–
CH_3COOH[b]	0.81	1.22	3.03	3.21
Products of hydrolysis of the volatile residue				
$CH_3COCH_2COCH_3$	1.22	1.09	–	–
t-BuOH	0.37	0.43	–	0.84
RCOOH[c]	0.23	0.17	0.14	0.17

[a] Mean results. [b] Pyruvic acid was identified qualitatively as 2,4-dinitrophenylhydrazone, and after treating with diazomethane its methyl ester was found. [c] Mixture of acetic and pyruvic acids.

Subsequent reaction of pentanetrione with hydroperoxode or the vanadium-containing peroxide analogous to that of α-diketones must lead to the mixed acetic-pyruvic anhydride. The latter may react with *t*-BuOH or *t*-BuOOH to form the acetic and pyruvic acids and also their *tert*-butyl esters and peresters [11–13] found by us (see the table). But it follows from the table that main reaction products of conversion of acetylacetone are CO_2 and acetic acid which are found already at the equimolar reagents ratio. For instance, at the 1:2 *t*-BuOOH:OV$(acac)_2$ ratio the liberation of CO_2 was observed already on the third minute of the propose. The participation of vanadium peroxides in oxidation may be seen from the alteration in the color of the reaction solutions. In the experiment described the claret coloration remained for 5 min. It may be suggested that further oxidation of mixed anhydride by the second α-dicarbonyl bond and hydrolysis of the oxidation products would take place [Eq. (3)].

Equation (3) may serve as the confirmation of H_2O formation according to scheme (2). With the purpose of testing the offered scheme the oxidation of acetylacetone with hydroperoxide **II** in the presence of vanadyl **I** was carried out at 10:20:1 molar ratio of reagents in benzene at 20ºC. Conversion of β-diketone was 40–50%. In this case 0.53 mol of CO_2 and 0.90 mol of acetic acid per 1 mol of diketone were isolated. The pentanetrione and its hydrate were also synthesized and their reaction with *t*-BuOOH was studied in benzene at 20ºC. The reaction of pentanetrione with hydroperoxide **II** at 1:1 molar ratio yielded 0.89 mol of *t*-BuOH, 0.59 mol of CH_3COOH, and 0.08 mol of *tert*-butyl acetate. The presence of CO_2, pyruvic acid, and unreacted triketone was established



(3)

qualitatively. In the reaction of pentanetrione hydrate with *t*-BuOOH at 1:2 molar ratio 0.60 mol of CO_2 and 1.04 mol of CH_3COOH were found [Eq. (3)].

In the IR spectra of volatile fractions of all the reactions described intense absorption bands characteristic of the acetic acid are observed, cm^{-1}: 1714, 1760 [C=O (dimer, monomer), 1290 (C–O), 1420 (C–O–H). After treating with diazomethane the acid was identified in a form of its methyl ester. At the 1:10 and higher molar ratio of vanadyl **I** and hydroperoxide **II** alongside with the products of transformation of the ligand the liberation of oxygen was observed. In this case some part of $VO(acac)_2$ is converted to the dark-green precipitate insoluble in benzene and containing no organic groups. Its IR spectrum contains absorption bands at 600, 763 (V–O–V), and 999 (V=O) cm^{-1}. Very intense absorption band at 3409 cm^{-1} was attributed to the bond vibrations of hydroxy group (V–OH), and the band at 1627 cm^{-1} was characteristic of the crystallization water (Fig. 1). Elemental analysis data show that the residue contains not more than 1% of carbon. Hydrogen content was evaluated at 2.23, 2.57%, the calculated value for $HOVO_2{\cdot}H_2O$ is 2.54%. Combustion of the substance under study gives V_2O_3 and V_2O_5. On the basis of IR spectroscopy and elemental analysis it may be concluded that the composition of vanadium-containing precipitate is close to $HOVO_2{\cdot}H_2O$.

Note that the IR spectrum of this precipitate is identical to the ethylbenzene-insoluble product of decomposition of the vanadium-containing peroxy-derivative in the $(t\text{-BuO})_4V$–*t*-BuOOH system in the presence of oxygen [14] [Eq. (4)].

$$>V(O)OOCH(Me)Ph \longrightarrow >V(O)OH + PhC(O)Me. \quad (4)$$

In spite of the extremely poor solubility of the precipitate in benzene it was found to decompose *t*-BuOOH at room temperature with the liberation of oxygen. Reaction of this precipitate with hydro-peroxide **II** in benzene (0.45 g of *t*-BuOOH and 0.02 g of precipitate, ~25:1 molar ratio) yielded 0.30 mol of O_2, 0.64 mol of *t*-BuOH, 0.05 mol of acetone and 0.04 mol of tert-butyl peroxide per 1 mol of hydroperoxide **II**. Selectivity of oxygen formation was 60%.

Reaction of $VO(acac)_2$ with *t*-BuOOH was studied by means of ESR spectrocopy in the absence as well as in the presence of spin traps such as 2-methyl-2-nitrosopropane and *C*-phenyl-*N*-*tert*-butyl-nitrone at 20ºC. The first trap occured to be ineffective most probably due to its oxidation to nitro compound. At the

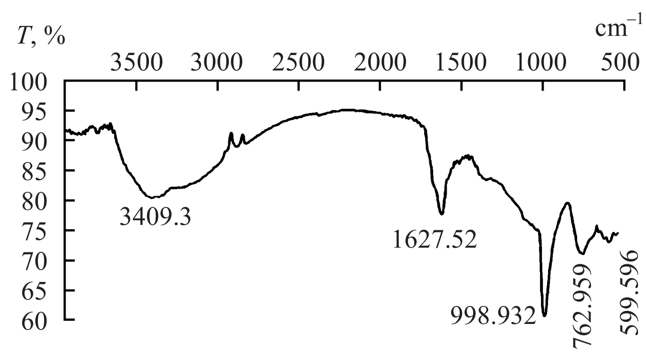


Fig. 1. IR spectrum of the benzene-insoluble product formed in the reaction of $(acac)_2VO$ with *t*-BuOOH excess (1:15 molar ratio) (KBr pellet).

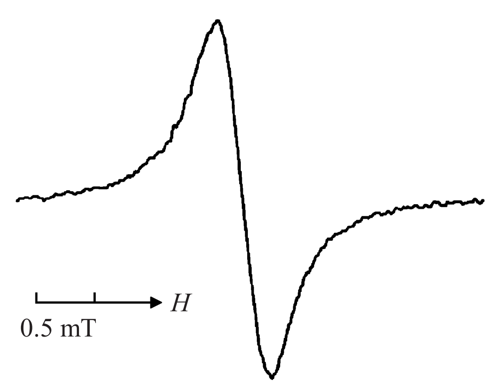


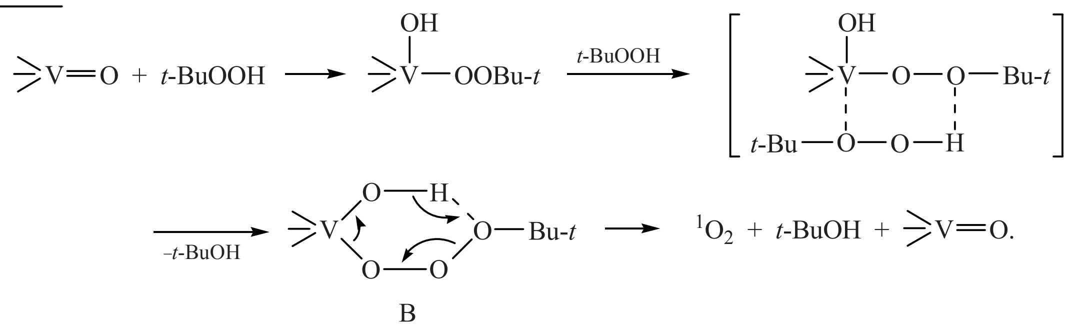
Fig. 2. ESR spectrum of $(acac)_2VO$–*t*-BuOOH (1:15) system registered just after mixing of reagents in the absence of spin traps, benzene, 20ºC, $c[(acac)_2VO]$ 0.005 M.

addition of *t*-BuOOH to VO(*acac*)$_2$ (2:1) in benzene intensity of the vanadyl signal increased 3.5 times and remained constant in the course of 30 min what indicated the presence of the V^{4+} compounds. The excess of hydroperoxide up to 10 mol/mol led to the complete disappearance of the V^{4+} signal showing the oxidation of V^{4+} to V^{5+}. At the increase in the amount of *t*-BuOOH to 15 mol per 1 mol of vanadyl **I** in the absence of spin traps in benzene at 20ºC ESR spectrum is a singlet, g_i 2.0156 (Fig. 2).

Intensity of the signal does not alter in the course of 40 min. Analogous signal with g_i 2.0150 is observed in the course of decomposition of *t*-BuOOH on the vanadium-containing precipitate. As *t*-BuOO$^·$ radicals were not found under these conditions we suggested that according to the value of *g*-factor the signal belonged to the vanadium-containing >V(O)OO$^·$ radical. A singlet with the same value of *g*-factor was registered in the(*t*-BuO)$_3$VO–*t*-BuOOH system and attributed to (*t*-BuO)$_2$V(O)OO$^·$ radical [14].

On the basis of data on the reactions of aluminum [15] and vanadium [14] *tert*-butylates with *tert*-butylhydroperoxide we think that the formation of oxygen in the reactions under study proceeds through the stages of formation of vanadium-containing peroxides and trioxides.

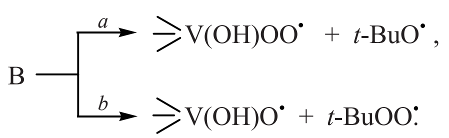
Vanadium peroxy compounds may be formed due to the displacement of ligand with hydroperoxide [Eq. (1)] and also as the result of addition of *t*-BuOOH to V=O bond [6, 7]. As it was shown above, excess hydroperoxide leads to substitution of ligands and formation of the vanadium hydroxocompounds. The latter take part in generation of oxygen, and the scheme of its formation may be presented as follows [Eq. (5)].



(5)

Reaction of peroxide A with *t*-BuOOH according to the analogous scheme also must lead to the liberation of oxygen through the stage of the vanadium-containing trioxide.

Simultaneosly to formation of oxygen homolysis of trioxide B takes place [scheme (6)] to $g_i$ve the vanadium-containing peroxy radical traced by means of ESR spectroscopy (Fig. 2).



(6a)

(6b)

Indirect confirmation of the reaction (6b) is the presence of *tert*-butylperoxide in the reaction products.

$$2t\text{-BuOO}^· \rightarrow t\text{-BuOOBu-}t + O_2. \qquad (7)$$

According to the scheme (5) oxygen must be formed in the singlet state. With the purpose of establishing this assumption reactions of the VO(*acac*)$_2$–*t*-BuOOH with the singlet oxygen acceptors such as anthracene and 1,1-diphenylethylene [16] were carried out [16]. It was established preliminary that $Ph_2C{=}CH_2$ does not react at room temperature with hydroperoxide **II** (C_6H_6, 3 days).

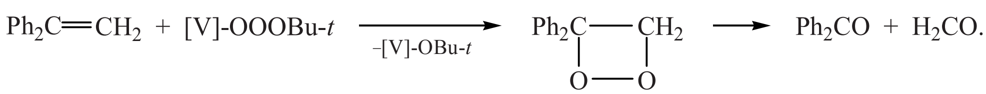
Products of the reaction of anthracene with the vanadyl **I**-*t*-BuOOH system at the 1:0.1:1.5 molar ratio in benzene at 20ºC (1 day) contain 0.30 mol of anthraquinone. Analogous reaction with 1,1-diphenylethylene yields 0.29 mol of benzoquinone and 0.20 mol of HCOOH. Formaldehyde was identified qualitatively in the volatile reaction products, while the products of hydrolysis contained epoxide, probably 1,1-diphenyloxirane.

All the above-mentioned substances were formed in the reaction of anthracene with *tert*-butylperoxide in the presence of the insoluble precipitate isolated from the reaction of VO(*acac*)$_2$ with hydroperoxide. Keeping of 0.02 g of the precipitate, 0.35 g of anthracene, and 0.45 g of *t*-BuOOH in 20 ml of benzene for 1 day yielded 0.08 g (20%) of anthraquinone, and after 3 days 0.17 g (41%) of it was found.

By an example of oxidation of 1,1-diphenylethylene it was shown that the vanadium-containing precipitate plays a role of heterogeneous catalyst. Small batch of it, 0.01 g, was placed in 10 ml of benzene and kept for 1 h. After that the precipitate was filtered off and dried. To the filtrate obtained 0.31 g of $Ph_2C=CH_2$ and 0.45 g of *t*-BuOOH were added (1:3 molar ratio), and the resulting mixture was kept at room temperature for 3 days. Only the traces of benzoquinone were found. Then the solution obtained was treated with the batch of precipitate isolated as described above. After 1 day of storage at 20ºC 0.26 mol of Ph_2CO and 0.18 mol of formic acid were found. After 4 days amount of benzoquinone reached 0.36 mol, and after 7 days, 0.49 mol.

Note that in the case of $OV(acac)_2$ and the vanadium-containing precipitate benzoquinone and formaldehyde were evaluated as 2,4-dinitro-phenylhydrazones by means of TLC 1 h after the beginning of the reaction.

Formation of anthraquinone may be regarded as the result of the reaction of anthracene either with the singlet oxygen or with the vanadium-containing trioxide through the stage of formation of 9,10 epidioxyanthracene [16]. Oxidation of $Ph_2C=CH_2$ to benzoquinone and formaldehyde may occur with the intermediate formation of 1,2-dioxetane and its decomposition. It is known that the reactivity of 1,1-diphenylethylene to the free singlet oxygen is low [17], and we suggest that the reaction of phenylalkene with the vanadium-containing trioxide takes place [16].



(8)

Formaldehyde mainly forms formic acid or enters the Condensation reactions.

Hence, reaction of $OV(acac)_2$ with the excess of *t*-BuOOH proceeds through decomposition of vanadium alkoxylate, oxidation of the ligand, and liberation of oxygen partially in the singlet form through the stage of formation of the vanadium-containing peroxides and trioxides.

EXPERIMENTAL

IR spectra were recorded on an IR-Prestige-21 spectrometer from KBr pellets or thin layer. ESR spectra were taken on a Bruker ER-200D-SRC spectrometer equipped with a double ER 4105DR resonator (working frequency 9.5 GHz), and the temperature-controlling ER 4111VT block. For evaluation of g factor diphenylpicrylhydrazyl was used as a reference substance. Analysis was carried out in the cell of ESR spectrometer. For the improvement of resolution in the ESR spectra and removing of oxygen liberating in the reaction of components **I, II** the reaction solutions were degased. Spin traps were added on the initial stages of the reactions. Vanadyl acetylacetonate concentration was no more than 0.005 mol l^{-1}.

GLC analysis of the liquid reaction products was carried out on a Tsvet-2-65 chromatograph equipped with a flame ionization detector. Argon was used as a carrier gas. In all the cases Chromaton N-AW- DMCS was used. Volatile components (acetone, *tert*-butanol, *tert*-butylperoxide, acetylacetone, methyl acetate) were analysed on a 2400×3 mm column filled with TZKM ceramic carrier containing 10% of PEGA, colunm temperature 50–80ºC. Analysis of *tert*- butyl acetate and *tert*-butyl peracetate was carried out on a 3000×3 mm column containing 5% of SP-2401 at 50ºC. Analysis of high boiling products (acetophenone, benzophenone, 1-phenyl-1-ethanol) was carried out on a 3000×3 mm column, stationary phase 5% of SE-30 on Inerton-AW, column temperature 100–190ºC. Anthracene, anthraquinone, and 1,1-diphenylethylene were analysed at 190–210ºC on a 1000×3 mm column filled with 5% of OV-17 on Inerton Super carrier. Chromatograms were solved by means of the internal standard method, in each case reference substances were used. Amount of aliphatic acids in nonvolatile residues was evaluated according to [18]. Carboxylic acids were identified as methyl esters after treating with diazomethane. Quantitative analysis of hydroperoxides was carried out by iodometric titration. Carbonyl compounds were identified as 2,4-dinitrophenylhydrazones by melting points, and by means of TLC comparing R_f values of the batch and reference substances.

Silpearl sorbent, the broad-pored silica gel on the aluminum foil (Silufol UV-254) was used, elution was carried out with benzene or 18:1 benzene–diethyl ether. Amount of oxygen liberated in the course of the reaction was measured by the amount of the benzoic acid formed in the reaction of O_2 with benzaldehyde [19]. Vanadyl acetylacetonate was prepared from V_2O_5 by in treating succession with freshly distilled acetylacetone and sodium carbonate solution [20], mp 252ºC [21].

Pentanetrione-2,3,4 was prepared by oxidation of acetylacetone with *p*-nitrosodimethylaniline, bp 55–57ºC (12 mm Hg) [22]. Concentration of *tert*-butyl hydroperoxide used was no less than 99.6–99.8%.

Reaction of vanadyl acetylacetonate with *tert*-butyl hydroperoxide (1:15) in benzene, 20ºC. A solution of 0.088 g of VO(*acac*)$_2$ in 15 ml of benzene was placed in a flask, and 0.448 g of *t*-BuOOH was added. The reaction mixture immediately acquired intense cherry coloration, and after 20 min it became light brown. After 2 h formation of fine dark green precipitate was observed. It was filtered off, and the filtrate was analyzed chromatographically. *tert*-Butanol, 0.27 g, *tert*-butyl peroxide, 0.017 g, 0.012 g of *tert*-butyl acetate, and 0.0034 g of acetone were found. By means of titration in the presence of $FeCl_3$ [23] 0.005 g of *tert*-butyl peracetate was found. Treating with diazomethane solution gave 0.075 g of methyl acetate corresponding to 0.061 g of acetic acid.

The precipitate obtained as a greenish brown mass was dissolved in diethyl ether, hydrolized with 10% H_2SO_4, extracted with ether, and dried over Na_2SO_4. Ether extract contained 0.02 g of *t*-BuOH. No *tert*-butyl hydroperoxide was found in the reaction products. In the parallel experiment the acid content was evaluated in the precipitate obtained after filtering the benzene solution [18]. Amount of carboxylic acids was 0.17 mol per 1 mol of vanadyl. For their identification the precipitate was treated with alkali, the solution obtained was filtered, and water was distilled off from the filtrate. The concentrated residue was acidified with 30% sulfuric acid, thoroughly extracted with the distilled diethyl ether, and dried over Na_2SO_4. Some part of the solution was treated with 2,4-dinitrophenylhydrazine to form the corresponding hydrazone of the pyruvic acid which was identified by means of TLC against the authentic sample. Residual solution was methylated with diazomethane and then treated with 2,4-dinitrophenylhydrazine to give the corresponding hydrazone of methyl pyruvate, mp 184ºC in agreement with the reported data [24].

In the reaction of VO(*acac*)$_2$ with *t*-BuOOH at 1:15 molar ratio in benzene the liberation of oxygen was observed. Its amount was evaluated by means of the procedure [19]. For this purpose the reaction was carried out in the H-shaped ampule. One of its bends was loaded with 0.4 ml of benzaldehyde, and another one with a solution of 0.088 g of VO(*acac*)$_2$ and 0.449 g of *tert*-butyl hydroperoxide in 10 ml of benzene. Both bends were frozen, degased, and sealed. After refreezing vigorous liberation of oxygen was observed, and the reaction solution aquired cherry color. After 12 h formation of finely dispersed green precipitate was observed, and the solution became light brown. Amount of benzoic acid was evaluated by weighting, and also by titration with 0.1 N NaOH solution in presence of phenolophthaleine.

Amount of benzoic acid was 0.30 g corresponding to 0.040 g of O_2 (3.78 mol per 1 mol of starting vanadyl acetylacetonate). For the evaluation of CO_2 liberated in the course of the reaction of VO(*acac*)$_2$ with *t*-BuOOH the process was carried out in a two-necked flask with the reflux condenser connected with a bubbler filled with the saturated $Ba(OH)_2$ solution. Another neck was supplied with a tube for the inert gas inlet. The flask was evacuated and then filled with dry argon to remove oxygen. After that a mixture of 0.095 g of VO(*acac*)$_2$, 0.480 g of *tert*-butyl hydroperoxide, and 15 ml of benzene was placed in the flask, and the argon flow was passed through it. Several minutes later formation of barium carbonate was observed. Argon was passed through the reaction mixture for 3 h until the complete formation of the precipitate. $BaCO_3$ was filtered off and dried. Yield 0.140 g, 1.99 mol/mol of starting vanadyl.

Oxidation of acetylacetone with VO(*acac*)$_2$–*t*-BuOOH (10:1:20) system in benzene. A solution of 0.13 g of vanadyl **I**, 0.88 g of *t*-BuOOH, and 0.49 g of acetylacetone was placed in the reaction vessel. Twenty minutes later heat evolution was observed. Amount of unreacted diketone after 20 h of keeping was evaluated at 0.24 g. Volatile products were recondensed in a trap cooled with liquid nitrogen. Residual red-brown mass after a day of storage became bluish green. Treating of the condensate with diazomethane permitted to find 0.32 g of methyl acetate. Amount of the acid (0.26 g) was confirmed also by titration of the condensate with 0.1 N NaOH. TLC analysis of volatile products before and after treating the condensate with diazomethane permitted to establish the formation of pyruvic acid and its methyl ester (corresponding 2,4-dinitrophenylhydrazones were found). In the parallel experiment formation of 0.51 g of $BaCO_3$ (0.53 mol per mol of diketone) was observed. In this case precipitation of the bluish green solid from the solution was observed. Its IR spectrum contained absorption bands characteristic of the *acac*-V, V=O, and V–OH (3400 cm^{-1}) bonds.

Reaction of anthracene with VO(*acac*)$_2$-*t*-BuOOH system (10:1:15) in benzene. VO(*acac*)$_2$, 0.088 g, 0.5 g of anthracene, and 0.45 g of *t*-BuOOH in 40 ml of benzene were in succession placed in the flask. Reaction mixture aquired bright yellow color. After 24 h yellow needle-like crystals were filtered off on a glass filter. Pure anthraquinone, 0.02 g, was obtained, mp 280ºC (in agreement with the reported data). The volatile products were recondensed, and 0.24 g of *t*-BuOH and 0.06 g of (*t*-BuO)$_2$ were found in this preparation by chromatography. Yellow residue was hydrolyzed in benzene with 10% sulfuric acid and extracted with freshly distilled benzene. The extract obtained was dried over sodium sulfate. Anthraquinone, 0.17 g, and 0.06 g of *t*-BuOH were found in it. Aqueous acidic hydrolizate contained 0.02 g of *t*-BuOH.

Reaction of 1,1-diphenylethylene with the insoluble vanadium-containing precipitate and *t*-BuOOH in benzene. The reaction mixture consisted of 0.01 g of the insoluble precipitate, 0.31 g of $Ph_2C=CH_2$, 0.45 g of *tert*-butylhydroperoxide, and 10 ml of benzene. After 1.5 h the aliquote of the solution was treated with 2,4-dinitrophenylhydrazine. By means of TLC dinitrophenylhydrazones of benzophenone and formaldehyde were found. Chromatographic analysis of the solution after 4 days of storage showed that it contained 0.14 g of benzophenone and 0.16 g of starting phenylalkene.

Benzene and volatile products were recondensed in a trap cooled with liquid nitrogen. The condensate contained 0.18 g of *t*-BuOH, 0.016 g of acetone, and 0.20 g of unreacted *t*-BuOOH. Presence of aldehyde was proved by the reaction with fuchsin sulfurous acid. Titration of the reaction solution with 0.1 N NaOH in the presence of phenolphthalein showed the presence of 0.025 g of formic acid identified by oxidation with 0.1 N $KMnO_4$ solution. In the parallel experiment the residue after removing benzene was analyzed to show the formic acid content 0.013 g [18]. The residue after removing volatile products is a brown mass. It $g_i$ves positive test on the presence of oxirane ring. We assume that formation of 1,1-diphenyloxirane may take place because the lack of the products of transformation of phenylalkene is observed.

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