ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 2, pp. 266–276. © Pleiades Publishing, Ltd., 2008. Original Russian Text © L.P. Stepovik, M.V. Gulenova, I.M. Martynova, B.A. Mar'yasin, V.K. Cherkasov, 2008, published in Zhurnal Obshchei Khimii, 2008, Vol. 78, No. 2, pp. 288–298.

## Titanium Tetra-tert-butoxide-tert-Butyl Hydroperoxide Oxidizing System: Physicochemical and Chemical Aspects

L. P. Stepovik<sup>*a*</sup>, M. V. Gulenova<sup>*a*</sup>, I. M. Martynova<sup>*a*</sup>, B. A. Mar'yasin<sup>*a*</sup>, and V. K. Cherkasov<sup>*b*</sup>

 <sup>a</sup>Lobachevskii Nizhni Novgorod State University, pr. Gagarina 23, Nizhni Novgorod, 603950 Russia e-mail: gulmv@rambler.ru
 <sup>b</sup>Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhni Novgorod, Russia

Received June 13, 2007

**Abstract** — The reaction of titanium tetra-*tert*-butoxide with *tert*-butyl hydroperoxide (1 : 2) ( $C_6H_6$ , 20°C) involves the steps of formation of the titanium-containing peroxide (*t*-BuO)<sub>3</sub>TiOOBu-*t* and peroxytrioxide (*t*-BuO)<sub>3</sub>TiOOBu-*t*. The latter decomposes with the release of oxygen, often in the singlet form, and also homolytically with cleavage of both peroxy bonds. The corresponding alkoxy and peroxy radicals were identified by ESR using spin traps. The title system oxidizes organic substrates under mild conditions. Depending on the substrate structure, the active oxidant species can be titanium-containing peroxide, peroxy-trioxide, and oxygen generated by the system. **DOI:** 10.1134/S1070363208020151

Titanium alcoholates are widely used as catalysts of hydroperoxide oxidation of various classes of organic substrates. They catalyze the synthesis of epoxidized alcohols from alkenes [1] and stereoselective epoxidation of allyl alcohols [2, 3]. When treated with *tert*-butyl hydroperoxide in the presence of Ti(OPr-i)<sub>4</sub>, primary and secondary benzyl alcohols selectively transform into the corresponding aldehydes and ketones [4], and substituted phenols and naphthols are oxidized to o-quinones [5]. The above oxygen-containing derivatives are oxidized along intramolecular pathway, without participation of free radicals.

The reaction of titanium tetra-*tert*-butoxide **I** with *tert*-butyl hydroperoxide **II** in 1:2 molar ratio in benzene at room temperature is accompanied by the release of oxygen (0.85–0.90 mol per mole of **I**) and regeneration of the starting titanium alcoholate [6] (Table 1). As the **II**: **I** molar ratio is increased to 10:1, the amount of the released oxygen increased to 4.2 mol. No products of solvent oxidation were detected. The above system oxidizes under mild conditions (20°C) the C–H bonds of the methyl (toluene), methylene (hexane, ethylbenzene), and methine (1,1-diphenylmethane, triphenylmethane) groups [6], and also the E–H bonds of organometallic hydrides R<sub>3</sub>EH (E = Si, Ge; R = Et, Ph) [7]. The composition of the

products suggests the radical mechanism of the reaction [6].

We suggested that the reaction of the components of the alcoholate I-hydroperoxide II system in benzene is similar to that observed in the aluminum tri-

**Table 1.** Reaction products formed in the  $(t-BuO)_4Ti-t-BuOOH$  system in benzene at 20°C (moles per mole of titanium alcoholate)

	(t-BuO) <sub>4</sub> Ti:t-BuOOH ratio				
Reaction products	1:2	1:10			
Volatile reaction products					
$O_2^{b}$	0.85	4.42			
t-BuOH	3.59	9.63			
$(t-BuO)_2$	0.08	0.29			
$(CH_3)_2 \tilde{C}=O$	0.02	Traces			
Products of hydrolysis of nonvolatile residue <sup>c</sup>					
t-BuOH	2.15	3.16			
$H_2O_2$	0.08	0.11			
СH <sub>3</sub> COOH	0.07	0.24			

<sup>a</sup> Averaged results. <sup>b</sup> Determined by the reaction with benzaldehyde. <sup>c</sup> ~1 mol of titanium in all the experiments. *tert*-butoxide–*tert*-butyl hydroperoxide system [8]. The initial step of the process is formation of the titanium-containing peroxide. The reaction of the latter with *tert*-butyl hydroperoxide leads to peroxytrioxide **III** 

which decomposes along two pathways: (1) release of oxygen and regeneration of titanium alcoholate and (2) homolytic pathway with the formation of alkoxy and peroxy radicals [scheme (1)] [6, 7, 9].

$$(t-\operatorname{BuO})_{4}\operatorname{Ti} + t-\operatorname{BuOOH} \xleftarrow{C_{6}H_{6}, 20^{\circ}\mathrm{C}}{t-\operatorname{BuOH} + (t-\operatorname{BiO})_{3}\operatorname{TiOOBu} - t,}$$

$$\mathbf{I} \qquad \mathbf{II}$$

$$(t-\operatorname{BuO})_{3}\operatorname{TiOOBu} - t + t-\operatorname{BuOOH} \longrightarrow t-\operatorname{BuOH} + (t-\operatorname{BiO})_{3}\operatorname{TiOOBu} - t,$$

$$\mathbf{III}$$

$$(1)$$

$$\begin{pmatrix} 0 \\ (t-\operatorname{BuO})_{3}\operatorname{Ti} \\ t-\operatorname{BuO} \end{pmatrix} \xrightarrow{0} \begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix} (t-\operatorname{BuO})_{4}\operatorname{Ti} + {}^{1}\operatorname{O}_{2},$$

$$(1)$$

$$\mathbf{IIIa}$$

The goal of this study was to examine and prove the processes indicated in scheme (1) by physicochemical and chemical methods.

The formation of radicals was monitored by ESR in the presence of spin traps and without them. As spin traps we used *C*-phenyl-*N*-tert-butylnitrone IV and 2-methyl-2-nitrosopropane V. The former scavenges alkylperoxy radicals, and the latter, alkyl and alkoxy radicals [10, 11]. It is known that nitroso compounds react with hydroperoxides to form adducts of alkoxy radicals. The possibility of using spin trap V as acceptor of free radicals in the system metal alcoholate–hydroperoxide was demonstrated in [8].

After mixing I and II (1:2) in benzene at room temperature without spin traps, a singlet ( $g_i$  2.0125) appears in the ESR spectrum (Fig. 1). This signal can be assigned to (*t*-BuO)<sub>3</sub>TiOO (VI), as alkylperoxy

radicals are detected only at low temperatures [12]. With time, this signal becomes strongly broadened, suggesting generation of oxygen in the reaction mixture [13]. In 30 min the signal fully disappears. In the vitrified solvent matrix (ethylbenzene,  $-90^{\circ}$ C), an anisotropic spectrum of (t-BuO)<sub>3</sub>TiOO· is observed. Its parameters are  $g_1 = 2.0249$ ,  $g_2 = 2.0092$ , and  $g_3 = 2.0025$ . The quantity  $\langle g_i \rangle = 2.0122$  calculated from these parameters is well consistent with the  $g_i$  value determined from the isotropic ESR spectrum (Fig. 2). This fact confirms that, at room temperature, only the titanium-containing peroxy radical is detected.

A mixture formed by the reaction of an authentic sample of  $(t-BuO)_3$ TiOOBu-*t* with *t*-BuOOH (20°C) also gives a broad singlet with the same *g*-factor in the absence of spin traps. Because tri-*tert*-butoxy-*tert*-butylperoxytitanium gives ESR signals neither at -90 (ethylbenzene) nor at 25°C (benzene),  $(t-BuO)_3$ TiOO



0.5 mT



**Fig. 2.** ESR spectrum of the reaction mixture (t-BuO)<sub>4</sub>Ti-t-BuOOH (1:2) in ethylbenzene  $(-90^{\circ}C)$ .

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 78 No. 2 2008



**Fig. 3.** ESR spectrum recorded in the  $(t-BuO)_4$ Ti–t-BuOOH system (1 : 2) in the presence of spin trap IV: (a) immediately after mixing the reactants,  $c[Ti(OBu-t)_4]$  0.025 M, and (b) 10 min after mixing the reactants,  $c[Ti(OBu-t)_4]$  0.1 M, the sample was degassed. Figures at peaks are compound nos.

is apparently generated in the step of the reaction of the titanium-containing peroxide with II.

Addition of C-phenyl-N-tert-butylnitrone IV into the reaction system in benzene gives rise to an ESR spectrum shown in Fig. 3. After mixing the reactants  $\{c[\text{Ti}(\text{OBu-}t)_4] = 0.025 \text{ M}\}, \text{ a triplet with isotropic parameters } [g_i = 2.0063, a_i^{15}\text{N}) = 0.795 \text{ mT}] \text{ typical}$ of benzoyl-tert-butylnitroxyl radical VII [10] appears in the ESR spectrum (Fig. 3a). Radical VII is formed by oxidation of the spin trap with either singlet oxygen or peroxy radicals [11]. A triplet of doublets with asymmetric lines was assigned to adducts of C-phenyl-N-tert-butylnitrone. With an increase in the concentration of titanium tert-butoxide to 0.1 M, a signal of radical VII practically disappears from the ESR spectrum in 10 min, and two triplets (1:1:1) of doublets (1:1) are recorded (Fig. 3b). Their constants were determined after degassing the samples. One of the signals with the parameters  $g_i = 2.0053$ ,  $a_i(^{15}N) =$ 1.450 mT should be assigned to the adduct of trap IVwith alkoxy radical VIII, *t*-BuO, or (*t*-BuO)<sub>3</sub>TiO [8]. At low concentrations of the starting alcoholate I (0.025 M), this signal is not detected (Fig. 3a), and at  $c[\text{Ti}(\text{OBu-}t)_4] = 0.1$  M its relative concentration is low, and within 10–15 min it fully disappears. The major signal in the spectrum (Fig. 3b) at  $g_i = 2.0056$ with the hyperfine coupling constants  $a_i({}^{15}N) = 1.323$ ,  $a_i(H) = 0.139$  mT belongs to an adduct of spin trap IV with one of peroxy radicals  $[(t-BuO)_3TiOO]$  or t-BuOO'] (IX) [14]. The first alternative is more probable, because  $(t-BuO)_3TiOO$  is more stable under these conditions.

The isotropic ESR spectrum (benzene, 20°C) of the reaction mixture in the presence of 2-methyl-2-nitro-

sopropane contains a symmetrical triplet (1:1:1)[ $g_i = 2.0056$ ,  $a_i(^{15}N) = 2.715$  mT] corresponding to the adduct of spin trap V with *t*-BuO radicals, *t*-Bu-N(O')-OBu-*t* (X) [8].

We determined the half-life of the  $(t-BuO)_3TiOO'$ radical in ethylbenzene, ~500 s. The kinetics of the decay of this radical follows a first-order equation, suggesting a monomolecular mechanism of its formation.

An indirect evidence for the formation of peroxy radicals *t*-BuOO and (t-BuO)<sub>3</sub>TiOO is the presence in reaction products of *tert*-butyl peroxide (~0.08 mol) and bound hydrogen peroxide (~0.10 mol) (per mole of starting alcoholate) (Table 1) [Eq. (2)]:

$$2\text{ROO}^{\cdot} \longrightarrow \text{ROOR} + \text{O}_2, \qquad (2)$$
$$\text{R} = t\text{-Bu}, \ (t\text{-BuO})_3\text{Ti}.$$

To prove the formation of peroxy radicals and quantitatively estimate their concentration, we performed the reactions of  $(t-BuO)_4Ti-t-BuOOH$  with sterically hindered phenols [2,6-di-*tert*-butyl-4-methylphenol (Ionol), 2,4,6-tri-*tert*-butylphenol], because it is known that alkylperoxy radicals are scavenged by 2,4,6-substituted phenols with the formation of 4-alkylperoxy-2,6-di-*tert*-butyl-4-alkylhexa-3,5-dienones [15–17].

In the absence of metal alcoholates ( $20^{\circ}$ C, C<sub>6</sub>H<sub>6</sub>), hydroperoxide **II** does not react with any of the abovementioned phenols. From the reactions of system **I–II** with these phenols, we isolated in both cases 2,6-di*tert*-butyl-4-*tert*-butylperoxy-4-alkylcyclohexa-2,5-dienone (~30%) and 2,5-di-*tert*-butyl-*p*-benzoquinone (0.04–0.17 mol) (Table 2).



The formation of the above products can be accounted for by scheme (3).

As seen from the scheme, the phenoxyl radical reacts either with *t*-BuOO or with  $(t-BuO)_3TiOO$  radical. In the former case, the reaction yields a peroxy ketone, and in the latter case, 2,6-di-*tert*-butyl*p*-benzoquinone via titanium-containing peroxide **XI**. The presence of peroxy ketones in the reaction mixtures is also confirmed by IR spectroscopy. The IR spectra of the reaction products contain strong absorption bands belonging to quinoid structures, cm<sup>-1</sup>: 1647 (C=C), 1667–1669 (C=O), 796–800 (O–O) [17, 18]. Thus, the formation of alkylperoxy ketones confirms the generation of peroxy radicals in the system I–II and allows quantitative estimation of their concentration.

Along with the peroxy ketone, with 2,4,6-tri-*tert*butylphenol we expected the formation of the corresponding alkoxy ketone, 2,4,6-tri-*tert*-butyl-4-*tert*butoxycyclohexa-2,5-dienone. However, we have not detected this product. It is known that the related compounds are not formed from Ionol [19]. In the case of 2,4,6-tri-*tert*-butylphenol, the phenoxyl radical interacts not only with peroxy radicals, but also with oxygen generated by the system (t-BuO)<sub>4</sub>Ti–t-BuOOH to form bis(1,3,5-tri-*tert*-butylcyclohexa-2,5-dien-4on-1-yl) peroxide.

Tri(*tert*-butoxy)titanium *tert*-butyl trioxide **III** cannot be subjected to an experimental structural study because of its instability and is postulated as the necessary unit in the chain of the general mechanism [scheme (1)]. To substantiate this approach theoretically, we performed a quantum-chemical calculation of the trioxide molecule (an isolated molecule in the gas phase was considered).

All the calculations were performed by the DFT method (density functional theory) in the B3LYP version using the 6-31G basis set and the 6-31G(d,p) basis set supplemented by polarized d,p functions. We used the standard version of the GAUSSIAN

**Table 2.** Products of oxidation of 2,6-di-*tert*-butyl-4-R-phenols (R = Me, *t*-Bu) with the system  $Ti(OBu-t)_4$ *t*-BuOOH (1 : 1 : 2), C<sub>6</sub>H<sub>6</sub>, 20°C (moles per mole of metal alcoholate)<sup>a</sup>

Departies products <sup>a</sup>	Ti(OBu-t) <sub>4</sub>				
Reaction products	R = Me	R = t-Bu			
Volatile reaction products					
t-BuOH	3.31	3.17			
Acetone	0.04	_			
Products of hydrolysis of nonvolatile residue <sup>b,c</sup>					
t-BuOH	2.64	2.75			
t-BuOOH	0.02	Traces			
2,6-Di-tert-butyl-p-	0.04	0.17			
benzoquinone					
2,6-Di-tert-butyl-4-tert-	0.30	0.30			
butylperoxy-4-R-cyclohexa-					
2,5-dienone					
Bis(1,3,5-tri- <i>tert</i> -butylcyclo-	_	0.07			
hexa-2,5-dien-4-on-1-yl)					
peroxide					
Starting phenol	0.29	0.24			

<sup>a</sup> Averaged results. <sup>b</sup> ~1 mol of titanium in all the experiments.
 <sup>c</sup> An unidentified epoxy compound (yield 0.10 mol) was also detected in the case of R = Me.

03W program package [20]. The results of geometry optimization and calculation of the total energy of peroxytrioxide **III** suggest that it should be fairly stable ( $\Delta E = E_1 - E_2 = 19.3 \text{ kcal mol}^{-1}$ ) (Fig. 4).

To determine whether this point on the potential energy surface is a minimum, we calculated the vibration frequencies of a molecule of this kind. In so doing, to decrease the number of heavy atoms and thus to simplify the calculation, we replaced *tert*-butyl groups by methyl groups. We assumed that this replacement would not cardinally alter the problem, because the *tert*-butyl groups are relatively remote from each other. Therefore, their repulsion in the open form of the trioxide molecule should not be significant, despite the fact that the strain strain caused by close location of *tert*-butyl groups is certainly higher compared to methyl groups. The calculation showed that the open form of titanium peroxytrioxide **III** corresponds to a minimum on the potential energy surface (Fig. 5), i.e., this molecule is an intermediate. Selected bond angles and bond lengths in this molecule are given in Table 3.

Thus, the results of a quantum-chemical calculation and evidences for the presence of the radicals  $(t-BuO)_3TiOO$ , t-BuO,  $(t-BuO)_3TiO$ , and t-BuOOconfirm the formation of titanium-containing peroxytrioxide **III** in the reaction of alcoholate **I** with hydroperoxide **II** and its homolytic decomposition across two peroxy bonds.

Table 1 shows that the major transformation pathway of **III** is the decomposition with the release of oxygen. In the process, the *tert*-butoxy group migrates to the metal atom with an electron pair, which, in accordance with the rule of spin preservation, should lead to the formation of singlet oxygen [scheme (1), pathway 1]. However, quantum-chemical calculations showed that cyclic form **IIIa** of the peroxytrioxide cannot be realized because of strong steric strain produced by the bulky *tert*-butyl groups. Presumably, simultaneous formation of oxygen and titanium alcoholate **I** is realized in a dimer of the open form of **III** [scheme (4)]:

**Table 3.** Selected interatomic distances d in  $(MeO)_3Ti \cdot OOOMe^a$ 

Distance	<i>d</i> , Å	Distance	<i>d</i> , Å
$\begin{array}{c} {\rm Ti}^{1} - {\rm O}^{6} \\ {\rm Ti}^{1} - {\rm O}^{7} \\ {\rm Ti}^{1} - {\rm O}^{8} \\ {\rm Ti}^{1} - {\rm O}^{2} \end{array}$	1.792 1.784 1.782 1.903	$O^{2}-O^{3}$ $O^{3}-O^{4}$ $O^{2}-O^{4}$	1.447 1.446 2.346

<sup>a</sup> Bond angle  $O^2O^3O^4 = 108.4^\circ$ .



**Fig. 4.** Results of calculation of the (t-BuO)<sub>3</sub>TiOOOBu-t molecule in the open form [FOPT (geometry optimization to reach the minimum); DFT-B3LYP; 6-31G; E = -1931.997810 au].

With the aim to identify and quantitatively determine  ${}^{1}O_{2}$ , we studied the reaction of the  $(t-BuO)_{4}Ti$ t-BuOOH system with typical acceptors of singlet oxygen: anthracene and 9,10-dimethylanthracene. The primary oxidation products are 9,10-epidioxyanthracenes. 9,10-Dihydro-9,10-epidioxyanthracene under the reaction conditions transforms into anthraquinone [21]; its yield reaches 0.30 mol. The reaction with 9,10-dimethylanthracene yields up to 0.45 mol of 9,10-dimethylepidioxyanthracene, which was isolated pure and characterized by <sup>1</sup>H NMR spectroscopy [22]. The formation of anthraquinone and 9,10-dimethyl-9,10-epidioxyanthracene unambiguously proves the occurrence of the reaction with singlet oxygen.

It is well known that  $\beta$ -carotene in concentrations of down to  $10^{-4}-10^{-5}$  M efficiently quenches free singlet oxygen irrespective of its generation pathway. One  $\beta$ -carotene molecule induces conversion of more than 250  ${}^{1}O_{2}$  molecules. The quenching is physical, occurs at a rate of  $(2.5-5.0) \times 10^{9}$  mol  $1^{-1}$  s<sup>-1</sup>, and consists in the energy transfer to the triplet level of  $\beta$ -carotene [23, 24]:

 $O_2(^1\Delta) + \beta$ -carotene  $\longrightarrow O_2(^3\Sigma) + {}^3(\beta$ -carotene). (5)

Addition of  $\beta$ -carotene in concentrations as high as  $10^{-4}-10^{-3}$  M to the system under consideration decreased the anthraquinone yield by a factor of no more than 2.

We studied the reaction of the system alcoholate I-hydroperoxide II (1:2) with anthracene and 9,10-dimethylanthracene simultaneously (molar ratio 1:1), taking into account that the rate constants of the reactions of free singlet oxygen with anthracene and 9,10dimethylanthracene differ by two orders of magnitude  $(k_1 = 7 \times 10^4, k_2 = 4 \times 10^6 \text{ 1 mol}^{-1} \text{ s}^{-1}$ , respectively) [25]. However, in our case the yield of 9,10-dimethyl-9,10-epidioxyanthracene (0.35 mol) exceeds the yield of anthraquinone (0.19 mol) by a factor of less than 2. These results, in combination with the lack of significant effect of  $\beta$ -carotene on the anthracene conversion, show that there is no free singlet oxygen in the system.

The  $(t\text{-BuO})_4\text{Ti}-t\text{-BuOOH}$  system oxidizes arylalkenes containing at the  $sp^2$ -carbon atom only phenyl substituents and hydrogen atoms (1,1-diphenylethylene, triphenylethylene). It is known that these compounds are relatively inert to free singlet oxygen. The [2+2]-cycloaddition reactions are performed by passing  ${}^1\text{O}_2$  through an arylalkene solution for 24 h and more [26].

By the example of the reaction of system **I**–**II** with  $Ph_2C=CH_2$ , we demonstrated that the reaction was complete within ~1–1.5 h, as judged from the disappearance of both the substrate and hydroperoxides. Prolongation of the reaction time to 24 h did not lead to higher conversion of the substrate and higher yields of oxidation products (carbonyl compounds, Table 4).

We assume that the oxidation of phenylethylenes with the (t-BuO)<sub>4</sub>Ti-t-BuOOH system involves the steps of the formation and subsequent decomposition of 1,2-dioxetanes [27]. With the aim to elucidate the pathways of formation of dioxetanes, we performed the reactions with 1,1-diphenylethylene in the presence of  $\beta$ -carotene. Addition of  $\beta$ -carotene exerted no appreciable effect on the quantitative composition of the Ph<sub>2</sub>C=CH<sub>2</sub> oxidation products and on the degree of its conversion (Table 4). Hence, in this case the active oxidizing agent is other than free singlet oxygen. The most probable agent is either singlet oxygen coordinated on the metal as in vanadium compounds [22, 28] or the metal-containing peroxytrioxide. However, in contrast to the systems based on vanadium compounds [22, 28] when the yield of benzaldehyde in oxidation of *trans*-stilbene reaches ~50%, in our system we have not detected the aldehyde or benzoic acid among products of similar reaction.

Thus, the products of the reactions of system I-II with anthracenes and phenylalkenes suggest that the substrates are oxidized with singlet oxygen. The data we obtained suggest that singlet oxygen is most prob-



Fig. 5. Results of calculation of trimethoxylitanium methyl trioxide molecule [FOPT (geometry optimization to reach the minimum); DFT-B3LYP; 6-31G(d, p); E = -1460.44767616 au; no imaginary frequencies].

**Table 4.** Products of reactions of phenylalkenes with the  $Ti(OBu-t)_4-t$ -BuOOH system (1 : 2) (benzene, 20°C, moles per mole of titanium alcoholate)<sup>a</sup>

Reaction products	Ph <sub>2</sub> C=	=CH <sub>2</sub>	Ph <sub>2</sub> C=CHPh	
Volatile reaction products				
<i>t</i> -BuOH PhCHO	2.78	2.86 <sup>b</sup>	2.85 0.04	
Products of hydrolysis of nonvolatile residue <sup>c</sup>				
t-BuOH	2.58	2.86 <sup>b</sup>	2.80	
Ph <sub>2</sub> C=O	0.59	0.65 <sup>b</sup>	0.19	
PhCOOH	_		0.12	
HCOOH <sup>d</sup>	0.33	0.36 <sup>b</sup>	_	
Starting alkylarene	0.35	0.30 <sup>b</sup>	0.73	

<sup>a</sup> Averaged results. <sup>b</sup> In the presence of  $\beta$ -carotene, concentration 7.7 × 10<sup>-4</sup> M;  $\nu(O_2 \text{ theor.}) : \nu(\beta\text{-carotene}) = 160$ . <sup>c</sup> ~1 mol of metal in all the experiments. <sup>d</sup> Formaldehyde was identified qualitatively.

ably generated in the step of the reaction of the substrates with peroxytrioxide III [Eq. (6)].

The possibility of the direct oxidation with organometallic polyoxides was demonstrated by the example

$$[(t-BuO)_{3}TiOOOBu-t] + \frac{Ph}{Ph}C=C \xrightarrow{R}_{H} \xrightarrow{-(t-BuO)_{4}Ti} \xrightarrow{Ph}C-C \xrightarrow{R}_{Ph} \xrightarrow{O-O}_{O-O} Ph_{2}C=O + RCHO,$$
(6)

of trialkylsilyl hydrotrioxides [29]. These compounds react with typical acceptors of singlet oxygen to form the corresponding products in 25–60% yield. At the same time, the amount of singlet oxygen determined by the chemiluminescence method does not exceed 0.1%. Oxygen released in the free form is triplet, because under the influence of oxygen-centered radicals present in the system the singlet–triplet transition occurs at a high rate, ~1 × 10<sup>10</sup> mol l<sup>-1</sup> s<sup>-1</sup> [13, 30, 31]:

$$\stackrel{\uparrow}{\operatorname{RO'}} \stackrel{\uparrow\downarrow}{} \stackrel{\downarrow}{\operatorname{O_2}} \stackrel{\downarrow}{\longrightarrow} \stackrel{\uparrow\uparrow}{\operatorname{RO'}} \stackrel{\uparrow\uparrow}{} \stackrel{(7)}{}$$

In the mixture from the reaction of system I-II with anthracene and 1,1-diphenylethylene simultaneously (1 : 1) in benzene, we detected benzophenone in a yield of up to 0.30 mol per mole of the initial titanium alcoholate. In the process, the yield of anthraquinone did not exceed 0.10 mol. Oxygen evolution was also observed.

According to Eq. (6), the oxidation of phenylalkenes should result in the regeneration of alcoholate I. Indeed, in the mixture from the reaction of 1,1-diphenylethylene with the  $(t-BuO)_4Ti-t-BuOOH$  system, we detected up to 0.50 mol of the starting alcoholate. The remaining 0.50 mol participates in the oxidation of formaldehyde (Table 4).

Aldehydes are oxidized with titanium-containing peroxide to metal acyloxy compounds [32] whose hydrolysis yields the corresponding acids [Eq. (7)]:

$$(t-BuO)_3 TiOOBu-t + RCHO$$
  
 $\longrightarrow (t-BuO)_3 TiOCH(R)OOBu-t$   
 $\longrightarrow (t-BuO)_3 TiOCOR + t-BuOH,$  (8)  
 $R = H, Ph.$ 

As noted above [6], system I–II oxidizes C–H bonds of hydrocarbons at 20°C. In all the cases, the reaction products were carbonyl compounds, alcohols, or their transformation products. Significant amounts of hydroperoxides were also detected, suggesting the radical character of the process. It was suggested that the oxidation is initiated by oxygen-centered radicals formed by decomposition of peroxytrioxide III [scheme (1)]. Carbon-centered radicals subsequently react with oxygen generated by the system to form the corresponding peroxy radicals responsible for the final products. With ethylbenzene as model substrate, the oxidation yielded acetophenone, 1-phenyl-1-ethanol, and 1-hydroperoxy-1-phenylethane.

To prove the homolytic character of the process, we examined the oxidation of ethylbenzene by ESR. On addition of 2-methyl-2-nitrosopropane (20°C), an ESR spectrum containing signals of adducts of the  $\alpha$ -phenylethyl radical PhCH(Me)N(O)Bu-t (XII) {triplet of doublets at  $g_i = 2.0062$  with hyperfine coupling constants  $a_i({}^{15}N) = 1.496$ ,  $a_i(H_{\alpha}) = 0.378$ ,  $a_i[H(CH_3)] = 0.048$  mT} [8, 33] and two triplets is recorded. One of these triplets with the parameters  $g_i$  = 2.0057,  $a_i({}^{15}N) = 2.715$  mT belongs to *tert*-butoxy*tert*-butylnitroxyl **X** [8], and the other  $[g_i = 2.0056,$  $a_i$ <sup>(15</sup>N) = 2.920 mT], to an adduct of spin trap V with an alkoxy radical, probably (t-BuO)<sub>3</sub>TiON(O)Bu-t. When the spectra are successively recorded in time (~30 min), the intensity of the signals from adducts of the  $\alpha$ -phenylethyl radical remains constant, whereas the intensity of the signals from *tert*-butoxy radicals drastically decreases. The peroxy radicals [PhCH(Me)· OO] were identified in the presence of C-phenyl-N*tert*-butylnitrone IV. The ESR spectrum is a triplet of doublets  $[g_i = 2.0062, a_i({}^{15}N) = 1.315, a_i(H) =$ 0.104 mT] [8]. These data suggest the radical character of the reaction of the system with ethylbenzene and prove that carbon-centered radicals escape into the bulk of the solvent. This conclusion can be confirmed by the results of the reaction of the  $(t-BuO)_{4}Ti$ t-BuOOH system (1:2) with ethylbenzene in atmospheres of argon and oxygen. In the latter case, the amount (in moles per mole of titanium alcoholate) of acetophenone increased from 0.43 to 1.38; that of 1-phenyl-1-ethanol, from 0.13 to 0.60; and that of 1-hydroperoxy-1-phenylethane, from 0.40 to 1.50.

Experiments with  $(t-BuO)_3$ TiOOBu-*t* showed that this compound does not oxidize hydrocarbons. In the experiments with ethylbenzene, either acetophenone was not detected at all, or its amount did not exceed 0.005 mol.

To elucidate the factors affecting the relative contributions of the decomposition pathways of **III**, we studied the reactions of system **I**–**II** with anthracene and ethylbenzene simultaneously. When the reaction of the (t-BuO)<sub>4</sub>Ti–t-BuOOH system with anthracene was performed in ethylbenzene as solvent, the prevalent pathway was radical oxidation of ethylbenzene to 1-hydroperoxy-1-phenylethane and products of its further transformations (acetophenone, 1-phenyl-1ethanol, styrene). Molecular oxidation of anthracene to anthaquinone is realized to 10-15%. The major pathway of the reaction of system I–II with a 1 : 1 mixture of ethylbenzene and anthracene in benzene (Table 5) is the oxidation of anthracene to anthraquinone. Products of ethylbenzene oxidation were detected in minor amounts.

As shown in scheme (1), the first step of the reaction of alcoholate I with hydroperoxide II yields titanium-containing peroxide  $(t-BuO)_3TiOOBu-t$ , which is also an oxidant. For example, it oxidizes aldehydes [Eq. (8)] and alcohols [6] by the molecular mechanism. We have monitored the reaction of the  $(t-BuO)_4Ti-t-BuOOH$  system with PhCH(OH)Me  $(1:1:1, benzene, 20^{\circ}C)$  by ESR. The absence of any radicals confirms the molecular reaction pathway. System I–II (1:2) oxidizes 3,6-di-*tert*-butylpyrocatechol to 3,6-di-*tert*-butyl-*p*-benzoquinone [34]. The reaction with the quinone occurs as nucleophilic 1,4-addition of the metal-containing peroxide to the system of conjugated bonds.

Thus, depending on the structure of molecules of organic substrates, the active oxidizing species in the titanium tetra-*tert*-butoxide-*tert*-butyl hydroperoxide system are metal-containing peroxide, peroxytrioxide, and oxygen generated by the system. The reaction of the titanium-containing peroxytrioxide with substrates occurs along either molecular (anthracenes, phenyl-alkenes) or homolytic pathway.

## **EXPERIMENTAL**

The IR spectra were recorded on a Specord IR-75 device (liquid film between windows of a KBr cell). The ESR spectra were taken on a Bruker ER-200D-SRC spectrometer equipped with an ER 4105DR double resonator (operating frequency ~9.5 GHz) and an ER 4111VT temperature-control block. In determination of the *g*-factor, we used diphenylpicrylhydrazyl as reference. The analysis was performed in the cell of the ESR spectrometer. To improve the resolution of ESR lines and remove oxygen released in the reaction of I with II, the reaction solutions were degassed. Spin traps IV and V were added in the initial steps of the reactions. The consumption of the peroxy radical (*t*-BuO)<sub>3</sub>TiOO was calculated with a special program, Store 1000.

Chromatographic analysis of reaction products in the liquid phase was performed with a Tsvet-2-65 device equipped with a flame-ionization detector; the carrier gas was argon. Readily volatile components (acetone, *tert*-butyl alcohol, *tert*-butyl hydroperoxide) **Table 5.** Products of the reaction of the  $Ti(OBu-t)_{4}$ *t*-BuOOH system with anthracene and ethylbenzene (1:2:1:1) in benzene at 20°C (moles per mole of titanium alcoholate)

Deastion meduate	$Ti(OBu-t)_4$ concentration, M				
Reaction products	0.05	0.12	0.05 <sup>a</sup>	0.30 <sup>a</sup>	
Volatile reaction products					
t-BuOH	3.16	2.99	3.22	3.04	
PhC(O)CH <sub>3</sub>	0.04	0.04	0.10	0.06	
Products of hydrolysis of nonvolatile residue <sup>b</sup>					
t-BuOH	2.68	2.88	2.90	3.13	
PhCH(OOH)CH <sub>3</sub>	0.04	0.05	0.27	0.21	
PhCH=CH <sub>2</sub>	Traces	Traces	0.02	0.02	
Anthraquinone	0.33	0.34	_	_	
Starting anthracene	0.68	0.64	_	_	
Starting $PhCH_2CH_3$	0.80	0.88	0.60	0.68	

<sup>a</sup> Experiments without anthracene. <sup>b</sup>  $\sim 1$  mol of titanium in all the experiments; the amount of PhCH(OH)CH<sub>3</sub> did not exceed 0.01 mol.

were analyzed on a  $2400 \times 3$ -mm column, stationary phase 10% poly(ethylene glycol adipate) on TZKM brick, temperature 55-80°C. For the analysis of titanium tetra-*tert*-butoxide, we used a  $2400 \times 3$ -mm column, stationary phase 15% Apiezon L, temperature 180°C. High-boiling products (benzaldehyde, acetophenone, benzophenone, phenol, 1-phenyl-1-ethanol, etc.) were identified with a  $3000 \times 3$ -mm column, stationary phase 5% SE-30, adsorbent Inerton AW, temperature 100-190°C. Anthracene, 9,10-dimethylanthracene, anthraquinone, 1,1-diphenylethylene, and triphenylethylene were analyzed at 190-210°C  $(1000 \times 3$ -mm column, stationary phase 5% OV-17 on Inerton Super). tert-Butyl hydroperoxide in benzene was determined with an LKhM-80 device,  $1200 \times$ 3-mm column, carrier gas helium, stationary phase 15% dinonyl phthalate on Chromaton N-AW-DMCS, 80°C. The chromatograms were calculated using authentic samples as external references.

All manipulations with titanium-containing compounds were performed under dry deoxygenated argon.

The amount of aliphatic acids in nonvolatile residues was determined according to [35], and the amount of *tert*-butoxy groups, by the Denigés method [36]. Carboxylic acids were identified as methyl esters after treatment with diazomethane. The quantitative analysis of hydroperoxides was performed by iodometric titration. 1-Hydroperoxy-1-phenylethane was identified by products of its acid decomposition (phenol and acetaldehyde) in the presence of p-toluenesulfonic acid [37]. Carbonyl compounds were identified in the form of 2,4-dinitrophenylhydrazones by the melting point and by TLC (comparison of  $R_f$ for the spots of the sample and authentic compounds). The sorbent, Silpearl, was wide-pore silica gel on aluminum foil (Silufol UV-254), and the eluent was benzene or benzene–diethyl ether (9 : 1). The amount of oxygen released in the reactions was determined from the weight of benzoic acid formed by the reaction of  $O_2$  with benzaldehyde [38]. The titanium content was determined after hydrolysis of the derivatives, by precipitation of hydroxides followed by calcination to the oxide.

Titanium tetra-tert-butoxide was prepared by treatment of TiCl<sub>4</sub> with *tert*-butyl alcohol in the presence of NH<sub>3</sub> [39], bp 82–83°C (2 mm Hg),  $n_D^{20}$  1.4420 [40]. Tri-tert-butoxy-tert-butylperoxytitanium was prepared from (t-BuO)<sub>3</sub>TiCl and t-BuOOH in the presence of diethylamine [41]. The activity of the peroxide obtained was no less than 95-96%. 2-Methyl-2nitrosopropane was prepared by oxidation of tertbutylamine with hydrogen peroxide in the presence of sodium tungstate [42]. C-Phenyl-N-tert-butylnitrone was prepared by rearrangement of 2-tert-butyl-3-phenvloxazirane [43]. The melting points of the spin traps obtained were in agreement with published data [42, 43]. 9,10-Dimethylanthracene was prepared by treatment of 9,10-dilithioanthracene with dimethyl sulfate, mp 183–184°C (from benzene) [44]. The concentration of tert-butyl hydroperoxide used in this study was no less than 99.6-99.8%.

Reaction of titanium tetra-*tert*-butoxide with *tert*butyl hydroperoxide (1 : 2) in benzene, 20°C. *tert*-Butyl hydroperoxide (0.32 g) was added to 0.62 g of Ti(OBu-t)<sub>4</sub> in 10 ml of benzene (room temperature), and evolution of oxygen was observed (19.04 ml, normal conditions). The reaction solution acquired intense straw color, and 0.49 g of titanium tetra-*tert*butoxide was found in this solution. On the next day, benzene and low-boiling products were removed at 20°C under reduced pressure. Treatment of a part of the condensate with 2,4-dinitrophenylhydrazine gave a precipitate of the corresponding acetone hydrazone (TLC monitoring). In the volatile fraction we found 0.48 g of *t*-BuOH, 0.002 g of acetone, and 0.02 g of (*t*-BuO)<sub>2</sub>.

The residue (dark yellow resinous mass) was hydrolyzed with 10% H<sub>2</sub>SO<sub>4</sub>, and the mixture was extracted with ether. In the ether extract we determined 0.27 g of *t*-BuOH, and in the aqueous acid layer, 0.02 g of *t*-BuOH and 0.005 g of hydrogen peroxide.

In a replicate run, the residue after removing benzene was analyzed for acetic acid (0.008 g) [35].

Reaction of anthracene and 9,10-dimethylanthracene with the Ti(OBu-t)<sub>4</sub>–t-BuOOH system (1 : 1: 1 : 2) in benzene. A flask was charged with 0.34 g of Ti(OBu-t)<sub>4</sub>, 0.18 g of anthracene, 0.21 g of 9,10-dimethylanthracene, and 0.18 g of t-BuOOH in 35 ml of benzene. The reaction solution immediately became yellow-brown. The solvent and low-boiling compounds were condensed in a trap cooled with liquid nitrogen. The condensate contained 0.20 g of t-BuOH.

The residue (yellow solid mass) was hydrolyzed in benzene with a 10% solution of sulfuric acid and extracted with freshly distilled benzene. The extract was dried with sodium sulfate. Chromatographic analysis revealed the presence of 0.14 g of unchanged 9,10-dimethylanthracene, 0.15 g of unchanged anthracene, 0.04 g of anthraquinone, and 0.15 g of *t*-BuOH. Then the solvent was removed at 20°C under reduced pressure. The residue was a yellow crystalline precipitate containing, along with anthracenes and anthraquinone, also 9,10-dimethyl-9,10-epidioxyanthracene (0.09 g). Its amount was determined by iodometric titration [13].

In a separate experiment, 9,10-dimethylepidioxyanthracene was isolated pure by column chromatography (Silicagel-60, 0.060–0.20 mm, eluent hexane) and characterized by <sup>1</sup>H NMR spectroscopy [CDCl<sub>3</sub>,  $\delta$ , ppm: 1.48 s (3H), 7.2 and 7.4 two m (AA'BB', 2H)] [22].

The aqueous layer was analyzed by the Denigés method for the content of t-BuO groups (0.09 g).

**Reaction of 1,1-diphenylethylene with the**  $Ti(OBu-t)_4$ -t-BuOOH system (1:1:2). A mixture of 1.19 g of Ti(OBu-t)<sub>4</sub>, 0.63 g of t-BuOOH, and 0.63 g of Ph<sub>2</sub>C=CH<sub>2</sub> in 10 ml of benzene was allowed to stand at room temperature for 2 h. The reaction solution became red-orange, and 0.58 g of I was found in this solution. The condensed solvent contained 0.70 g of t-BuOH. Formaldehyde was identified qualitatively by TLC in the form of 2,4-dinitrophenylhydrazone. The residue after removing the solvent and low-boiling products was a red-brown gelatinous mass. It was hydrolyzed in ether with a 10% H<sub>2</sub>SO<sub>4</sub> solution, and the mixture was extracted with distilled ether. In the ether extract we found 0.57 g of t-BuOH, 0.23 g of the starting alkene, and 0.36 g of Ph<sub>2</sub>C=O (melting point of benzophenone 2,4-dinitrophenylhydrazone and its mixture with an authentic sample 240°C).

In a replicate run, the residue after removing benzene was analyzed for formic acid (0.06 g), which was identified in the form of methyl formate [35, 37]. The aqueous acidic hydrolyzate contained 0.08 g of *t*-BuOH [36].

The reaction of 1,1-diphenylethylene with system I–II in the presence of  $\beta$ -carotene was performed similarly. After the reaction completion,  $\beta$ -carotene was detected by TLC (eluent hexane–petroleum ether, 7 : 1).

## REFERENCES

- Adam, W., Braun, M., Griesbeck, A., Lucchini, V., Staab, E., and Will, B., *J. Am. Chem. Soc.*, 1989, vol. 111, no. 1, p. 203.
- Finn, M.G. and Sharpless, K.B., J. Am. Chem. Soc., 1991, vol. 113, no. 1, p. 113.
- 3. Dryuk, V.G. and Kartsev, V.G., Usp. Khim., 1999, vol. 68, no. 3, p. 206.
- Krohn, K., Khanbabaee, K., and Rieger, H., Chem. Ber., 1990, vol. 123, no. 6, p. 1357.
- Krohn, K., Khanbabaee, K., and Rieger, H., Chem. Ber., 1989, vol. 122, no. 12, p. 2323.
- Stepovik, L.P., Gulenova, M.V., and Martynova, I.M., *Zh. Obshch. Khim.*, 2005, vol. 75, no. 4, p. 545.
- Stepovik, L.P., Gulenova, M.V., Martynova, I.M., Skvortsov, N.S., and Cherkasov, V.K., *Zh. Obshch. Khim.*, 2005, vol. 75, no. 7, p. 1161.
- Stepovik, L.P., Martynova, I.M., Dodonov, V.A., and Cherkasov, V.K., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2002, no. 4, p. 590.
- Stepovik, L.P., Dodonov, V.A., Gulenova, M.V., Martynova, I.M., and Cherkasov, V.K., Abstracts of Papers, XI Mezhdunarodnaya konferentsiya po khimii organicheskikh i elementorganicheskikh peroksidov (XI Int. Conf. on Chemistry of Organic and Organometallic Peroxides), Moscow, 2003, p. 25.
- 10. Zubarev, V.E., Belevskii, V.N., and Buchachenko, A.L., *Usp. Khim.*, 1979, vol. 48, no. 8, p. 1361.
- Zubarev, V.E., *Metod spinovykh lovushek. Primenenie* v khimii, biologii, meditsine (Method of Spin Traps. Applications to Chemistry, Biology, and Medicine), Moscow: Mosk. Gos. Univ., 1984.
- 12. Khursan, S.L., Khalizov, A.F., and Shereshovets, V.V., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1997, no. 5, p. 924.
- Moiseeva, N.I., Gekhman, A.E., Minin, V.V., Larin, G.M., Bashtanov, M.E., Krasnovskii, A.A., and Moiseev, I.I., *Kinet. Katal.*, 2000, vol. 41, no. 2, p. 191.
- Zubarev, V.E., Belevskii, V.N., and Yarkov, S.P., *Dokl. Akad. Nauk SSSR*, 1979, vol. 244, no. 6, p. 1392.
- Bartlett, P.D., Gunter, P., J. Am. Chem. Soc., 1966, vol. 88, no. 14, p. 3288.

- Pokhodenko, V.D., Ganyuk, L.N., and Brodskii, A.I., Dokl. Akad. Nauk SSSR, 1962, vol. 145, no. 4, p. 815.
- 17. Campbell, B.T.W. and Coppinger, G.M., J. Am. Chem. Soc., 1952, vol. 74, no. 6, p. 1469.
- Horswill, E.C. and Ingold, K.U., *Can. J. Chem.*, 1966, vol. 44, no. 3, p. 269.
- Ershov, V.V., Nikiforov, G.A., and Volod'kin, A.A., *Prostranstvenno-zatrudnennye fenoly* (Sterically Hindered Phenols), Moscow: Khimiya, 1972.
- 20. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Montgomery, J.A., Jr., Vreven, T., Kudin, K.N., Burant, J.C., Millam, J.M., Iyengar, S.S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G.A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J.E., Hratchian, H.P., Cross, J.B., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Ayala, P.Y., Morokuma, K., Voth, G.A., Salvador, P., Dannenberg, J.J., Zakrzewski, V.G., Dapprich, S., Daniels, A.D., Strain, M.C., Farkas, O., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Ortiz, J.V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Gonzalez, C., and Pople, J.A., Gaussian 03, Revision B.05, Pittsburgh PA: Gaussian, 2003.
- Gekhman, A.E., Makarov, A.P., Nekipelov, V.I., Talzi, K.P., Polotnyuk, O.Ya., Zamaraev, K.I., and Moiseev, I.I., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, no. 7, p. 1686.
- 22. Gekhman, A.E., Stolarov, I.P., Moiseeva, N.I., Rubaijlo, V.L., Vargaftik, M.N., and Moiseev, I.I., *Inorg. Chim. Acta*, 1998, vols. 275–276, p. 453.
- 23. Fotte, C.S. and Denny, R.W., J. Am. Chem. Soc., 1968, vol. 90, no. 22, p. 6233.
- 24. Cantrell, A., McGarvey, D.J., Truscott, T.G., Rancan, F., and Bohm, F., *Arch. Biochem. Biophys.*, 2003, vol. 412, no. 1, p. 47.
- 25. Razumovskii, S.D., *Kislorod elementarnye formy i svoistva* (Oxygen: Elemental Species and Properties), Moscow: Khimiya, 1979, p. 214.
- 26. Rio, G. and Berthelot, J., *Bull. Soc. Chim. Fr.*, 1969, no. 10, p. 3609.
- Sharipov, G.L., Kazakov, V.P., and Tolstikov, G.A., *Khimiya i khemilyuminestsentsiya 1,2-dioksetanov* (Chemistry and Chemiluminescence of 1,2-Dioxetanes), Moscow: Nauka, 1990.

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 78 No. 2 2008

- 28. Gekhman, A.E., Amelichkina, G.E., Moiseeva, N.I., Vargaftik, M.N., and Moiseev, I.I., *J. Mol. Catal. A: Chem.*, 2000, vol. 162, no. 1, p. 111.
- Grabovskii, S.A., Ivanova, E.V., Kabal'nova, N.N., and Katliyaloglu, K., Abstracts of Papers, XI Mezhdunarodnaya konferentsiya po khimii organicheskikh i elementorganicheskikh peroksidov (XI Int. Conf. on Chemistry of Organic and Organometallic Peroxides), Moscow, 2003, p. 13.
- 30. Darmanyan, A.P., Foote, C.S., and Jardon, P., *J. Phys. Chem.*, 1995, vol. 99, no. 31, p. 11854.
- Darmanyan, A.P., Gregory, D.D., Guo, Y., Jenks, W.S., Burel, L., Eloy, D., and Jardon, P., *J. Am. Chem. Soc.*, 1998, vol. 120, no. 2, p. 396.
- Dodonov, V.A., Stepovik, L.P., and Sofronova, S.M., *Zh. Obshch. Khim.*, 1981, vol. 51, no. 12, p. 2730.
- Janzen, E.G. and Blackburn, B.J., J. Am. Chem. Soc., 1969, vol. 91, no. 16, p. 4481.
- Stepovik, L.P., Gulenova, M.V., Shavyrin, A.S., and Fukin, G.K., *Zh. Obshch. Khim.*, 2006, vol. 76, no. 8, p. 1329.
- 35. Bauer, K.H., Die organische Analyse, Leipzig: Geest und Portig, 1950. Translated under the title Analiz organicheskikh soedinenii, Moscow: Inostrannaya Literatura, 1953, p. 234.

- 36. Polyanskii, N.G. and Safronenko, E.D., *Zh. Prikl. Khim.*, 1961, vol. 34, no. 6, p. 1376.
- Stepovik, L.P., Martynova, I.M., and Dodonov, V.A., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 2, p. 267.
- Dodonov, V.A., Stepovik, L.P., Soskova, A.S., and Zaburdaeva, E.A., *Zh. Obshch. Khim.*, 1994, vol. 64, no. 10, p. 1715.
- 39. US Patent 2684972, 1954, *Ref. Zh. Khim.*, 1955, no. 19, p. 348.
- 40. Feld, R. and Cowe, P.L., *The Organic Chemistry of Titanium*, London: Butterworths, 1965.
- Dodonov, V.A., Stepovik, L.P., Sofronova, S.M., and Zinchenko, V.A., *Zh. Obshch. Khim.*, 1990, vol. 60, no. 5, p. 1125.
- 42. Stowell, J.C., *J. Org. Chem.*, 1971, vol. 36, no. 20, p. 3055.
- 43. Emmons, W.D., J. Am. Chem. Soc., 1957, vol. 79, no. 21, p. 5739.
- Kocheshkov, K.A. and Talalaeva, T.V., Sinteticheskie metody v oblasti metalloorganicheskikh soedinenii litiya, natriya, kaliya, rubidiya i tseziya (Synthetic Methods in Organometallic Chemistry of Lithium, Sodium, Potassium, Rubidium, and Cesium), Moscow: Akad. Nauk SSSR, 1949, issue 1, parts I–V, pp. 103, 112.

Copyright of Russian Journal of General Chemistry is the property of Springer Science & Business Media B.V. and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.