ESR study of the thermal decomposition of di-*tert*-butoxy-*tert*-butyl alumotrioxide formed in the reaction of tri-*tert*-butoxyaluminum with *tert*-butyl hydroperoxide

L. P. Stepovik,[a] I. M. Martinova,[a] V. A. Dodonov,[a] and V. K. Cherkasov[b]*

[a]*N. I. Lobachevsky State University of Nizhny Novgorod, 23 prosp. Gagarina, 603600 Nizhny Novgorod, Russian Federation. Fax: +7 (831 2)65 8592. E-mail: guav3@uic.nnov.ru*

[b]*G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, 49 pr. Tropinina, 603600 Nizhny Novgorod, Russian Federation. Fax: +7 (831 2) 66 1497. E-mail: cherkasov@imoc.sinn.ru*

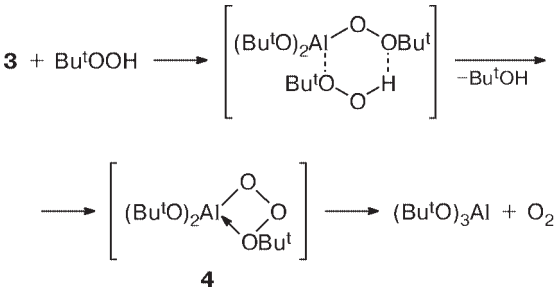
Tri-*tert*-butoxyaluminum reacts with *tert*-butyl hydroperoxide to produce di-*tert*-butoxy-*tert*-butyl alumotrioxide, which decomposes heterolytically to form singlet dioxygen and homolytically with the O—O bond cleavage. The $Bu^tOO^{\bullet}$, $(Bu^tO)_2AlOO^{\bullet}$, $Bu^tO^{\bullet}$, and $(Bu^tO)_2AlO^{\bullet}$ radicals were identified by ESR using spin traps. These findings confirm the formation of aluminum-containing trioxide. The above radicals initiate alkylarene oxidation by the tri-*tert*-butoxyaluminum—*tert*-butyl hydroperoxide system. The carbon-centered and alkylperoxy radicals originated from the oxidized substrates were identified.

Key words: tri-*tert*-butoxyaluminum, *tert*-butyl hydroperoxide, di-*tert*-butoxy-*tert*-butyl alumotrioxide, spin traps, oxidation, alkoxy and alkylperoxy radicals, ESR spectra.

The tri-*tert*-butoxyaluminum (**1**)—*tert*-butyl hydroperoxide (**2**) system efficiently oxidizes the C—H bonds of the methylene and methine groups in alkanes, arylarenes, alkenes, ketones, ethers, and esters.[1—8] The methylene groups are predominantly oxidized to keto and hydroxyl groups, and the methine groups are transformed into the hydroperoxyl groups. In the case of tri- and tetrasubstituted alkenes, the interaction of the methyl group with the **1**—**2** system is accompanied by allyl rearrangement and affords tertiary hydroperoxides.[5] Oxidation occurs at ~20 °C and completes in most cases by the C—C bond cleavage in the initial compound.[4,5] The C—H bonds of benzyl, benzhydryl, and allyl groups react most easily, whereas the C—H bonds of the benzene cycle and methyl group (except the Me group in toluene) do not undergo oxidation.

In inert solvents (tetrachloromethane, benzene, chlorobenzene) at 298 K the **1**—**2** system generates molecular dioxygen,[1] whose yield at the 1 : 2 reactant ratio reaches 80%. The O_2 evolution remains the main process also when the ratio of the **1**—**2** reaction components increases to 1 : 10. It was established that dioxygen is not the product of decomposition of di-*tert*-butoxy-*tert*-butyl peroxyaluminum (**3**) but forms when the latter reacts with hydroperoxide **2**. Previously[2] we assumed that aluminum-containing trioxide **4** is the intermediate of this reaction:

$$(Bu^tO)_3Al + Bu^tOOH \rightleftharpoons Bu^tOH + \underset{\mathbf{3}}{(Bu^tO)_2AlOOBu^t}, \qquad (1)$$



(2)

The O_2 evolution was also found in the synthesis and decomposition of organic dialkyl trioxides[9—13] and organoelement trioxides R_3EOOOR, $R_3EOOOER_3$ (E = Si, Ge, Sn, Pb).[14,15] In the case of dialkyl trioxides, a portion of the formed dioxygen, depending on the reaction conditions, exists in the singlet state.[11,12] Dialkyl trioxides decompose homolytically to form alkoxy and alkylperoxy radicals. The latters were detected by both chemical methods[9,10] and ESR.[13] The O—O bond en-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 590—595, April, 2002.

1066-5285/02/5104-638 $27.00

ergy in dialkyl trioxides slightly depends on the structure of the radical and ranges within 88—96 kJ mol^{-1},[11,16] which is almost twice as low than the bond energy of the corresponding peroxides. The pronounced dependence of the yield of $^1O_2$ on the medium nature confirms that the solvent is involved in the chemical reaction of formation of luminescence emitters. Singlet dioxygen is formed by recombination of the peroxy radicals originated from the trioxide and solvent.[11,12]

In this work we studied by ESR the reaction of alcoxide **1** with hydroperoxide **2** to reveal the role of trioxide **4** in the oxidation of alkylarenes (ethylbenzene, isopropylbenzene) containing the reactive C—H bonds. 2-Methyl-2-nitrosopropane (MNP) and *C*-phenyl-*N*-*tert*-butylnitron (PBN) were used as spin traps. 2-Methyl-2-nitrosopropane allows the capture of the alkyl and alkoxy radicals but it does not form stable adducts with alkylperoxy radicals, which are accepted by the PBN molecules.[17,18]

As known,[19] nitroso compounds react with hydroperoxides to form adducts with alkoxy radicals. We found that MNP reacts slowly with hydroperoxide **2**. Traces of the MNP adduct with the Bu^{t}O$^\cdot$ radical were detected. For the reaction of MNP with Bu^{t}OOH (1 : 1, C_6H_6, 298 K, without light), the color of the nitroso compound disappears within 4-5 days. Therefore, MNP can be used in the above system as an acceptor of free radicals.

Experimental

Solvents (benzene, ethylbenzene, and isopropylbenzene, all reagent grade) were purified by distillation above P_2O_5 and stored above metallic sodium. Tri-*tert*-butoxyaluminum was prepared by the reaction of *tert*-butyl alcohol and aluminum[20] followed by sublimation (160—170 °C, 1 Torr). Found (%): Al, 11.12. $C_{12}H_{27}AlO_3$. Calculated (%): Al, 10.96. MNP was synthesized by the oxidation of *tert*-butylamine with hydrogen peroxide in the presence of sodium tungstate,[21] and PBN was prepared by the rearrangement of 2-*tert*-butyl-3-phenyloxazirane.[22] The melting points of the spin traps corresponded to the published data.[21,22] The concentration of *tert*-butyl hydroperoxide was at least 99.5—99.8%. All reactions with aluminum alcoxide were carried out in an argon flow.

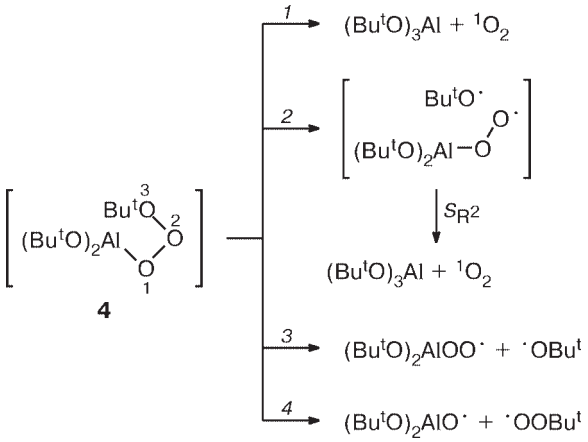
ESR spectra were recorded on a Bruker ER200D-SRC spectrometer equipped with an ER 4105 DR double resonator (working frequency ~9.5 GHz) and an ER 4111 VT thermocontrolling unit. To determine the *g* factor, DPPH was used as a standard.

Reaction of (Bu^{t}O)$_3$Al with Bu^{t}OOH (1 : 2) in different solvents. Bu^{t}OOH (0.41 g, 4.5 mmol) was added to a solution of (Bu^{t}O)$_3$Al (0.56 g, 2.3 mmol) in 8 mL of a solvent (ethylbenzene, isopropylbenzene, benzene, or tetrachloromethane). The resulting solution was placed in an ESR cell, and the ESR spectra of the reaction mixture were monitored in time. The reaction solutions were degassed to enhance resolution of ESR lines in the spectra and to remove O_2 evolved during the reaction between components **1** and **2**. Then PBN or MNP (0.3 mol L^{-1}) in the corresponding hydrocarbon was added after specified time.

Results and Discussion

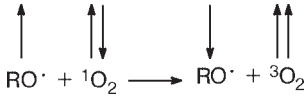
The O_2 evolution with the simultaneous regeneration of metal alcoxide and the homolytic decomposition of aluminum-containing trioxide **4** to form the oxygen-centered radicals (identified by ESR) prove the existence of the aluminum-containing trioxide. The decomposition of this trioxide can be presented as a sequence of molecular and homolytic reactions (Scheme 1).

Scheme 1



According to the rule of spin conservation, singlet dioxygen is formed by the molecular decomposition of trioxide **4** through the migration of the *tert*-butoxy group with an electron pair to the aluminum atom (see Scheme 1, direction *1*). Singlet dioxygen can also be generated through a peculiar S_R2 substitution reaction (see Scheme 1, direction *2*). The formation of $^1O_2$ in the reaction of alcoxide **1** with hydroperoxide **2** was established by IR spectroscopy. The $^1O_2$ yield determined by the reaction of singlet dioxygen with anthracene and 9,10-dimethylanthracene was from 40% (in benzene) to 50% (in tetrachloromethane).

As mentioned above, the total O_2 yield in the reaction of *tert*-butoxyaluminum with *tert*-butyl hydroperoxide reaches 80%. We assume that the free radicals and aluminum atom in the compounds participate in singlet dioxygen quenching.



(3)

R = Bu^t, Bu^{t}O, (Bu^{t}O)Al, (Bu^{t}O)$_2$AlO.

For example, for the oxygen-centered radicals this process was found in the work.[23]

Trioxide **4** decomposes homolytically through two O—O bonds to form the corresponding radical pairs (see Scheme 1, routes *3* and *4*).

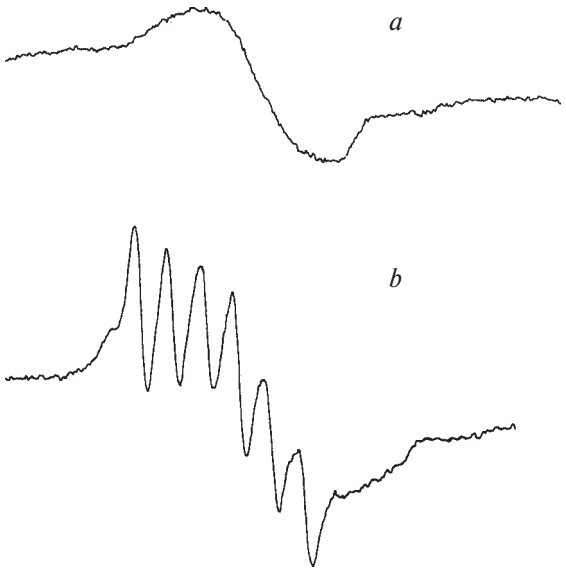


Fig. 1. ESR spectrum of the $(Bu^tO)_3Al—Bu^tOOH$ (1 : 2) system 10 min after mixing of the reactants (without spin traps, 298 K, $[(Bu^tO)_3Al] = 0.3$ mol L^{-1}). Solvents: *a*, benzene, chlorobenzene; and *b*, ethylbenzene.

In benzene or chlorobenzene, when spin traps are absent, after 10—15 min at ~20 °C, the ESR spectrum is a singlet with $\Delta H \approx 2.5$ mT. Based on $g = 2.014$—2.015, this signal can be attributed to the peroxy radical[9,10] (Fig. 1, *a*). The broad unresolved singlet in the absence of spin traps was detected not only in the **1**—**2** system but also in the reaction of **3** with **2** or with cumyl hydroperoxide (298 K, C_6H_6). The absence of the hyperfine structure (HFS) from the ESR spectra of the radical in the above solvents is associated with O_2 accumulation in the solution, which, as known,[23,24] broadens the lines. When the reaction mixture contains compounds easily oxidized by dioxygen (ethylbenzene, isopropylbenzene, diphenylethane, *etc.*), a hyperfine structure of the peroxy radical appears in the ESR spectrum (*viz.*, six components with the same intensity with $a_i = 0.46$ mT) (see Fig. 1, *b*). This splitting can be a result of the hyperfine coupling (HFC) of an unpaired electron with the ^{27}Al magnetic nucleus (100%; $\mu_N = 3.6385$; $I = 5/2$).[25] This suggests an aluminum-containing peroxyl radical $(Bu^tO)_2AlOO^\bullet$ (**5**) to form in the **1**—**2** system at ~20 °C.

The ESR spectrum of the **1**—**2** system in the presence of MNP in benzene exhibits an intense triplet with $a_N = 2.72$ mT and $g = 2.0057$, which is attributed to *tert*-butoxy-*tert*-butylnitroxyl (**6**). The constants for $Bu^tON(O^\bullet)Bu^t$ agree with the published data[26] and those obtained by us for di-*tert*-butyl peroxalate decomposition in benzene[27] in the presence of MNP. After MNP consumption (evidenced by decoloration of the latter and the spectrum of the nitroxyl adduct), the initial broad signal with $g = 2.014$ appears again.

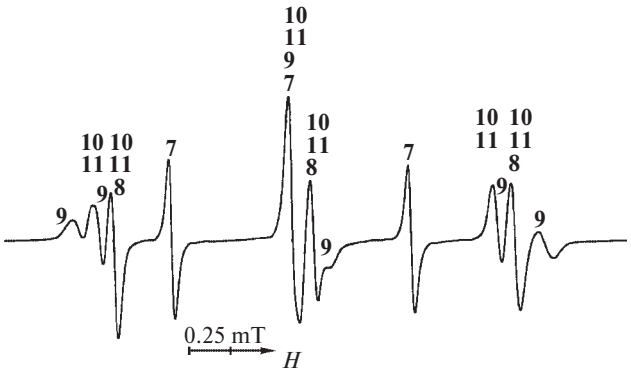
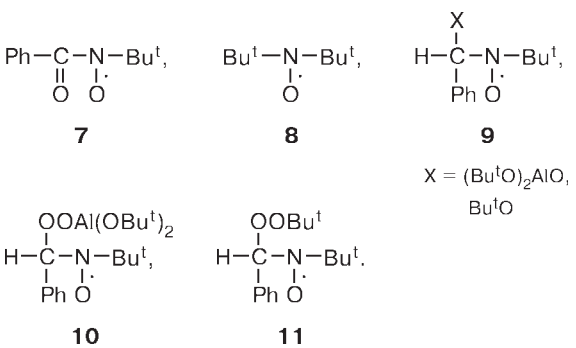


Fig. 2. ESR spectrum of the $(Bu^tO)_3Al—Bu^tOOH$ (1 : 2) system in benzene 90 min after mixing of the reactants (in the presence of PBN, 298 K, $[(Bu^tO)_3Al] = 0.3$ mol L^{-1}, degassed sample). Figures in the spectrum correspond to numbers of compounds.

The introduction of PBN into the system in non-oxidized solvents (benzene, chlorobenzene) followed by degassing of the solutions produces the ESR spectrum containing five different signals (Fig. 2): two triplets (1 : 1 : 1) and three triplets (1 : 1 : 1) of doublets. One of two triplet signals with the parameters $g = 2.0066$ and $a_N = 0.794$ mT, according to the published data,[17] belongs to the benzoyl-*tert*-butylnitroxyl radical (**7**), which is formed due to the oxidation of the spin trap by either singlet dioxygen or peroxy radicals.[18] Based on the isotropic parameters $g = 2.0057$ and $a_N = 1.519$ mT, we can attribute the second signal to di-*tert*-butylnitroxyl (**8**), which is formed by PBN decomposition.[18] One of three triplet-doublet signals with the parameters $g = 2.0056$, $a_N = 1.35$ mT, and $a_H = 0.181$ mT should be assigned to the PBN adduct with the alkoxy radical **9**, $Bu^tO^\bullet$, or $(Bu^tO)_2AlO^\bullet$. When modeling the formation of the PBN adduct with $Bu^tO^\bullet$ (di-*tert*-butyl peroxalate was used as the source of the latter), we observed the ESR spectrum with the parameters $g = 2.0056$, $a_N = 1.422$—1.433 mT, and $a_H = 0.180$—0.182 mT, which is in agreement with the published data.[18,19] Based on the HFC constant a_N, nitroxyl **9** can be treated as the PBN adduct either with $(Bu^tO)_2AlO^\bullet$ or its superposition with $Bu^tO^\bullet$. Two



other signals, virtually coinciding with **9** in parameters (g = 2.0057), differ from it by lower HFC constants: a_N = 1.330 and a_N = 1.350 mT; a_H = 0.099—0.102 and a_H = 0.130 mT, respectively. The published data for these HFC constants are characteristic of the PBN adducts with peroxy radicals **10** and **11**.[28,29]

We believe that nitroxyls **10** and **11** are the PBN adducts with $(Bu^tO)_2AlOO^\bullet$ and $Bu^tOO^\bullet$, respectively.

The $Bu^tOO^\bullet$ radical was identified as an adduct with PBN in di-*tert*-butyl peroxalate decomposition in benzene containing hydroperoxide **2**. The ESR spectrum coinciding with the published one[27] exhibits the signal from adduct **7** and two triplets of doublets with a_N = 1.411 and a_N = 1.345 mT; a_H = 0.183 and a_H = 0.130 mT. According to the a_N HFC constants, the first of them belongs the PBN adduct with $Bu^tO^\bullet$, and the second one belongs to that with $Bu^tOO^\bullet$.

Thus, the reaction of the components of the **1**—**2** system produces the intermediate aluminum-containing trioxide **4**, whose decomposition through two O^1—O^2 bonds (see Scheme 1, routes *3* and *4*) affords free radicals $Bu^tOO^\bullet$, $(Bu^tO)_2AlOO^\bullet$, $Bu^tO^\bullet$, and $(Bu^tO)_2AlO^\bullet$.

Homolysis of the corresponding aluminum peroxide **3** can also serve as a source of alkoxy radicals.

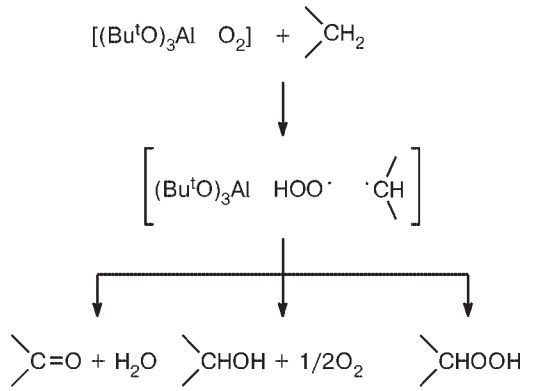
$$\mathbf{3} \longrightarrow (Bu^tO)_2AlO^\bullet + Bu^tO^\bullet \qquad (4)$$

However, peroxide **3** is rather stable at ~20 °C and does not form radicals on heating in benzene to 333 K. Di-*tert*-butylnitroxyl **8** and *tert*-butoxy-*tert*-butylnitroxyl **6** were detected at this temperature. This finding agrees with the previously obtained data[30] showing that even at 343 K compound **3** only slightly undergoes homolytic decomposition.

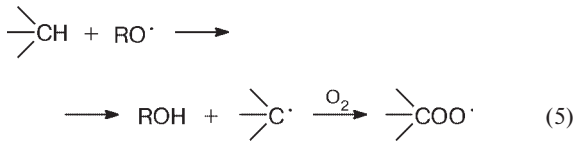
The formation of the alkoxy and peroxy radicals in the **1**—**2** system was indirectly confirmed by the use as a spin trap of the PBN—2,4,6-tri-*tert*-butylphenol equimolar mixture, which like *C*-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-4-*tert*-butylnitron can capture both alkyl and alkoxy radicals.[18,31] However, in our case, no ESR signals were detected in the reaction of compounds **1** and **2** in benzene, regardless of the presence or absence of the oxidized substrate. This agrees with the published data[9] that the reaction of alkoxy and alkylperoxy radicals with substituted phenols affords diamagnetic peroxyketone. Moreover, besides *tert*-butanol and dioxygen, the reaction of **1** with **2** (1 : 2, C_6H_6, 298 K) and of **3** with **2** (1 : 1) produced *tert*-butyl peroxide (0.04—0.07 mol), bound hydrogen peroxide (0.04—0.09 mol), and acetic acid (0.04—0.05 mol) (all per mole of the peroxide consumed), whose formation is due to further transformations of the radicals formed in trioxide decomposition (see Scheme 1, routes *3* and *4*).

In our previous works[1—8] we described the oxidation of substrates in the presence of **1**—**2** system using the following scheme: dioxygen generated at the first stage reacts with the C—H bond of the substrate molecule to produce the carbon-centered and hydroperoxy radicals. The latter oxidizes the carbon-centered radical to form the oxo, hydroxy, and hydroperoxy derivatives of hydrocarbons (Scheme 2).

Scheme 2



Taking into account the new data, we assume that the radicals formed according to Scheme 1 (routes *3* and *4*) eliminate the H atom from the C—H bond in the substrate molecule and form the carbon-centered radical. The latter reacts with dioxygen generated by the system to form alkylperoxy radicals.



(5)

R = Bu^t, BuO^t, $(Bu^tO)_2Al$, $(Bu^tO)_2AlO$

It was of interest to identify the carbon-centered and related peroxy radicals and to determine the role in oxidation of the radicals formed in Scheme 1. However, we were not able to detect alkylaryl radicals involved in the oxidation of toluene, ethylbenzene, and 1,1-diphenylethane at ~20 °C in the presence of MNP at the initial stages of the process. In the all cases, only *tert*-butoxy-*tert*-butylnitroxyl (**6**) was found. This fact can be explained by the difference between the rate constants of the reactions of alkyl radicals with dioxygen (k_1 ~10^9 L (mol s)$^{-1}$)[12] compared to MNP (k_2 ~10^6 L (mol s)$^{-1}$).[18] It follows from this that alkyl radicals can be detected at the final stages of the reaction when the major amount of dioxygen has already been consumed and when the product of the steady-state concentration of dioxygen by k_1 is comparable to the product of the MNP concentration by k_2.

Indeed, when MNP was added to a solution of a mixture of **1** and **2** in ethylbenzene (20 °C), after 1.5 h of

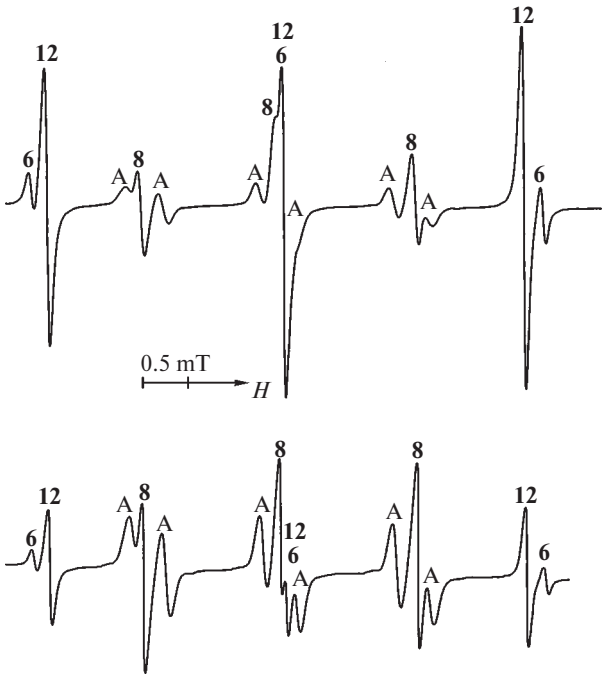


Fig. 3. ESR spectrum of the $(Bu^tO)_3Al—Bu^tOOH$ (1 : 2) system in ethylbenzene 90 min after mixing the reactants (in the presence of MNP, 298 K, degassed sample). The spectra were recorded successively at an interval of 15 min. Figures in the spectrum correspond to numbers of compounds; A is $PhCH(Me)N(O^{\bullet})Bu^t$.

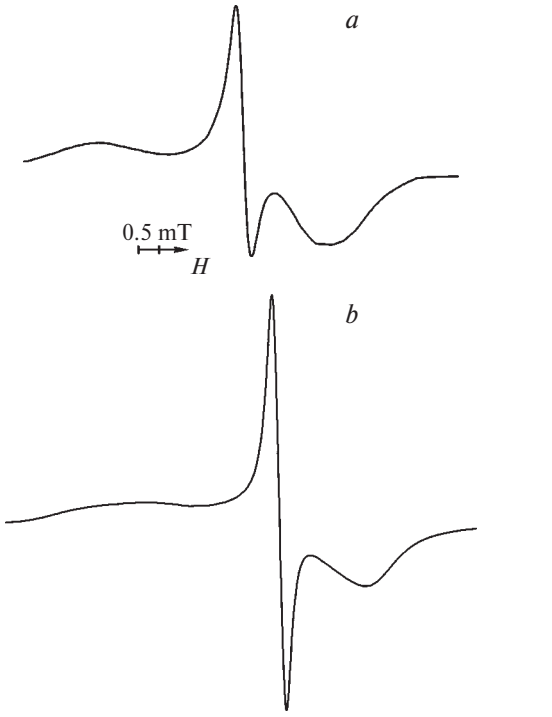


Fig. 4. ESR spectrum of the $(Bu^tO)_3Al—Bu^tOOH$ (1 : 2) reaction mixture in ethylbenzene at 180 K: *a*, superposition of the signal with $g = 2.015$ and the anisotropic spectrum of $(Bu^tO)_2AlOO^{\bullet}$; and *b*, theoretical spectrum obtained by the WINEPR SimFonia program.

mixing of the reactants, we obtained the ESR spectrum (Fig. 3) containing, along with the signals from *tert*-butyl and *tert*-butoxyl adducts **8** and **6**, a triplet of doublets with the HFC constants $a_N = 1.49$, $a_H = 0.349$ mT and $g = 2.0050$ corresponding to the adduct of the α-phenylethyl $PhCH(Me)N(O^{\bullet})Bu^t$ radical[32] and a triplet with $a_N = 2.906$ mT and $g = 2.0051$ attributed to the adduct of the alkoxy (perhaps, alumooxy) radical with MNP **12**.[17] When the spectra were successively recorded in time (at ~15-min intervals), we observed a decrease in the intensity of signals from the adducts of the alkoxy radicals and an increase in the intensity of signals from the adducts of the alkyl radical (see Fig. 3).

Unlike alumoperoxy radical (**5**), which is stable at ~20 °C, the alkylperoxy radicals formed from the substrate are stable only at low temperatures and manifest themselves as a symmetric singlet in the ESR spectrum.[13] When the reaction mixture of alkoxide **1** with hydroperoxide **2** in ethylbenzene or isopropylbenzene is cooled, in the ESR spectrum, beginning from 250 K, the HFC of radical **5** disappears and an additional signal appears, whose isotropic *g* factor ($g = 2.015$) also indicates that it belongs to the peroxy radical. The relative intensity of this signal reversibly changes with the temperature: it increases with the temperature decrease and decreases with its increase. The spectrum of an ethylbenzene solution cooled to 180 K exhibits a superposition of this signal with the anisotropic spectrum of $(Bu^tO)_2AlOO^{\bullet}$ (see Fig. 4, *a*). Using the WINEPR SimFonia program for ESR spectra simulation, we plotted the theoretical spectrum for this sample (see Fig. 4, *b*). The parameters of the anisotropic ESR spectrum of $(Bu^tO)_2AlOO^{\bullet}$ found at 180 K in ethylbenzene ($g_{||} = 2.037$; $A_{||}(^{27}Al) = 0.55$ mT; $g_{\perp} = 2.002$; $A_{\perp}(^{27}Al) = 0.40$ mT) are in good agreement with the parameters of its isotropic ESR spectrum.

The temperature evolution of the ESR spectrum indicates the formation of the carbon-centered $ROO^{\bullet}$ radicals in the reaction system, along with the aluminum-containing peroxyl radicals $(Bu^tO)_2AlOO^{\bullet}$. Their steady-state concentration at ~20 °C is much lower than the concentration of the $(Bu^tO)_2AlOO^{\bullet}$ radicals. With the temperature decrease the lifetime of these radicals increases and, correspondingly, their steady-state concentration increases.

To identify the $\equiv COO^{\bullet}$ peroxyl radicals, we studied the reaction of **1** with **2** in ethylbenzene and isopropylbenzene in the presence of PBN. The obtained spectra exhibit, along with the signal from adduct **7**, triplets of doublets: in the case of ethylbenzene $a_N = 1.331$, $a_H = 0.101$ mT (**13**), and in the case of isopropylbenzene $a_N = 1.317$ and $a_H = 0.099$ mT (**14**) (Fig. 5). Their anisotropic parameters correspond to those of the peroxy radicals.

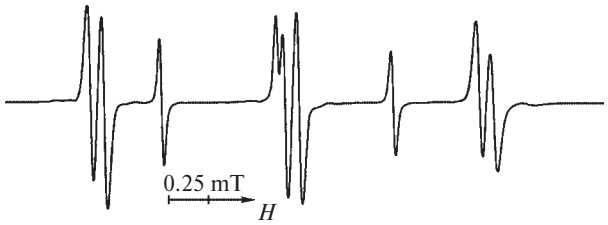
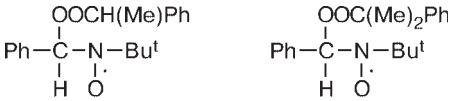


Fig 5. ESR spectrum of the $(Bu^tO)_3Al—Bu^tOOH$ (1 : 2) reaction mixture in ethylbenzene (isopropylbenzene) at 298 K in the presence of PBN.

The HFC constants of the found adducts differ from those of adduct **11** and are close to those for adduct **10**. However, the absence of HFC of the radicals studied, unlike the situation for radical **5**, allows us to assign them to the PBN adducts with the peroxy radicals formed from the oxidized substrates: **13** is formed from ethylbenzene and **14** is formed from isopropylbenzene.



13 **14**

This assumption was confirmed by the decomposition of di-*tert*-butyl peroxalate in ethylbenzene in the presence of hydroperoxide **2** and PBN without removal of the air oxygen. The ESR spectrum for this mixture represents a triplet of doublets with $a_N = 1.351$ and $a_H = 0.102$ mT.

Published data concerning the stability of the adducts of peroxy radicals with PBN and their subsequent transformations are contradictory. In the opinion of the authors,[18,26,27] the PBN adducts with peroxy radicals are unstable at temperatures >250—260 K and transformed into alkoxyl adducts. The authors[33] assert that similar adducts are stable at ~20 °C but in the dark. The PBN adducts detected by us at ~20 °C should be attributed to peroxy radicals based on the HFC parameters and published data.

Thus, the presence of the $(Bu^tO)_2AlOO^{\bullet}$, $Bu^tO^{\bullet}$, $(Bu^tO)_2AlO^{\bullet}$, and $Bu^tOO^{\bullet}$ radicals confirms the formation of di-*tert*-butoxy-*tert*-butyl alumotrioxide in the reaction of alcoxide **1** with hydroperoxide **2** (in a ratio of 1 : 2) and the homolytic decomposition of the latter. The radicals that formed initiate oxidation, which is proved by the presence in the reaction mixture of alkylaryl and the corresponding peroxy radicals from the oxidized substrates. However, the main pathway of aluminum-containing trioxide transformation is its decomposition with 80% O_2 evolution (to 80%), and 50% of this amount are in the singlet state. Note that, unlike organic dialkyl trioxides, where singlet dioxygen is the product of the recombination of the peroxy radicals from trioxide, it forms in this case due to the molecular decomposition of intermediate **4**.

Spectral studies were performed at the Analytical Center of the G. A. Razuvaev Institute of the RAS and financially supported by the Russian Foundation for Basic Research (Project No. 00-03-42004) and the Federal Target Program "Integration" (No. 372/2001).

The authors thank G. A. Abakumov for interest in the work and helpful discussion of the experimental results.

References

1. V. A. Dodonov, L. P. Stepovik, and S. M. Sofronova, *Zh. Obshch. Khim.*, 1990, **60**, 1839 [*J. Gen. Chem. USSR*, 1990, **60** (Engl. Transl.)].
2. V. A. Dodonov, L. P. Stepovik, A. S. Soskova, and E. A. Zaburdaeva, *Zh. Obshch. Khim.*, 1994, **64**, 1715 [*Russ. J. Gen. Chem.*, 1994, **64** (Engl. Transl.)].
3. V. A. Dodonov, L. P. Stepovik, and E. A. Zaburdaeva, *Zh. Obshch. Khim.*, 1997, **67**, 116 [*Russ. J. Gen. Chem.*, 1997, **67** (Engl. Transl.)].
4. V. A. Dodonov, E. A. Zaburdaeva, N. V. Dolganova, L. P. Stepovik, and T. I. Zinov´eva, *Zh. Obshch. Khim.*, 1997, **67**, 988 [*Russ. J. Gen. Chem.*, 1997, **67** (Engl. Transl.)].
5. I. M. Martynova, L. P. Stepovik, and V. A. Dodonov, *Zh. Obshch. Khim.*, 2001, **71**, 785 [*Russ. J. Gen. Chem.*, 2001, **71** (Engl. Transl.)].
6. L. P. Stepovik, E. A. Zaburdaeva, and V. A. Dodonov, *Zh. Obshch. Khim.*, 1997, **67**, 282 [*Russ. J. Gen. Chem.*, 1997, **67** (Engl. Transl.)].
7. E. A. Zaburdaeva, L. P. Stepovik, V. A. Dodonov, and I. M. Martynova, *Zh. Obshch. Khim.*, 1997, **67**, 2015 [*Russ. J. Gen. Chem.*, 1997, **67** (Engl. Transl.)].
8. L. P. Stepovik, I. M. Martynova, and V. A. Dodonov, *Zh. Obshch. Khim.*, 1999, **69**, 267 [*Russ. J. Gen. Chem.*, 1999, **69** (Engl. Transl.)].
9. P. D. Bartlett and P. Günter, *J. Am. Chem. Soc*, 1966, **88**, 3288.
10. N. A. Milas and B. Plesničar, *J. Am. Chem. Soc*, 1983, **105**, 1498.
11. S. L. Khursan, V. V. Shereshovets, A. F. Khalizov, A. I. Voloshin, V. D. Komissarov, and V. P. Kazakov, *Izv. Akad. Nauk*, *Ser. Khim.*, 1993, 2056 [*Russ. Chem. Bull.*, 1993, **42**, No. 12 (Engl. Transl.)].
12. S. L. Khursan, A. F. Khalizov, and V. V. Shereshovets, *Izv. Akad. Nauk*, *Ser. Khim.*, 1997, 924 [*Russ. Chem. Bull.*, 1997, **46**, 884 (Engl. Transl.)].
13. S. L. Khursan, V. V. Shereshovets, N. M. Shishlov, A. F. Khalizov, and V. P. Komissarov, *React. Kinet. Catal. Lett.*, 1994, **52**, 249.
14. Yu. A. Alexandrov and B. I. Tarunin, *J. Organomet. Chem.*, 1982, **238**, 125.
15. Yu. A. Aleksandrov, N. G. Sheyanov, *Zh. Obshch. Khim.*, 1969, **39**, 141 [*J. Gen. Chem. USSR*, 1969, **39** (Engl. Transl.)].

16. A. Pryor, D. G. Prier, and D. F. Church, *J. Am. Chem. Soc.*, 1983, **105**, 2883.
17. V. E. Zubarev, V. N. Belevskii, and L. T. Bugaenko, *Usp. Khim.*, 1979, **43**, 1392 [*Russ. Chem. Rev.*, 1979, **43** (Engl. Transl.)].
18. V. E. Zubarev, *Metod spinovykh lovushek. Primenenie v khimii, biologii, meditsine* [*Spin-trap Method. Application in Chemistry, Biology, and Medicine*], Izd-vo MGU, Moscow, 1984, 186 (in Russian).
19. S. Terabe and R. Konaka, *J. Chem. Soc., Perkin Trans. 2*, 1972, 2163.
20. *Organic Syntheses. An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals*, Wiley, New York; Chapman, London, 1950, **32**.
21. J. C. Stowell, *J. Org. Chem.*, 1971, **36**, 3055.
22. W. D. Emmons, *J. Am. Chem. Soc.*, 1957, **72**, 5739.
23. N. I. Moiseeva, A. E. Gekhman, V. V. Minin, G. M. Larin, M. E. Bashtanov, A. A. Krasnovskii, and I. I. Moiseev, *Kinet. Katal.*, 2000, **41**, 191 [*Kinet. Catal.*, 2000, **41** (Engl. Transl.)].
24. J. E. Wertz and J. R. Bolton, *Electron Spin Resonance. Elementary Theory and Practical Applications*, Wiley, New York, 1972.
25. B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 142.
26. J. A. Howard and J. Ch. Tain, *Can. J. Chem.*, 1978, **56**, 176.
27. E. Niki, S. Yokoi, J. Tsuchiya, and Y. Kamiya, *J. Am. Chem. Soc.*, 1983, **105**, 1498.
28. M. V. Merritt and R. A. Johnson, *J. Am. Chem. Soc.*, 1977, **99**, 3713.
29. V. E. Zubarev, V. N. Belevskii, and S. P. Yarkov, *Dokl. Akad. Nauk SSSR*, 1979, **244**, 1392 [*Dokl. Chem.*, 1979 (Engl. Transl.)].
30. V. A. Dodonov, L. P. Stepovik, S. M. Sofronova, and V. A. Zinchenko, *Zh. Obshch. Khim.*, 1990, **60**, 1125 [*Russ. J. Gen. Chem.*, 1990, **60** (Engl. Transl.)].
31. C. H. Camaggi and M. J. Perkins, *J. Chem. Soc., Perkin Trans. 2*, 1972, 507.
32. E. G. Janzen and B. Blackburn, *J. Am. Chem. Soc.*, 1969, **91**, 4481.
33. E. G. Janzen and C. A. Evans, *J. Am. Chem. Soc.*, 1973, **95**, 8205.

Received July 1, 2001;
in revised form September 14, 2001