

# Oxygen activation on metallic centers and oxidizing abilities of such oxygen

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## Abstract

It was shown that metallcontaining peroxides such as  $\text{XOOBu-}t$  [ $\text{X} = (t\text{-BuO})_2\text{Al}, (t\text{-BuO})_3\text{Ti}$ ] generate molecular oxygen in the electron-excited singlet state ( $^1\text{O}_2$ ). These ozonides and  $\eta^2$ -peroxocomplex  $\text{Ph}_3\text{Bi}(\eta^2\text{O}_2)$  demonstrate high oxidative activity towards some classes of organic substances under mild conditions (20 °C).

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## 1. Introduction

It has been found that the reaction of tri-*tert*-butoxyaluminum (1) with *tert*-butyl hydroperoxide (2) and tetra-*tert*-butoxytitanium (3) with (2) (1:2) under mild conditions (20 °C) in  $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{H}_5\text{Cl}$  or  $\text{CCl}_4$  results in oxygen evolution in a yield  $\sim 80\%$ . Using typical  $^1\text{O}_2$  acceptors – anthracene and 9,10-dimethylanthracene it has been determined that there  $\sim 50\%$  of the oxygen is in the electron-excited singlet state. Oxygen is evolved through the intermediate formation of aluminium (or titanium)-containing peroxide and trioxide (4) according to Scheme 1.

Ozonide 4 ( $\text{M} = \text{Al}$ ) eliminates the electron-excited oxygen and in parallel generates oxygen-centred radicals:  $t\text{-BuOO}\cdot$ ,  $t\text{-BuO}\cdot$ ,  $(t\text{-BuO})_2\text{AlOO}\cdot$  and  $(t\text{-BuO})_2\text{AlO}\cdot$ . The latter were identified by EPR using spin traps [2-methyl-2-nitrosopropane (MNP) and *C*-phenyl-*N-tert*-butylnitron (PBN)] [1]. These radicals confirm the existence of trioxide 4.

At the same time in our group the system triphenylbismuth (5)–(2) (1:3) in hydrocarbons was proposed (see Scheme 2).

Radicals such as  $\text{Ph}\cdot$  and  $t\text{-BuO}\cdot$  were identified by EPR using the same spin traps. Biphenyl was also obtained in the pure state. Oxygen evolution was not been observed in this case.

Metal-containing peroxide intermediates such as  $\text{XOOBu-}t$  (4) [ $\text{X} = (t\text{-BuO})_2\text{Al}, (t\text{-BuO})_3\text{Ti}$ ] and  $\text{Ph}_3\text{Bi}(\eta^2\text{O}_2)$  demonstrate a high oxidative activity toward C–H bonds in methylene fragments of hydrocarbons and their derivatives. In the first stage reactions form corresponding ketones and hydroxyl derivatives (see Scheme 3).

In the case of ethylbenzene the radical  $\text{Ph}\dot{\text{C}}\text{HCH}_3$  was detected by EPR with MNP [1].

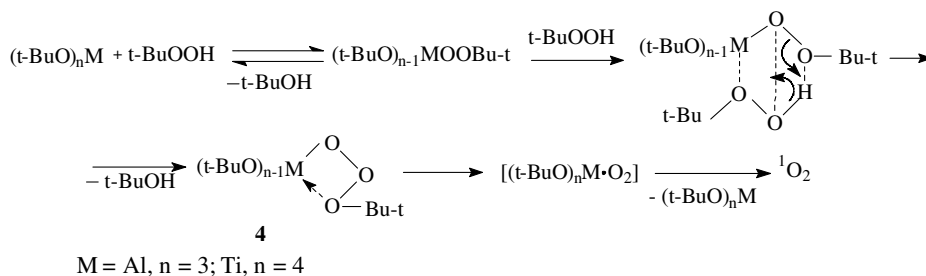
Oxidation of alkylarenes containing tertiary C–H bonds results in hydroperoxides (see Scheme 4).

It should be noted that C–H bonds of benzene and methyl groups of hydrocarbons (except toluene) are not oxidized in such conditions.

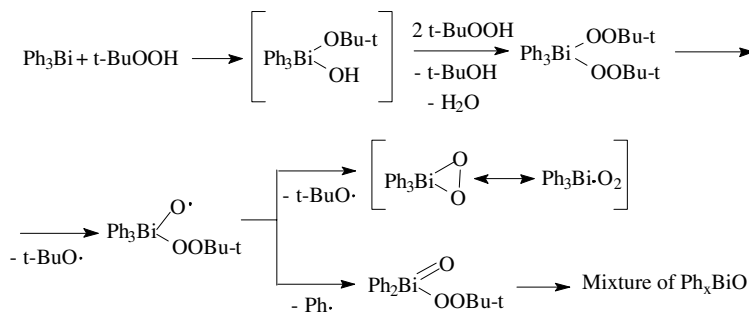
Besides C–H bonds (1)–(2) and (5)–(2) systems oxidize N–H bonds of aromatic amines at the same conditions. Oxidation proceeds via the intermediate formation of nitrogen-containing *N*-peroxide compounds [2] (see Scheme 5).

All nitroxyl radicals were proved by EPR. In the case of diphenylamine the intermediate formation of the nitrogen-centered radical is indicated by the formation of

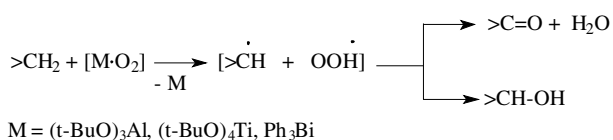
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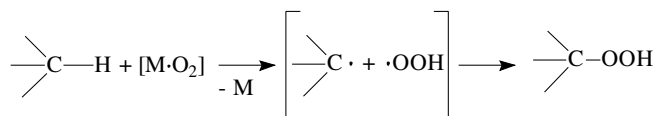
Scheme 1.



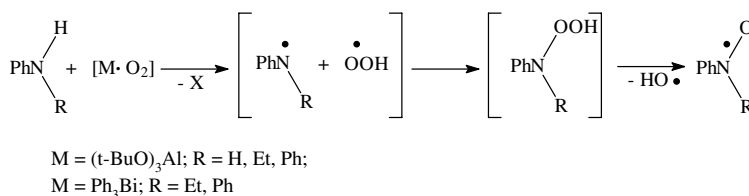
Scheme 2.

M = (t-BuO)<sub>3</sub>Al, (t-BuO)<sub>4</sub>Ti, Ph<sub>3</sub>Bi

Scheme 3.

M = (t-BuO)<sub>3</sub>Al, (t-BuO)<sub>4</sub>Ti, Ph<sub>3</sub>Bi

Scheme 4.



Scheme 5.

tetraphenylhydrazine, which is the dimerization product of the radicals.

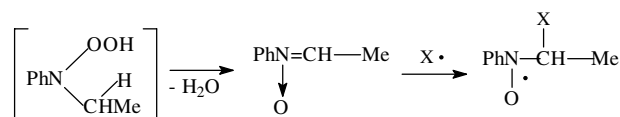
Reactions (1)–(2) with *N*-ethylaniline not only form phenylethyl nitroxyl radical, but *N*-hydroperoxide also decomposes to form the corresponding nitron that can serve as a good spin trap.

The adduct of this nitron with the X<sup>•</sup> radical was also found by EPR. The X<sup>•</sup> radical is most likely the *t*-BuO<sup>•</sup> radical.

*N*-ethylaniline is partially oxidized at the CH<sub>2</sub>-group of the Et fragment, which is indicated by the presence of acetic acid and azoxybenzene in the reaction products. These products are formed due to the cleavage of the N–C bond of the substrate. However, their minor yield indicates that

the attack of the oxygen is predominately directed to the amino group of the initial compound (see Scheme 6).

The active oxygen generated by (1)–(2) and (3)–(2) systems seems to be the oxidant of the S atom of sulfides [3,4]. The reactions are completed within an hour in high yields of sulfones (80–96%) (Table 1). We suppose that the electron-excited oxygen reacts with sulfides not as a



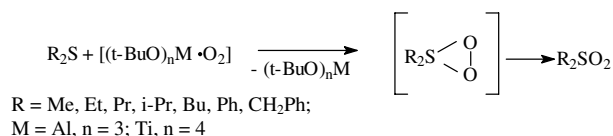
Scheme 6.

Table 1  
Oxidation of sulfides R<sub>2</sub>S by the system (*t*-BuO)<sub>3</sub>Al–*t*-BuOOH(1:1:2), 20 °C, benzene

N	R	Products/mole of sulfide <sup>a</sup>						
		Volatile fraction			After hydrolysis of nonvolatile residue			
		<i>t</i> -BuOOH	<i>t</i> -BuOH	R <sub>2</sub> S	<i>t</i> -BuOOH	<i>t</i> -BuOH	R <sub>2</sub> S	R <sub>2</sub> SO <sub>2</sub>
1	Me	0.04	2.26	0.04	0.03	1.62	–	0.94
2	Et	0.06	2.30	Traces	– <sup>b</sup>	– <sup>b</sup>	–	0.79
3	Pr	0.06	1.73	Traces	0.15	2.22	Traces	0.96
4	<i>i</i> -Pr	0.08	2.16	–	– <sup>b</sup>	– <sup>b</sup>	–	0.95
5	Bu	0.05	2.40	–	0.14	1.92	0.03	0.96
6	Ph	–	2.24	–	–	2.46	0.12	0.80
7	PhCH <sub>2</sub>	0.05	2.29	–	0.22	– <sup>b</sup>	–	0.96

<sup>a</sup> Averaged data are presented.

<sup>b</sup> Not determined.



Scheme 7.

kinetically independent molecule but oxidizes the substrate to sulfones directly in the coordination sphere of the metal with the intermediate formation of thiadioxirane (Scheme 7).

It should be noted that the action of the Ph<sub>3</sub>Bi–*t*-BuOOH system on the sulfides differs from that described above. The main direction is not the oxidation of the S atom but the cleavage of the S–C bond of the substrate. For example in the case of dibenzylsulfide ~50% benzaldehyde has been found. At the same time interaction of diisopropylsulfide with (5)–(2) system leads to acetone (26%). We offer a radical mechanism for this transformation.

## 2. Experimental

*Reaction of 1,1-diphenylethane with tri-tert-butoxyaluminum–tert-butylhydroperoxide (1:1:2) system.* The mixture of (*t*-BuO)<sub>3</sub>Al (2.38 g), *t*-BuOOH (1.74 g) and Ph<sub>2</sub>CHCH<sub>3</sub> (1.77 g) in 25 mL of benzene was left for 4 days at room temperature. Then the solvent and volatile components from the red-brown solution were condensed off a trap cooled with liquid nitrogen. The volatile fraction contained *t*-BuOH (1.85 g) and PhC(O)CH<sub>3</sub> (0.02 g). The residue, red oil, was hydrolyzed with 10% H<sub>2</sub>SO<sub>4</sub>, extracted with diethyl ether, and dried with Na<sub>2</sub>SO<sub>4</sub>. In the ether solution of *t*-BuOH (1.23 g), PhC(O)CH<sub>3</sub> (0.07 g), PhOH (0.07 g), Ph<sub>2</sub>CO (0.03 g), Ph<sub>2</sub>C(OH)CH<sub>3</sub> (0.27 g), Ph<sub>2</sub>C=CH<sub>2</sub> (0.10 g), Ph<sub>2</sub>C(OOH)CH<sub>3</sub> (0.27 g), PhCOOH (0.04 g) and non-reacted Ph<sub>2</sub>CHCH<sub>3</sub> (0.85 g) were detected. In the aqua-acid part 0.27 g of aluminum were found.

Ph<sub>2</sub>C(OOH)CH<sub>3</sub> was also identified by paper chromatography. The ether from the part of ether solution was condensed and the residue was dissolved in benzene. The

eluent used was a mixture benzene–hexane (9:1), developer acetic acid and than 40% potassium iodide. The R<sub>f</sub> of the analyzing solution and known peroxide is identical. *t*-BuOOH in such conditions was not determined.

Oxidation and analyses of other hydrocarbons were carried out analogously.

*Reaction of aniline with the tri-tert-butoxyaluminum–tert-butylhydroperoxide (1:1:2) system.* To *t*-BuOOH (0.72 g) was added a mixture of (*t*-BuO)<sub>3</sub>Al (0.98 g) and PhNH<sub>2</sub> (0.37 g) in benzene (20 mL) and left for 1 day at ~20 °C. Then the solvent and the volatile components were condensed off a trap cooled with liquid nitrogen. The volatile fraction contained PhNO<sub>2</sub> (0.04 g) and *t*-BuOH (0.91 g). The residue, dry yellow powder, was hydrolyzed with 10% H<sub>2</sub>SO<sub>4</sub>, extracted with diethyl ether, and dried with Na<sub>2</sub>SO<sub>4</sub>. GLC analysis of the ether hydrolyzate detected PhNO<sub>2</sub> (0.04 g), *t*-BuOH (0.33 g), *t*-BuOOH (0.09 g), PhN=NPh (0.01 g) and PhN(O)=NPh (0.29 g).

EPR spectra were detected on a Bruker ER200D-SRC spectrometer equipped with an ER 4105 DR double resonator (working frequency ~9.5 GHz) and an ER 4111 VT temperature-controlling unit. Diphenylpicrylhydrazyl (DPPH) was used as a standard in the determination of the *g*-factor.

The reactions with other amines were carried out analogously.

*Oxidation of dipropyl sulfide by tri-tert-butoxyaluminum–tert-butylhydroperoxide (1:1:2) system.* *t*-BuOOH (1.44 g) was added to a solution of (*t*-BuO)<sub>3</sub>Al (1.96 g) and Pr<sub>2</sub>S (0.94 g) in benzene (20 mL). After 1–2 min, the reaction mixture was self-heated. The formation of Pr<sub>2</sub>SO<sub>2</sub>, whose amount obtained was 0.78 g (65%) in 4.5 h, was monitored by GLC. Then the solvent and volatile components of the reaction mixture were condensed in a trap cooled with liquid nitrogen. The volatile fraction contained *t*-BuOH (0.84 g) and *t*-BuOOH (0.02 g). Sulphuric acid (10%) was added to a colorless powder-like residue, the mixture was extracted with Et<sub>2</sub>O, and the extract was dried with Na<sub>2</sub>SO<sub>4</sub> and analyzed by GLC. Pr<sub>2</sub>SO<sub>2</sub> (1.12 g, 94%), *t*-BuOH (1.53 g) and *t*-BuOOH (0.11 g) were found.

Me<sub>2</sub>S, Et<sub>2</sub>S, *i*-Pr<sub>2</sub>S and Bu<sub>2</sub>S were oxidized similarly.

Ether-insoluble but water-soluble Me<sub>2</sub>SO<sub>2</sub>, Et<sub>2</sub>SO<sub>2</sub> and *i*-Pr<sub>2</sub>SO<sub>2</sub> were isolated by the treatment of the reaction mixture with acetic acid taken in an exactly calculated amount. Aluminum acetate that formed was filtered off, and volatile components were removed under a reduced pressure.

*Oxidation of dibenzyl sulfide by tetra-tert-butoxytitanium-tert-butylhydroperoxide (1:1:2) system.* *t*-BuOOH (0.34 g) was added to a solution of (*t*-BuO)<sub>4</sub>Ti (0.64 g) and (PhCH<sub>2</sub>)<sub>2</sub>S (0.41 g) in benzene (10 mL). After 1 min, the reaction mixture was self-heated. When the mixture was cooled, colorless crystals of (PhCH<sub>2</sub>)<sub>2</sub>SO<sub>2</sub> (0.25 g) were filtered. The filtrate was hydrolyzed with 10% H<sub>2</sub>SO<sub>4</sub> and dried with Na<sub>2</sub>SO<sub>4</sub>. Then the solvent was condensed in a trap cooled with liquid nitrogen and 0.21 g of (PhCH<sub>2</sub>)<sub>2</sub>SO<sub>2</sub> was obtained.

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