# Liquid-phase oxidation of sulfides by an aluminum (and titanium) tert-butoxide—tert-butyl hydroperoxide system

V. A. Dodonov, E. A. Zaburdaeva,\* and L. P. Stepovik

N. I. Lobachevsky Nizhny Novgorod State University, 23 prosp. Gagarina, 603950 Nizhny Novgorod, Russian Federation. Fax: +7 (831 2) 65 8592. E-mail: zaea4@rambler.ru

A system aluminum (and titanium) *tert*-butoxide—*tert*-butyl hydroperoxide (1 : 2) under mild conditions (20 °C, 1 h) oxidizes aliphatic and alkylaromatic sulfides and diphenyl sulfide to the corresponding sulfones in yields close to ~100%. The oxidation is induced by electronexcited dioxygen formed upon thermal decomposition of intermediate metal-containing peroxy trioxides (ozonides). The latter are formed as a result of the reversible reaction of aluminum or titanium *tert*-butoxides with *tert*-butyl hydroperoxide followed by the interaction of di-*tert*butoxy-*tert*-butylperoxyaluminum and tri-*tert*-butoxy-*tert*-butylperoxytitanium that formed with another Bu<sup>t</sup>OOH molecule. Aluminum-containing peroxide (Bu<sup>t</sup>O)<sub>2</sub>AlOOBu<sup>t</sup> oxidizes sulfides to sulfoxides.

**Key words:** sulfides, sulfones, aluminum and titanium *tert*-butoxides, *tert*-butyl hydroperoxide, oxidation, metal-containing trioxides, electron-excited dioxygen.

The oxidation of sulfides by such strong agents as peroxy acids and by a series of mineral oxidants (nitric acid, chlorine dioxide, and others) includes their subsequent transformation into sulfoxides and then into sulfones. The synthesis of sulfones in the individual state needs, as a rule, drastic conditions: prolonged heating and excess oxidant.<sup>1,2</sup>

We have shown<sup>3</sup> that the tri-*tert*-butoxyaluminum (1)—*tert*-butyl hydroperoxide (2) system even at room temperature oxidizes dibenzyl and diphenyl sulfides in benzene to the corresponding sulfones in 80-96%yields.

It has been found<sup>4,5</sup> that the reaction of alkoxide 1 and 2 equivalents of peroxide 2 in  $C_6H_6$  or  $CCl_4$  results in oxygen evolution in a yield >80%. Oxygen is formed due to several consecutive reactions (Scheme 1). In the first step, alkoxide 1 reacts reversibly with Bu<sup>t</sup>OOH (2) to form di-*tert*-butoxy-*tert*-butylperoxyaluminum (3). The latter reacts with the second molecule of peroxide 2 in a six-membered reaction complex with the intermediate

#### Scheme 1



formation of an aluminum-containing ozonide, *viz.*, di-*tert*-butoxy-*tert*-butyltrioxyaluminum (**4**).

The existence of aluminum-containing ozonide **4** is confirmed by its parallel homolytic decomposition resulting in oxygen-centered radicals  $Bu^tO^{\bullet}$ ,  $Bu^tOO^{\bullet}$ ,  $(Bu^tO)_2AlO^{\bullet}$ , and  $(Bu^tO)_2AlOO^{\bullet}$  identified by ESR using spin traps.<sup>5</sup>

The thermal decomposition of trioxide **4** is assumed<sup>5</sup> to occur due to the intramolecular transfer of the Bu<sup>t</sup>O group (with an electron pair or, which is more probable, as a radical) to the Al atom ( $S_R$ 2 substitution). According to the spin conservation rule, singlet dioxygen is evolved. Its yield was determined by the reactions with anthracene and 9,10-dimethylanthracene and equaled to 40% in benzene and 50% in CCl<sub>4</sub>. It should be taken into account that free radicals escaping to the solvent bulk are efficiently involved in quenching of electron-excited oxygen.<sup>5</sup>

The purpose of this work is to study the oxidation of typical representatives of aliphatic, alkylaromatic, and aromatic sulfides by electron-excited dioxygen generated by systems 1-2 and tetra-*tert*-butoxytitanium (5)–2 in benzene at room temperature. It was of interest to compare the reactivities of dioxygen formed in these systems and singlet oxygen  ${}^{1}O_{2}(\Delta g)$  obtained by photoinduced excitation.

# Experimental

Commercial solvents (analytical and reagent grades) were used. Benzene was purified by distillation from  $P_2O_5$  and stored over metallic sodium; chlorobenzene and  $CCl_4$  were distilled

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and stored over Na<sub>2</sub>SO<sub>4</sub>. Dimethyl, diphenyl, and methyl phenyl sulfides (pure) were distilled before use. Dibenzyl sulfide (pure) was recrystallized from ethanol, and anthracene ("scintillation") was recrystallized from benzene. Dialkyl sulfides were synthesized by the reaction of Na<sub>2</sub>S with the corresponding alkyl halides according to a described procedure.<sup>6</sup> The method of synthesis and properties of aluminum tri-tert-butoxide (1) have been described previously.<sup>5</sup> Di-tert-butoxy-tert-butylperoxyaluminum was synthesized by the reaction of di-tert-butoxyaluminum chloride with Bu<sup>t</sup>OOH in the presence of Et<sub>2</sub>NH.<sup>7</sup> The content of the main substance was 90-96%. Di-tert-butoxyaluminum chloride is the product of the treatment of a solution of alkoxide 1 in benzene with anhydrous HCl.<sup>8</sup> Titanium tetratert-butoxide was synthesized by a known procedure.9 All procedures with aluminum and titanium derivatives were carried out in an atmosphere of dry oxygen-free argon. tert-Butyl hydroperoxide was synthesized according to a described procedure.<sup>10</sup> The content of active oxygen in Bu<sup>t</sup>OOH was 99.5–99.8%.

IR spectra were recorded on a Specord-M80 instrument in an interval of 4000–400 cm<sup>-1</sup>. Volatiles (Bu<sup>t</sup>OH, Me<sub>2</sub>S, MeSEt, and Et<sub>2</sub>S) were analyzed by GLC on an LKhM-80 chromatograph (helium as a carrier gas, column 120 cm long, 30% dinonyl phthalate on Chromaton N-AW-DMCS). The temperature was varied within 50–120 °C. The chromatographic analysis of Pr<sub>2</sub>S, Pr<sup>i</sup><sub>2</sub>S, and Bu<sub>2</sub>S, as well as Pr<sub>2</sub>SO<sub>2</sub>, Pr<sup>i</sup><sub>2</sub>SO<sub>2</sub>, and Bu<sub>2</sub>SO<sub>2</sub>, was carried out on a Tsvet-2-65 instrument (flame-ionization detector, helium as a carrier gas, column 300 cm long, Apieson-L, 15% on the support indicated above, temperature 150–180 °C). Anthracene, Ph<sub>2</sub>S, and MeSPh were analyzed on the same instrument (column 300 cm long, 5% SE-30 on Inerton Super) at 180–270 °C.

Qualitative analysis for sulfoxides was carried out according to a published procedure.<sup>11</sup>

Oxidation of dipropyl sulfide by the  $(Bu^tO)_3Al(1)-Bu^tOOH$ (2) system (1 : 2). Peroxide 2 (16 mmol) was added to a solution of compound 1 (8 mmol) and Pr<sub>2</sub>S (8 mmol) in benzene (20 mL). After 1–2 min, the reaction mixture self-heated. The formation of Pr<sub>2</sub>SO<sub>2</sub>, whose amount achieved 5.2 mmol 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 Bu<sup>t</sup>OH (11.4 mmol) and Bu<sup>t</sup>OOH (0.2 mmol). Sulfuric 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> (94%, 7.5 mmol), Bu<sup>t</sup>OH (20.7 mmol), and Bu<sup>t</sup>OOH (1.2 mmol) were found.

Other sulfides were oxidized similarly.

Ether-insoluble but water-soluble  $Me_2SO_2$ ,  $Et_2SO_2$ , and  $Pr_2SO_2$  were isolated by the treatment of the reaction mixture with AcOH 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 an equivalent amount of ditert-butoxy-tert-butylperoxyaluminum (3).  $(Bu^tO)_2AIOOBu^t$  (3) (2.1 mmol),  $Bn_2S$  (2.1 mmol), and benzene (10.5 mL) were mixed. Then the solvent and volatiles were condensed in a trap cooled with liquid nitrogen. The volatile fraction contained  $Bu^tOH$  (1.4 mmol). Sulfuric acid (10%) was added to the residue, the mixture was extracted with  $Et_2O$ , and the extract was dried with  $Na_2SO_4$  and analyzed by GLC.  $Bu^tOH$  (2.7 mmol) and  $Bu^tOOH$  (0.1 mmol) were found. Then unreacted  $Bn_2S$  (1.4 mmol) and  $Bn_2SO$  (0.5 mmol) were isolated. In addition,  $Bu^tOH$  (1.9 mmol) was found in the aqueous-acidic layer.

# **Results and Discussion**

Sulfides  $R^1SR^2$  (**6a**—**h**) and  $Ph_2S$  (**6i**), which does not react with  $O_2({}^{1}\Delta g)$ , <sup>12</sup> were chosen for the study. They were oxidized by the system **1**—**2** using either an equimolar amount of peroxide **2** or its twofold excess in benzene at room temperature. In the latter case, the only reaction products were sulfones **7a,c**—**i** (Scheme 2, Table 1).





Sulfones are formed during mixing accompanied by noticeable self-heating of the reaction mixture. After 10 min, 50%  $Pr_2SO_2$  were found chromatographically. The reactions are completed within an hour in high yields (79–96%).

When using a twofold excess of peroxide **2**, the system of titanium tetra-*tert*-butoxide (**5**)—Bu<sup>t</sup>OOH (**2**) oxidizes sulfides **6d,f,h** under similar conditions and with the same rate and efficiency (Scheme 3).

## Scheme 3

6d.f.h 
$$\xrightarrow{5-2}$$
 7d.f.h

The corresponding sulfones were the single products in all entries. According to the GLC data, the yields of  $Pr_2SO_2$  and  $Bu_2SO_2$  were 85–99%.

All sulfones were isolated in the individual state. The IR spectra correspond to those of authentic samples.<sup>13</sup>

Electron-excited dioxygen seems to be the oxidant of the S atom of sulfide. The data of several works<sup>14–17</sup> performed in our laboratory show that dioxygen evolved is consumed to the oxidation of C—H groups. The methylene groups of alkanes, alkylarenes, ketones, *etc.* are transformed into carbonyl groups by ketonization, whereas methine groups are transformed into hydroperoxy groups. The CH<sub>2</sub> groups in the benzyl and allyl fragments are oxidized especially easily.<sup>16,17</sup> The oxidation is accompa-

Entry	Sulfide	Products/mole per mole of sulfide <sup>b</sup>								
		volatile fraction			after hydrolysis of a nonvolatile residue					
		Bu <sup>t</sup> OOH	Bu <sup>t</sup> OH	R <sup>1</sup> SR <sup>2</sup>	Bu <sup>t</sup> OOH	Bu <sup>t</sup> OH	$R^1SR^2$	$R^1SO^2R^2$		
1 c	6a	0.04	2.26	0.04	0.03	1.62	_	0.94		
2 c	6c	0.06	2.30	Traces	d	d	_	0.79		
3 c	6d	0.06	1.73	Traces	0.15	2.22	Traces	0.96		
4 <sup>c</sup>	6e	0.08	2.16	—	d	d	_	0.95		
5 c	6f	0.05	2.40	—	0.14	1.92	0.034	0.96		
6 <sup>c</sup>	6g	0.04	1.96	0.05	0.04	2.38	0.02	0.93		
7 <sup>c</sup>	6h	0.05	2.29	—	0.22	d	_	0.96		
8 c	6i	_	2.24	—	_	2.46	0.12	0.80		
9 e,f	6a	0.02	0.69	0.44	0.15	2.19	_	0.17		
10 e,f	6b	0.08	1.95	0.28	d	d	_	0.20		
11 <sup>e,f</sup>	6d	0.06	0.72	0.23	0.26	2.06	0.16	0.41		

Table 1. Oxidation of sulfides 6a-i by the (Bu<sup>t</sup>O)<sub>3</sub>Al (1)-Bu<sup>t</sup>OOH (2) system<sup>a</sup>

<sup>*a*</sup> 20 °C, solvent: benzene (entries 1, 3-5, 7-11), chlorobenzene (entry 2), and CCl<sub>4</sub> (entry 6).

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

<sup>*c*</sup> 1 equiv. of  $(Bu^{t}O)_{3}Al + 2$  equiv. of  $Bu^{t}OOH$ .

<sup>d</sup> Not determined.

<sup>*e*</sup> 1 equiv. of  $(Bu^{t}O)_{3}Al + 1$  equiv. of  $Bu^{t}OOH$ .

<sup>f</sup> The corresponding sulfoxides were qualitatively identified in entries 9–11.

nied by the cleavage of the C–C bonds in the organic substrate. Photoinduced dioxygen  $O_2(^{1}\Delta g)$  does not react with C–H bonds in hydrocarbons. Thus, the oxidating system **1–2** is a more efficient oxidant.

Sulfides can be oxidized by oxidating systems based on Bu<sup>t</sup>OOH and alkoxides 1 or 5 directly under the action of Bu<sup>t</sup>OOH or metal-containing peroxides of the (Bu<sup>t</sup>O)<sub>n</sub>MOOBu<sup>t</sup> type (M = Al, n = 2; M = Ti, n = 3), which are present in the reaction mixture (see Scheme 1).

It is established that peroxide 2 does not oxidize sulfides under the reaction conditions. To reveal how metalcontaining peroxides are involved in oxidation, we studied the interaction of a series of sulfides (**6d,f,h,i**) with aluminum-containing peroxide **3**. The results are presented in Table 2.

According to the data from this study, the main reaction products at an equimolar sulfide : peroxide **3** ratio are sulfoxides **8d,f,h,i**, which were qualitatively identified in all experiments. Sulfoxides **8h,i** were isolated in yields of 22 and 19%, respectively. It should be noted that only a half of sulfide is oxidized, while ~30% are oxidized in the case of diphenyl sulfide. No sulfones were found. Sulfoxides are formed, probably, due to the nucleophilic attack of the peroxy group on the S atom. The attack is favored by the coordination of sulfide with the Al atom as an S-ligand<sup>18</sup> (Scheme 4).

Sulfide (R <sub>2</sub> S)	R	Products/mole per mole of sulfide <sup>b</sup>								
		volatile fraction <sup>c</sup>		after hydrolysis of a nonvolatile residue						
		Bu <sup>t</sup> OH	R <sub>2</sub> S	Bu <sup>t</sup> OOH	Bu <sup>t</sup> OH	R <sub>2</sub> S	R <sub>2</sub> SO	$R_2SO_2$		
6d	Pr	0.71	0.41	0.25	2.04	0.10	d	_		
6f	Bu	0.59	0.29	0.37	1.86	0.29	d	0.10		
6h	Bn	0.62	_	0.06	2.03	0.67	0.22	_		
6i	Ph	0.32	—	0.14	2.00	0.71	0.19	_		

**Table 2.** Oxidation of sulfides **6d,f,h,i** by di-*tert*-butoxy-*tert*-butylperoxyaluminum (3) (1 equiv.)<sup>a</sup>

<sup>*a*</sup> 20 °C, benzene.

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

<sup>c</sup> Traces of Bu<sup>t</sup>OOH are present.

<sup>d</sup> Qualitative determination.

# Scheme 4



R = Pr(d), Bu(f), Bn(h), Ph(i)

Simultaneously aluminum-containing peroxide **3** thermally decomposes, which followed from the detection of Bu<sup>t</sup>OH in the volatile fraction.<sup>8</sup>

In all cases, a twofold increase in the amount of peroxide 3 results in the corresponding sulfones 7 through the intermediate formation of sulfoxides 8. The S atom in the latter is more electrophilic and, as a consequence, more active toward peroxide 3, which acts as a nucleophilic agent (Scheme 5).

## Scheme 5

$$\begin{array}{c} \mathsf{R}_2 \mathsf{S} = \mathsf{O} + (\mathsf{Bu}^{\mathsf{t}}\mathsf{O})_2 \mathsf{A} \mathsf{I} \mathsf{OOBu}^{\mathsf{t}} \longrightarrow \mathsf{R}_2 \mathsf{SO}_2 + (\mathsf{Bu}^{\mathsf{t}}\mathsf{O})_3 \mathsf{A} \mathsf{I} \\ \mathbf{8} \quad \mathbf{3} \quad \mathbf{7} \quad \mathbf{1} \end{array}$$

Thus, the reaction of peroxide 3 with  $Ph_2SO$  is completed by the formation of  $Ph_2SO_2$  in 86% yield.

The data presented indicate that peroxide 3 reacts with sulfides and sulfoxides as a nucleophilic reagent, while it reacts with Bu<sup>t</sup>OOH directly (see Scheme 1) to form metal-containing ozonide 4, due to which the direction of sulfide oxidation changes.

This conclusion is confirmed by the results of the oxidation of dimethyl, ethyl methyl, and dipropyl sulfides **6a,b,d** by the system 1-2 in benzene at an equimolar ratio of reactants 1, 2, and the sulfide (see Table 1, entries 9-11). Under these conditions, the yield of sulfones is halved ( $\leq 41\%$ ). In addition to the sulfones, unconsumed sulfides were isolated, and the corresponding sulfoxides **8a,b,d** were qualitatively identified. In this case, the two-fold decrease in the yield of sulfones is a result of the adequate decrease in aluminum-containing ozonide 4, which is an efficient oxidant of sulfides.

The low-temperature oxidation of organic substrates by the system 1-2 and oxidation by hydroperoxides catalyzed by compounds of `transition and nontransition metals occur due to the intermediate formation of metalcontaining peroxides in 10-90% yields during the time from fractions of a second to several minutes.<sup>19</sup>

In the studied reactions of sulfide oxidation by the systems 1-2 and 5-2, the formation of metal-containing aluminum and titanium peroxides is determined by a

higher nucleophilicity of hydroperoxide **2** over that of Bu<sup>t</sup>OH or water<sup>20</sup> and, hence, the peroxide anion Bu<sup>t</sup>OO<sup>-</sup> is a stronger nucleophile than the corresponding anions Bu<sup>t</sup>O<sup>-</sup> or HO<sup>-</sup>. All these facts cause the formation of peroxides of the (Bu<sup>t</sup>O)<sub>n</sub>MOOBu<sup>t</sup> type (M = Al, n = 2; M = Ti, n = 3), which react with the second molecule of **2** in a six-membered reaction complex involving, for example, an Al atom (inner-sphere reaction),<sup>21</sup> and the strong Bu<sup>t</sup>O base eliminates a proton to form trioxide **4** (Scheme 6).

## Scheme 6



Thus, the physicochemical activation of dioxygen occurs in the systems under study (see Schemes 1 and 6). Dioxygen is evolved in the catalytic cycle, which is confirmed by the independent reactions of peroxides 2 and 3 and by the oxidation of  $Ph_2S$  and  $Bn_2S$ .<sup>3</sup>

The energy of dioxygen formation calculated from the dissociation energies of covalent bonds of aluminum peroxytrioxide exceeds that of the first excitation state  $O_2(^{1}\Delta g)$  and equals 43.5–51.45 kcal mol<sup>-1</sup>. The standard dissociation energy of  $O_2(^{3}\Sigma g^{-})$  equal to 118 kcal mol<sup>-1</sup> was taken into account in the calculations, and the O–O bond energy in hydrogen peroxide is 44–51 kcal mol<sup>-1</sup>.<sup>21</sup>

To compare the data on the reactivity of dioxygen generated by the systems under study and that of singlet oxygen  $O_2(^{1}\Delta g)$  generated by photoirradiation, we used the known results<sup>22,23</sup> indicating that  $O_2(^{1}\Delta g)$  oxidizes sulfides to sulfoxides according to Scheme 7.

# Scheme 7

$$2 \operatorname{Et}_2 S + {}^1O_2 \longrightarrow 2 \operatorname{Et}_2 SO$$

Minor amounts of sulfone were also found among the reaction products. Unlike aliphatic sulfides,  $Ph_2S$  is not oxidized by singlet oxygen under these conditions. However, as mentioned previously,<sup>22,23</sup>  $Ph_2S$  is oxidized to  $Ph_2SO$  only in a mixture with  $Et_2S$ . Based on the experimental kinetic data and quantum-chemical calculations,<sup>24,25</sup> we assumed that the oxidation proceeds *via* peroxide intermediates (Scheme 8).

Intermediate 9 (probability of its formation is preferential) oxidizes the next molecule of the starting sulfide, including  $Ph_2S$ , to the corresponding sulfoxide (Scheme 9).



Scheme 8

Scheme 9

$$R_2^+ S^- O^- O^- + R_2^- S^- \longrightarrow 2 R_2^- SO$$

Thiadioxirane **10**, whose stability is favored by aprotic solvents, <sup>12,22</sup> is responsible for the formation of sulfones. The yield of the latter is much lower than that of sulfoxides. It should be noted that, when reacting in benzene, thiadioxirane **10** decomposes to the starting sulfide and dioxygen in the triplet state  $O_2(^3\Sigma g^-)$  (Scheme 10).

### Scheme 10



Thus, the reactivity of photoinduced  $O_2({}^{1}\Delta g)$  differs sharply from that of electron-excited dioxygen formed by the reaction of alkoxide 1 or 5 with Bu<sup>t</sup>OOH with the intermediate formation of the corresponding trioxides (ozonides) (see Scheme 1). The conversion of singlet dioxygen to the triplet in the liquid phase is especially intense, as known, in the presence of paramagnetic species (Scheme 11).

### Scheme 11

$$O_2(^{1}\Sigma g^+) \longrightarrow O_2(^{1}\Delta g) \longrightarrow O_2(^{3}\Sigma g^-)$$

The average lifetime of the  $O_2({}^{1}\Sigma g^{+})$  state is  $10^{-11}-10^{-10}$  s, and that of the  $O_2({}^{1}\Delta g)$  state is longer by four—five orders of magnitude.<sup>26</sup> Naturally, the chemical properties of singlet dioxygen molecules should differ from both each other and those in the triplet state. Photochemical studies of dioxygen  $O_2({}^{1}\Delta g)$  concerning its reactions with different substrates, such as alkenes, dienes, furan derivatives, anthracenes, *etc.*, have been performed to date.<sup>27</sup> As for the electron-excited state  $O_2({}^{1}\Sigma g^{+})$ , the results obtained exclude unambiguously any chemical reactions with the substrates listed above. It has also been

noted<sup>27</sup> that the physical deactivation of  $O_2({}^{1}\Sigma g^{+})$  occurs simultaneously, under any conditions of its transition state, to form  $O_2({}^{1}\Delta g)$ . This is favored by the lability of the reagent, its spin-allowed or -forbidden transition, deactivation due to collisions with solvent molecules, *etc.* 

Electron-excited dioxygen generated by the systems 1-2 and 5-2 reacts with sulfide not as a kinetically independent molecule in the solvent bulk but oxidizes the substrate to sulfone directly in the coordination sphere of the metal with the intermediate formation of thiadioxirane 10 (Scheme 12).

## Scheme 12

$$R_{2}S + [(Bu^{t}O)_{n}M \cdot O_{2}] \xrightarrow[-(Bu^{t}O)_{n}M]{} \left[R_{2}S \underbrace{\bigcirc}_{O}^{O}\right] \longrightarrow R_{2}SO_{2}$$
10

M = Al, *n* = 3; M = Ti, *n* = 4

We cannot exclude another alternative route of sulfone synthesis: the direct oxidation of sulfide by ozonide **4** in the step of formation of radical pairs  $(Bu^tO)_2AIOO^*$ and  $Bu^tO^*$ . The oxidation of coordinated sulfide is accompanied by the elimination of electron-excited dioxygen during the intramolecular  $S_R2$  substitution of the  $Bu^tO$  radical at the metal atom without oxygen escape to the solvent bulk.

Our hypothesis was checked for the oxidation of  $Pr_2S$  by system 1–2 (1:2) in benzene in the presence of anthracene. In this reaction, the yield of  $Pr_2SO_2$  was ~100%, and anthracene was isolated from the reaction mixture in an unchanged state. This fact indicates that electron-excited dioxygen does not escape to the solvent bulk, under these conditions, but reacts with sulfide directly in the coordination sphere of the Al atom.

In addition, for  $Bn_2S$  oxidation, one could assume the oxidation of the C–H bonds in the methylene groups followed by sulfide degradation to benzaldehyde, which occurs when this substrate is oxidized by  $O_2(^{1}\Delta g)$ .<sup>28</sup> No products of the oxidation of C–H bonds were found when  $Bn_2S$  was oxidized by the systems 1–2 and 5–2.

It should be noted in conclusion that sulfones are formed by the action of electron-excited dioxygen without its escape to the solvent bulk and involving sulfide in a reaction complex. Therefore, some sulfides, in particular,  $Pr_2S$  and  $Ph_2S$ , can be used as the test reagents to electron-excited states of oxygen in the liquid phase. These compounds, unlike substituted alkenes, dienes, anthracenes, <sup>5,26</sup> and others, have donor S atoms with a low electronegativity and, hence, a high polarizability. They form, as known, <sup>18</sup> stable complexes with "soft" metal ions, and coordination bonds in these complexes are characterized by a considerable covalent contribution. All these facts result in the easy oxidation of sulfides through the intermediate formation of persulfoxides **9** and thiadioxiranes **10** responsible for the formation of the target products. Sulfoxides and sulfones are synthesized very rapidly and specifically in high yields, as well as without secondary reactions.

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