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Soft Liquid-Phase Oxidation Sulfides with the Systems on the Base of the Element-Containing Alkoxides and *Tert*-Butylhydroperoxide

Elena A. Zaburdaeva^a; Viktor A. Dodonov^a; Larisa P. Stepovik^a; Irina A. Kapuskina^a

^a N. I. Lobachevsky Nizhny Novgorod State University, Nizhny Novgorod, Russia

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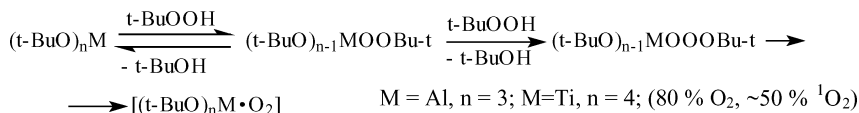
Irina A. Kapuskina

N. I. Lobachevsky Nizhny Novgorod State University,
 Nizhny Novgorod, Russia

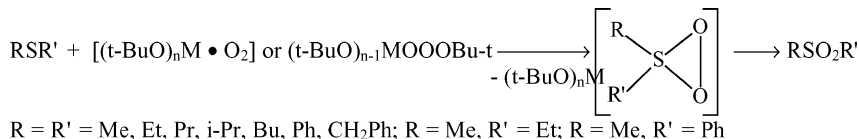
Keywords Electron-excited dioxygen; metal containing trioxides; oxidation; sulfides; sulfones; *tert*-butoxides of aluminum and titanium; *tert*-butylhydroperoxide

The tri-*tert*-butoxyaluminum (1)-*tert*-butylhydroperoxide (2) and tetra-*tert*-butoxytitanium (3)-hydroperoxide (2) systems in molar ratio alkoxide:(2) = 1:2 in soft conditions (rt, 1 h) oxidize alkyl and alkylaryl sulfides to corresponding sulfones with practically quantitative yields (Table I).

Oxidation proceeds under the action of the electron-excited (singlet) dioxygen generating by the (1)-(2) or (3)-(2) systems. Such active dioxygen forms by the consecutive reactions with participation of the coordinative sphere of the atoms of the elements (Al or Ti).^{1,2}



The intermediate formation of thiadioxirane is supposed.²



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Address correspondence to Elena A. Zaburdaeva, N. I. Lobachevsky Nizhny Novgorod State University, 23 prosp. Gagarina, 603950 Nizhny Novgorod, Russia. E-mail: zaea4@rambler.ru

TABLE I Oxidation of Sulfides RSR' with the Tri-*tert*-butoxyaluminum-*tert*-butylhydroperoxide System (1:2)^{a,b}

N	Sulfide		Products in volatile fraction, mol per 1 mol RSR'			Products after hydrolyzes of insoluble residue, mol per 1 mol RSR'			
	R	R'	t-BuOOH	t-BuOH	RSR'	t-BuOOH	t-BuOH	RSR'	RSO ₂ R'
1	Me	Me	0.04	2.26	0.04	0.03	1.62	—	0.94
2	Et	Et	0.06	2.30	Traces	—	—	—	0.79
3	Pr	Pr	0.06	1.73	Traces	0.15	2.22	Traces	0.98
4	Bu	Bu	0.05	2.40	—	0.14	1.92	0.03	0.96
5	Me	Ph	0.04	1.96	0.05	0.04	2.38	0.02	0.93
6	Ph	Ph	—	2.24	—	—	2.46	0.12	0.80
7	Bn	Bn	0.05	2.29	—	0.22	—	—	0.96

^a20°C, solvent C₆H₆; C₆H₅Cl (N 2) and CCl₄(N 6).^bMiddle dates, mol per 1 mol RSR'.

It is known^{3,4} that photooxidation of sulfides forms the corresponding sulfoxides. Hydroperoxide (**2**) and (t-BuO)_{n-1}MOOBu-t present in our systems do not oxidize sulfides to sulfones under the same conditions.

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