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Reaction of Organoelement Hydrides R_3EH (E = Si, Ge) with Metal *tert*-Butylate (M = Al, Ti)–*tert*-Butyl Hydroperoxide Oxidative Systems

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Abstract—Trialkyl(aryl)silanes and -germanes effectively react with metal (Al, Ti) *tert*-butylate–*tert*-butylhydroperoxide under mild conditions (room temperature, benzene or tetrachloromethane) mainly by the element–hydrogen bond. The character of the products depends on the nature of the element, the structure of the radical bound to it, and the solvent. The process is radical in nature. It includes the stages of formation of element-centered radicals and their reaction with the oxygen generated by the system. The intermediate organometallic peroxides can also acts as oxidants for the element (Si, Ge)–hydrogen bonds.

The oxidative activity of organosilicon and organogermanium hydrides depends on the structure of the radicals bound with the heteroatom and the nature of the oxidant. Potassium permanganate [1], hydrogen peroxide on a Zeolite catalyst [2], and perbenzoic acid [3] convert trialkyl(aryl)silanes to corresponding hydroxy derivatives. Triethylsilane and triethylgermane react with mineral acids (H_2SO_4, HNO_3), as well as with Ag_2O at the boiling points of the hydrides to form siloxane and germanoxane [4].

Over the past years dimethyldioxirane [5, 6] has been offered as a mild oxidant that converts trialkylsilanes of various structure to hydroxysilanes. The reaction involves the Si–H bond and occurs at temperatures ranging from –70°C to 20°C with a high conversion and selectivity by the molecular and radical mechanisms, the first prevailing.

The reaction of organosilicon hydrides with ozone at –70°C to –80°C involves formation of hydrotrioxides $R_3SiOOOH$ [6–9]. At elevated temperatures, the latter decompose with liberation of singlet oxygen, hydroxysilane, and, to a smaller degree, siloxane [6, 8]. The mechanism of the decomposition of silicon hydrotrioxides is mostly molecular.

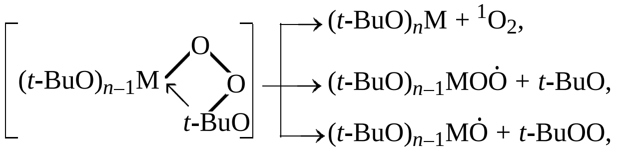
Silicon and germanium monohydrides are sufficiently stable toward free oxygen. Triphenylsilane undergoes oxidation to Ph_3SiOH, initiated by benzoyl peroxide (C_6H_6, 95°C) [10]. However, the ability of R_3GeH to oxidation is much dependent on the structure of the radical. Triphenylgermane is extremely slowly oxidized by atmospheric oxygen [11, 12], but tricyclohexylgermane is fast oxidized on exposure to air to form tricyclohexylgermanol.

Hence, E–H can bonds can be oxidized with a fairly broad range of reagents, and the reactions are accelerated by radical initiators. There is no information in the literature concerning reactions of silicon and germanium hydrides with oxidative systems comprising organoelement compounds or element alcoholates and hydroperoxides, that are known as effective and selective oxidants for C–H bonds in various substrates [13].

It was previously shown that aluminum and titanium *tert*-butylates (**I** and **II**) react with *tert*-butylhydroperoxide (**III**) at a 1 : 2 ratio under mild conditions (C_6H_6, CCl_4, 20°C) via formation of metal-containing trioxides [14, 15]. The latter decompose with evolution of oxygen, including singlet oxygen, as well as homolytically by the peroxide bonds with generation of alkoxyl and peroxyl radicals [scheme (1)].

$$(t\text{-BuO})_nM + t\text{-BuOOH} \rightleftarrows \underset{\mathbf{A}}{(t\text{-BuO})_{n-1}MOOBu\text{-}t} + t\text{-BuOH}, \qquad (1)$$

$$\mathbf{A} + t\text{-BuOOH} \longrightarrow \underset{\mathbf{B}}{(t\text{-BuO})_{n-1}MOOBu\text{-}t} + t\text{-BuOH},$$



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

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The oxygen generated by the systems is a selective oxidant for methylene and methine C–H bonds in alkanes, alkylarenes, alkenes [16–19], and some of their functional derivatives (ethers [20], esters [21], ketones [22], etc.). Oxidation of methylene and methyne C–H bonds leads, depending on the structure of the starting compounds, to introduction of oxo, hydroxy, and hydroperoxy groups. Methyl groups are insusceptible to oxidation, except for those in toluene [16] and α-methylethylenes [18]. The conversion of the starting substrate and the character of the resulting compounds is strongly dependent on whether the radicals formed on the initial stage are sufficiently stable and easy to form. The final stage of the process most frequently involves destruction of the skeleton of the starting substrate. The great role in the formation of secondary products belongs to metal peroxides. For example, the major products of the oxidation of triphenylmethane with systems containing alcoholate **I** or **II** and hydroperoxide **III** were triphenylmethyl hydroperoxide, phenol and benzophenone [23, 24], formed by scheme (2).

$$\begin{aligned} &Ph_3COOH + (t\text{-}BuO)_3Al \xrightarrow[-t\text{-}BuOH]{} Ph_3COOAl(OBu\text{-}t)_2 \\ &\longrightarrow PhOC(Ph)_2OAl(OBu\text{-}t)_2 \\ &\longrightarrow Ph_2CO + PhOAl(OBu\text{-}t)_2. \qquad (2) \end{aligned}$$

As to organoelement compounds, the oxidation of amines [25] and dialkyl sulfides [26] with the alcoholate **I**–hydroperoxide **III** system proceeds mainly through the attack either on the N–H bond, leading to formation of nitrogen-containing peroxy derivatives, or on the heteroatom (in R_2S) even in the presence of such readily oxidized groups as benzyl. The oxidants here are both oxygen and metal-containing trioxides **B** [scheme (1)].

In the present work we have studied reactions of oxidative systems consisting of alcoholate **I** or **II** and hydroperoxide **III** with organosilicon and organogermanium, aiming at assessing the effect of carbon hetero analogs on the regularities of the oxidation and the nature of its intermediates and final products. It is known that in the series C–H, Si–H, and Ge–H the bond length increases (0.109, 0.148, and 0.153 nm, respectively) and the bond energy decreases (411, 326, and 288 kJ mol^{-1}) [27].

For the starting substrates we chose both compounds containing reactive element–hydrogen bonds only (triphenylsilane and triphenylgermane) and containing, along with such bonds, methylene groups that exibit different reactivity toward the oxidative systems (triethylsilane, triethylgermane, and tribenzylsilane). All reactions were carried out at room temperature in benzene and tetrachloromethane at the element hydride–metal alcoholate–hydroperoxide ratio of 1 : 1 : 2. By special experiments we showed that in our chosen conditions the substrates react neither with CCl_4 nor with the components of the oxidative systems.

To find out whether the methylene group of the ethyl radical bound with an element is susceptible to oxidation, we reacted Et_4Si and Et_4Ge with the Al(OBu-*t*)$_3$–*t*-BuOOH system (C_6H_6, room temperature, 36 h). It was established that the conversion of Et_4Si is about 5%, and that of Et_4Ge is no higher than 10%. Acetaldehyde, acetic acid (0.05–0.08 mol) and hexaalkylelementoxanes (0.02–0.03 mol) were identified among the reaction products.

The example of tribenzylsilane was used to show that replacement of the ethyl radical by benzyl favors convertion of the methylene group and of the whole substrate (to 0.35–0.40 mol). Among the reaction products we found (mol/mol tribenzylsilane): benzaldehyde (0.05–0.10), benzyl alcohol (0.006), benzoic acid (0.06–0.10), and tribenzylhydroxysilane (0.12–0.15). The formation of aldehydes on the first stage is consistent with a radical mechanism of oxidation of the methylene fragment of silanes [14, 18–20]. Presence of tribenzylhydroxysilane implies reaction of the oxidative system with the Si–H bond. Note that the quantities of benzyl C–H and tribenzylsilane Si–H oxidation products are roughly equal, which suggests almost equal probabilities of formation of $R_2Si^{\cdot}$ and $R_3SiCH^{\cdot}Ph$ (R = $PhCH_2$) radicals.

Hence, the reaction of the Al(OBu-*t*)$_3$–*t*-BuOOH system with the methylene group is not prevailing even with benzyl radicals on silicon and is insignificant with ethyl radicals on silicon or germanium.

Oxidation of element–hydrogen bonds with the **I** (or **II**)–**III** system was considered using the example of silicon and germanium monohydrides R_3EH (R = Et, Ph). The conversions of the starting element hydrides were close to 100% with phenyl derivatives, 95% with triethylgermane, and 50–80% with Et_3SiH. At the same time, about 40–50% of oxygen is evolved in the free state (Table 1).

As seen from Table 1, the major transformation products of Et_2SiH, Ph_3SiH, and Ph_3GeH are either hydroxy compounds or hexaalkyl(aryl)elementoxanes. Unlike silicon monohydrides and Ph_3GeH, in the case of triethylgermane significant amounts of (*tert*-butylperoxy)triethylgermane (0.30–0.50 mol) and small amounts (0.01–0.02 mol) of *tert*-butoxytriethylgermane were found. The nature of the metal atom in the alcoholate has no significant effect either the com-

Table 1. Reaction products of trialkyl(aryl)element hydrides R_3EH (E = Si, Ge) with oxidative systems $(t\text{-BuO})_nM\text{–}t\text{-BuOOH}$ (M = Al, *n* = 3; Ti, *n* = 4, molar ratio 1 : 1 : 2)[a], (mol/mol element hydride, benzene, 20°C)

Reaction products	R = Et, E = Si		R = Et, E = Ge		R = Ph, E = Si		R = Ph, E = Ge	
	M = Al	M = Ti	M = Al	M = Ti	M = Al	M = Ti	M = Al	M = Ti
Products in the volatile fraction								
t-BuOH	2.39	3.14	2.50	3.12	2.89	3.03	2.81	3.62
t-BuOOH	0.11	–	0.06	–	0.05	–	–	–
O_2	0.38	0.41	0.36	Qualitatively	0.48	0.42	0.37	Not determined
Me_2CO	0.05	Traces	0.04	–	0.07	–	0.02	Traces
R_6E_2O	Traces	0.05	0.04	0.04	–	–	–	–
$R_3EOOBu\text{-}t$	–	–	0.53[b]	0.31[b,c]	–	–	–	–
R_3EH (initial)	0.20	0.49	0.06	–	–	–	–	–
Hydrolysis products of the nonvolatile residue[d]								
t-BuOH	1.88	2.69	1.23	2.22	1.45	2.92	1.87	2.18
R_3EOH	0.39	Traces	–	–	0.96	0.79	–	–
R_6E_2O	0.16	0.23	0.15	0.19	–	–	0.49	0.49[e]
PhOH	–	–	–	–	0.02[f]	0.12[f]	–	0.01

[a] Averaged results. [b] *tert*-Butoxytriethylgermane (0.01–0.02 mol) was found. [c] About 0.20 mol of an unidentified organogermanium peroxy compound was found among the hydrolysis products. [d] About 1 mol of metal in all experiments. [e] R_6Ge_2O, 0.44 mol, was isolated before hydrolysis. [f] Dihydroxydiphenylsilane, 0.06 mol, was found.

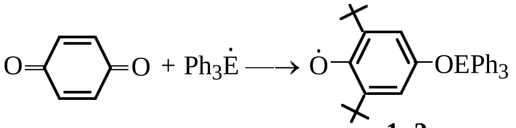
position of the products or on their yield. The low conversion of Et_3SiH in the case of titanium alcoholate can only be noted.

The formation of the compounds shown in Table 1 can be explained in terms of the radical nature of the oxidation reactions. It is known that element-centered radicals $R_3E^{\cdot}$ are most commonly prepared by reaction of element hydrides with the *tert*-butoxyl radicals generated by photolysis of *tert*-butyl peroxide [28]. In the reactions under study, radicals R_3E can be formed by hydrogen abstraction from the starting substrates by the oxygen-centered radicals generated by the systems in the course of decomposition of metal-containing trioxides **B** [scheme (1)].

$$R_3EH + XO^{\cdot} \longrightarrow R_3E^{\cdot} + XOH, \quad (3)$$

R = Et, Ph; E = Si, Ge; X = *t*-Bu, *t*-BuO, $(t\text{-BuO})_{n-1}M$, $(t\text{-BuO})_{n-1}MO$; M = Al, *n* = 3; M = Ti, *n* = 4.

We identified the $Ph_3Si^{\cdot}$ and $Ph_3Ge^{\cdot}$ radicals in the reaction of the corresponding hydrides with $Al(OBu\text{-}t)_3$–hydroperoxide **III** in benzene at 20°C by means of ESR in the form of spin adducts **1** and **2** with 2,6-di-*tert*-butyl-*p*-benzoquinone [29] [scheme (4)].



(4)

1, 2

E = Si (**1**), Ge (**2**).

The formation of radicals **1** and **2** proved only possible on final stages, when most oxygen has already been consumed for substrate oxidation and when the multiplication product of the steady-state concentration of oxygen on the rate constant of its reaction with radicals becomes comparable with the product of the concentration of the spin trap on the rate constant of the reaction with the same radicals [14].

The isotropic ESR spectra of spin adducts **1** and **2** are 1 : 2 : 1 triplets characteristic of 2,4,6-substituted aroxyls. Furthermore, the spectra show additional superfine structure formed by interaction with ^{29}Si, ^{73}Ge, and ^{13}C magnetic nuclei. The parameters of the ESR spectrum of adduct **1** of the triphehylsilyl radical, g_i = 2.0048, $a_i(^{29}Si)$ = 1.134 mT, and $a_i(H_m)$ = 0.116 mT, are close to those reported in the literature [29]. No data concerning the germanium analog are available. Our registered parameters of adduct **2** are as follows: g_i = 2.0048, $a_i(^{73}Ge)$ = 0.090 mT, $a_i(H_m)$ = 0.087 mT, and $a_i(^{13}C)$ = 1.030 mT. Evidence for the identification of the radicals formed by reactions (3) and (4) was obtained by modeling the formation of the above-mentioned quinone adducts with $Ph_3E^{\cdot}$.

Di-*tert*-butylperoxalate was used as the source of *tert*-butoxyl radicals [30]. The ESR spectra of the model adducts, and their parameters are identical to the above-listed data.

It was previously shown [14, 15] that alcoholate **I** (**II**)–hydroperoxide **III** systems generate oxygen both in benzene and in CCl_4. Using of the latter as the solvent in the oxidation of element hydrides, we can assess its effect on the qualitative and quantitative composition of the reaction products.

In view of the uniform reaction pathways of oxidative systems containing element hydrides, we considered the reaction in CCl_4 on an example of the Al(OBu-*t*)$_3$–hydroperoxide **III** system. The resulting data are listed in Table 2.

The presence of element chlorides among the reaction products provides one more evidence for the formation of element-centered radicals.

$$R_3E^{\cdot} + CCl_4 \longrightarrow R_3ECl + {}^{\cdot}CCl_3, \qquad (5)$$

$$R = Et,\ Ph;\ E = Si,\ Ge.$$

The highest yield of R_3ECl (up to 0.25–0.30 mol) was obtained with ethyl- and phenylgermanium compounds. Et_3SiCl and Et_3GeCl were identified by GLC. The presence of analogous phenyl derivatives was proved by IR spectroscopy. The IR spectrum of the nonvolatile residue of Ph_3SiH oxidation products contains bands at 510 and 560 cm^{-1}, characteristic of Si–Cl stretching vibrations, which was confirmed by the spectrum of an authentic Ph_3SiCl. However, in CCl_4, too, the preferred reaction pathway of the oxidative systems with element hydrides R_3EH is the competing oxidation of element–hydrogen bonds.

In view of the facility of the reaction of the $R_3E^{\cdot}$ radicals with oxygen [28, 31], we can propose their subsequent transformations to trialkyl(aryl)element hydroperoxides.

$$R_3E^{\cdot} + O_2 \longrightarrow R_3EOO^{\cdot}, \qquad (6)$$

$$R_3EOO^{\cdot} + R_3EH \longrightarrow R_3EOOH + R_3E^{\cdot}. \qquad (7)$$

We consider that the latter compounds can also be formed by direct reaction of metal-containing trioxides **B** with the starting substrates, similarly to the oxidation of amines [26]. It is known that in the initiated oxidation of element hydrides no hydroperoxides were found. Hence, the example of the oxidation of Ph_3SiH was used to show that triphenylsilyl hydroperoxide acts as inhibitor [10].

$$Ph_3SiOOH + Ph_3Si^{\cdot} \longrightarrow Ph_3SiO^{\cdot} + Ph_3SiOH, \qquad (8)$$

$$Ph_3SiO^{\cdot} + Ph_3SiH \longrightarrow Ph_3Si^{\cdot} + Ph_3SiOH. \qquad (9)$$

The formation in our studied reactions of small amounts of phenol and dihydroxydiphenylsilane (Table 1) points to formation of hydroperoxides Ph_3EOOH and metal-containing peroxides [scheme (2)].

The high degree of conversion of element hydrides R_3EH, as well as the fact that the reactions in benzene give 0.4–0.5 mol of free oxygen suggest intermolecular oxidation reactions leading to hydroxy derivatives R_3EOH, that probably occur by schemes (7) and (8). However, in view of the polarity of the E–H bond, we can also suggest that it is oxidized by organometallic peroxides.

To find out the role of the latter in the formation of the final products, we have studied the reaction of Ph_3EH with hydroperoxides Ph_3EOOH in the presence of alcoholates **I** or **II** in a 1 : 1 : 1 molar ratio in benzene at room temperature.

Special experiments established that the reactions of triphenylelement hydroperoxides with alcoholates **I** and **II** in 1 : 1 or 1 : 2 molar ratios in benzene at

Table 2. Reaction products of trialkyl(aryl)element hydrides R_3EH (E = Si, Ge) with the Al(OBu-*t*)$_3$–*t*-BuOOH system (molar ratio 1 : 1 : 2)[a], (mol/mol element hydride), CCl_4, 20°C

Reaction products[b]	R = Et		R = Ph	
	E = Si[c]	E = Ge	E = Si	E = Ge
Products in the volatile fraction[d]				
t-BuOH	2.80	2.80	2.85	2.78
t-BuOOH	0.08	Traces	0.12	–
O_2	0.20	0.23	0.37	0.20
Me_2CO	0.03	0.03	Traces	0.03
R_3ECl	0.10	0.30	–	–
R_6E_2O	0.19	0.03	–	–
R_3EOOBu-*t*	–	0.44	–	–
R_3EOBu-*t*	–	0.08	–	–
Hydrolysis products of the nonvolatile residue[e]				
t-BuOH	1.88	1.10	1.50	1.71
R_3EOH	0.41	–	0.85	–
R_6E_2O	0.04	0.06	–	0.37
R_3ECl	–	–	0.12	0.20
Cl^-	0.22	0.23	0.40	0.28

[a] Averaged results. [b] Hexachloroethane, about 0.04 mol, was found directly in the reaction mixture. [c] Unreacted Et_3SiH, 0.10 mol. [d] Phosgene was qualitatively identified. [e] About 1 mol of aluminum in all experiments.

Table 3. Reactiom products of triphenylelement hydrides Ph_3EH with hydroperoxides Ph_3EOOH (E = Si, Ge) in the presence of alcoholates $(t\text{-}BuO)_nM$; M = Al, n = 3: Ti, n = 4) at a 1 : 1 : 1 molar ratio, C_6H_6, 20°C (mol/mol hydroperoxide)

Reaction products[b]	Ph_3SiOOH	Ph_3GeOOH		
	Ph_3SiH, M = Al	Ph_3GeH, M = Al	Ph_3GeH, M = Ti	Ph_3SiH, M = Ti
Products in the volatile fraction				
t-BuOH	1.63	1.28	1.05	0.98
Hydrolysis products of the nonvolatile residue[a]				
t-BuOH	1.04	1.16	2.20	2.44
Ph_3SiOH	1.69[b]	–	–	0.77
Ph_3GeOH	–	–	0.10	–
Ph_6Ge_2O	–	0.88[c]	0.82[d]	0.43[e]
PhOH	0.03	–	0.17	0.14
Ph_3EH (initial)	0.23	0.10	0.03	0.18

[a] About 1 mol of metal in all experiments. [b] $Ph_2Si(OH)_2$, 0.05 mol, was found. Ph_6Ge_2O isolated before hydrolysis: [c] 0.34 mol, [d] 0.58 mol, and [e] 0.13 mol.

room temperature result in no oxygen evolution. That means that reactions similar to those involving *t*-BuOOH [scheme (1)] fail to occur. Evidence for this conclusion was obtained by using the readily oxidized ethylbenzene as solvent instead of benzene. The yield of acetophenone in this case was no more than 2%. It was found that hydroperoxides Ph_3EOOH fail to react with the corresponding hydrides in benzene at room temperature within a day.

The reactions of element hydrides with Ph_3EOOH in the presence of alcoholates **I** and **II** are complete within 1.5–2 h. The conversion of Ph_3SiH is 77–80%, and that of Ph_3GeH is higher than 90% (Table 3). The absence of oxygen and alkoxyl radicals in Ph_3EOOH–metal alcoholate systems rules out the radical oxidation pathway in this case.

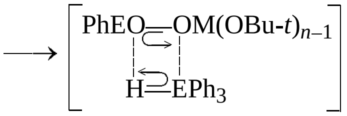
The high yield of t-BuOH and the presence of phenol point to the possible formation of peroxides **C**.

$$Ph_3EOOH + (t\text{-}BuO)_nM \xrightarrow[-t\text{-}BuOH]{} \underset{\mathbf{C}}{(t\text{-}BuO)_{n-1}MOOEPh_3}. \qquad (10)$$

We suggest that the oxidation of triphenylelement hydrides with peroxides **C** is favored by electron density redistribution in the intermediate reaction complex [scheme (11)].

Evidence for this scheme was provided by the isolation of hydroxytriphenylsilane in the oxidation of Ph_3SiH with the Ph_3GeOOH–$Ti(OBu\text{-}t)_4$ system.

$$Ph_3EH + Ph_3EOOM(OBu\text{-}t)_{n-1}$$



$$\longrightarrow \left[\begin{array}{l} PhEO{-}OM(OBu\text{-}t)_{n-1} \\ \quad H{-}EPh_3 \end{array}\right]$$

$$\longrightarrow Ph_3EOH + Ph_3EOM(OBu\text{-}t)_{n-1}, \qquad (11)$$

E = Si, Ge; M = Al, n = 3; M = Ti, n = 4.

The fact that the peroxide bond in the metal-containing peroxide can be oxidized with element hydrides was confirmed by the reactions of a fairly stable peroxide $(t\text{-}BuO)_2AlOOBu\text{-}t$ [22] with Et_3GeH, as well as with triethyl- and triphenylsilanes (C_6H_6, room temperature). The reactions with di-*tert*-butoxy-(*tert*-butylperoxy)aluminum proceed rather slowly. Within 20 h, 0.60–0.80 mol of the peroxide, 0.67 mol of Et_3GeH, 0.66 mol of Et_3SiH, and 0.61 mol of Ph_3SiH were consumed. No $Et_3EOBu\text{-}t$ was found. In the volatile fraction, 0.56–0.73 mol of *t*-BuOH was found, and hydrolysis of nonvolatile residues gave 0.54 mol of Et_3SiOH, 0.20 mol of Et_6Ge_2O, and 0.60 mol of Ph_3SiOH. The isolated products are indicative of the preferred coordination of the hydride hydrogen atom by the oxygen atom of the *tert*-butoxy group of the peroxide.

$$(t\text{-}BuO)_2AlOOBu\text{-}t + R_3EH \longrightarrow t\text{-}BuOH + R_3EOAl(OBu\text{-}t)_2. \qquad (12)$$

Hence, the Si–H and Ge–H bonds of trialkyl(aryl)-element hydrides can be oxidized both the oxygen generated by the $Al(OBu\text{-}t)_3$ [or $Ti(OBu\text{-}t)_4$]–*tert*-butylhydroperoxide system or by the intermediate organometallic peroxides of type **C**.

Trialkylhydroxysilanes and -germanes, as stronger acids, further react with metal alcoholates, expelling *tert*-butanol.

$$R_3EOH + (t\text{-}BuO)_nM \longrightarrow R_3EOM(OBu\text{-}t)_{n-1} + t\text{-}BuOH. \qquad (13)$$

Hydrolysis of unsymmetrical alkoxy compounds gives hexaalkyl(aryl)elementoxanes formed by dehydration of hydroxy compounds. However, these compounds were also found before hydrolysis (Tables 1 and 3). In the oxidation of triphenylgermane with the $Ti(OBu\text{-}t)_4$–*t*-BuOOH system, almost 90% of Ph_6Ge_2O was evolved. Special experiments were performed to establish that the dehydrating agent for hydroxytriphenylgermane can be alcoholate **II**. Hence, mixing of benzene solutions of $Ti(OBu\text{-}t)_4$ and Ph_3GeH (molar ratio 1 : 1, 20°C) resulted in precipitation of about 0.5 mol of hexaphenylgermanoxane within 5–10 min. Therewith, about 0.1 mol of *t*-BuOOH was liberated.

Equations (3) and (6)–(11) describe formation of hydroxy derivatives for all the element hydrides R_3EH studied. However, with triethylgermane, one of the major products of the reactions with the oxidative systems is (*tert*-butylperoxy)triethylgermane (**IV**) (Tables 1 and 2) whose presence can be explained by recombination of two peroxyl radicals [31] [scheme (14)].

$$Et_3GeOO^{\cdot} + t\text{-}BuOO^{\cdot} \longrightarrow Et_3GeOOBu\text{-}t + O_2. \quad (14)$$

Alternatively, peroxide **IV** can be formed by dimerization of the $Et_3Ge^{\cdot}$ and *t*-$BuOO^{\cdot}$ radicals. To obtain evidence for this suggestion, we reacted Et_3GeH with di-*tert*-butylperoxalate and hydroperoxide **III** at a 1 : 1 : 1 ratio in benzene at 50°C. The reaction in complete within 1 h. The yield of CO_2 is close to quantitative, implying complete conversion of di-*tert*-butylperoxalate. Among the reaction products we identified $Et_3GeOOBu$-*t* (–0.90 mol) and Et_3GeOBu-*t* (0.03 mol), that are probably formed by schemes (15)–(19).

$$[C(O)OOBu\text{-}t]_2 \longrightarrow 2CO_2 + 2t\text{-}BuO^{\cdot}, \quad (15)$$

$$t\text{-}BuO^{\cdot} + t\text{-}BuOOH \longrightarrow t\text{-}BuOO^{\cdot} + t\text{-}BuOH, \quad (16)$$

$$t\text{-}BuO^{\cdot} + Et_3GeH \longrightarrow Et_3Ge^{\cdot} + t\text{-}BuOH, \quad (17)$$

$$t\text{-}BuOO^{\cdot} + Et_3Ge^{\cdot} \longrightarrow Et_3GeOOBu\text{-}t, \quad (18)$$

$$t\text{-}BuO^{\cdot} + Et_3Ge^{\cdot} \longrightarrow Et_3GeOBu\text{-}t. \quad (19)$$

Equations (15) and (16) model generation of *tert*-butylperoxyl radicals. The insignificant yield of Et_3GeOBu-*t* suggests that *t*-$BuO^{\cdot}$ radicals are mostly consumed for formation of triethylgermyl and *tert*-butylperoxyl radicals.

Together the above data provide evidence for the homolytic formation of peroxide **IV** and for the formation of *tert*-butylperoxyl radicals in the reaction of alcoholates **I** and **II** with hydroperoxide **III** [scheme (1)].

Note that the amount of free oxygen in the reactions carried out in CCl_4 is always smaller than in benzene (Table 2). Among the hydrolysis products we always found the chloride anion. The IR spectrum of the nonvolatile products contains a strong band at 1621 cm^{-1}, assignable to Al–Cl stretching vibrations [comparison with the spectrum of an authentic $(PhCH_2O)_2AlCl$]. It was previously shown that Ph_3ECl (E = Si, Ge) do not change under the hydrolysis conditions.

We suggest that the Al–Cl bond is formed by the consecutive transformations of the trichloromethyl radical, presented in schemes (20)–(24). The trichloromethylperoxyl radical either abstracts hydrogen to give hydroperoxide or undergoes dimerization like tertiary alkylperoxyl radicals.

$$Cl_3C^{\cdot} + O_2 \longrightarrow Cl_3COO^{\cdot}, \quad (20)$$

$$Cl_3COO^{\cdot} \xrightarrow[-R_3E^{\cdot}]{R_3EH} Cl_3COOH, \quad (21)$$

$$\xrightarrow{Cl_3COO^{\cdot}} 2Cl_3CO^{\cdot} + O_2. \quad (22)$$

The subsequent reactions of the trichloromethoxyl radical and trichloromethylhydroperoxide may give rise to trichloromethanol that decomposes into phosgene and hydrogen chloride. One of such pathways is described by scheme (23).

$$>Al\text{–}OBu\text{-}t + HOOCCl_3 \xrightarrow[-t\text{-}BuOH]{} >AlOOCCl_3$$

$$\xrightarrow{R_3EH} >AlOER_3 + [Cl_3COH] \longrightarrow Cl_2CO + HCl. \quad (23)$$

Phosgene was qualitatively identified among the reaction products. Hydrogen chloride reacts with the alkoxy group on aluminum.

$$>Al\text{–}OBu\text{-}t + HCl \longrightarrow t\text{-}BuOH + >Al\text{–}Cl. \quad (24)$$

Note that schemes (20)–(24) describe not all the processes that occur in CCl_4, since the quantity of element chlorides is always smaller than the amount of chlorine bound with metal.

The above results led us to conclude that alcoholate **I** (**II**)–hydroperoxide **III** systems effectively oxidize trialkyl(aryl)silanes and -germanes. The reactions proceed mainly by the element–hydrogen bond and involves the $R_3E^{\cdot}$ radicals. The nature of the resulting products depends primarily on the structure of the radical and the nature of the element (Si, Ge). The specific character of the reaction of triethylgermane with the oxidative systems can be explained by the fact that the spin density in $R_3Ge^{\cdot}$ is concentrated on the element [32], as well as by the higher stability of the germanium-containing peroxyl radicals $R_3GeOO^{\cdot}$ as compared to their silicon analogs [28]. Comparing the reactions of the systems with identical compounds of carbon, silicon, and germanium one can see that the degree of conversion significantly increases in going from Ph_3CH (~30%) [23] to Ph_3SiH and Ph_3GeH (~100%). Moreover, unlike the reaction with triphenylmethane, that resulted in isolation of (triphenylmethyl)hydroperoxide and its rearramgement and decomposition products [23, 24, 33], in the case of element hydrides alcohols R_3EOH were found. We explain this result by the high oxidative activity of the intermediate organometallic peroxides toward the more polar and weaker E–H bonds.

EXPERIMENTAL

The IR spectra were recorded on Specord IR-75 and Specord-1000 IR instruments (liquid film between KBr windows). The ESR spectra were registered on a Bruker ER-200D-SRC spectrometer equipped with an ER 4105 DR double resonator (working frequency ~9.5 GHz) and an ER4111VT temperature control unit. The *g* factors were determined using diphenylpicrylhydrazyl as reference. Chromatographic analysis of the reaction products in the liquid phase was carried out on a Tsvet-2-65 gas chromatograph with a flame ionization detector and argon as carrier gas. High-boiling products (benzyl alcohol, benzaldehyde, phenol, Et_6Si_2O, Et_6Ge_2O, $Et_3GeOOBu$-*t*, Et_3GeCl, Ph_3SiH, $PhCH_2SiH$, etc.) were analyzed using a 3000 × 3 mm column packed with 5% SE-30 on Inerton-AW, oven temperature 100–230°C. Hexachloroethane was analyzed on a 2400 × 3 mm column packed with 15% of Apieson-L on Chromaton-N-AW-DMCS, oven temperature 140°C. Acetone, *tert*-butylhydroperoxide, tetraethylgermane, and tetraethylsilane were analyzed on an LKhM-80 gas chromatograph using a 1200 × 3 mm column packed with 15% of dinonyl phthalate on Chromaton N-AW-DMCS, carrier gas helium, oven temperature 40–80°C. The chromatograms were treated by the external calibration technique. All manipulations with metal-containing compounds were carried out under oxygen-free dry argon.

The quantities of unreacted Ph_3SiH and Ph_3GeH, apart from GLC, were determined by the volume of hydrogen evolved after treatment of the samples with a solution of KOH in *tert*-butanol [10]. Analysis for *tert*-butoxy groups was performed by the Deniges method [34] and analysis for acetic acid, by the procedure in [35]. Carbonyl compounds were identified as 2,4-dinitrophenylhydrazones by the melting points and by TLC on Silufol UV-254 plates in benzene or 9 : 1 benzene–diethyl ether. The quantity of oxygen evolved during the reactions was determined by the weigh of benzoic acid formed by the reaction of oxygen with benzaldehyde [16].

Titanium tetra(*tert*-butylate) was prepared by treatment of $TiCl_4$ with *tert*-butanol in the presence of NH_3 [36], bp 82–83°C (2 mm Hg), n_D^{20} 1.4420 [37]. Aluminum tri(*tert*-butylate) was obtained by the reaction of aluminum with *tert*-butanol [38] and purified by sublimation at 160-170°C (1 mm Hg). Found Al, %: 11.08. $C_{12}H_{27}AlO_3$. Calculated, %: Al 10.98. $(PhCH_2)_3SiH$, Et_3SiH, Ph_3SiH, Et_4Si, Ph_4Ge, and Et_4Ge were prepared by treatment of $SiHCl_3$ or $SiCl_4$ with Grignard reagents by published procedures. Ph_3GeBr and Et_3GeBr were prepared by bromination of Ph_4Ge and Et_4Ge in 1,2-dibromoethane. Their melting and boiling points and refractive indices agree with published data. Ph_3GeH and Et_3GeH were synthesized by reduction of the corresponding bromine derivatives of germanium with lithium alumohydride [39]. Ph_3SiOOH was prepared from Ph_3SiCl and 96% hydrogen peroxide, mp 110–111°C [40]. Ph_3GeOOH was synthesized by an analogous procedure from Ph_3GeBr, mp 136°C [41]. $Et_3GeOOBu$-*t* was obtained by reaction of Et_3GeCl with *t*-BuOOH, bp 79°C (14 mm Hg), n_D^{20} 1.3458 [42]. The activity of the peroxides was no less than 98%. The concentration of *tert*-butylhydroperoxide was no less than 99.6–99.8%.

According to the standard procedure, a mixture of a metal alcoholate and a substrate in a solvent was treated with the hydroperoxide. The reactions were complete within 1.5–2 h, as judged from the disappearance of the oxidized substance or hydroperoxide. Increase of the reaction time to 1 day did not affect the conversion of the substrate and the yield of the oxidation products. The solvent and volatile products were condensed in a trap cooled with liquid nitrogen. Nonvolatile residues were hydrolyzed in ether with 10% sulfuric acid and thoroughly extracted with ether. The volatile fractions and ethereal hydrolyzates were analyzed by GLC. The aqueous acidic hydrolyzates were analyzed for *t*-BuOH [34]. Metals were precipitated as hydroxides and then calcined to oxides.

Oxidation of tribenzylsilane with the $(t\text{-}BuO)_3Al$–*t*-BuOOH system (1 : 1 : 2) in benzene. A mixture of 1.61 g of $(t\text{-}BuOH)_3Al$, 1.18 g of *t*-BuOOH, and 1.98 g of $(PhCH_2)_3SiH$ in 20 ml of benzene was kept at room temperature for a day. Hydrogen evolution was observed. The reaction solution was dark orange. The volatile fraction contained 1.40 g of *tert*-butanol, 0.02 g of acetone, and 0.07 g of benzaldehyde. The residue was a brown dry material. During hydrolysis, a solid material insoluble in ether or aqueous acids formed on the phase interface. According to the IR spectrum [ν, cm^{-1}: 1060 (Al–O), 1590 (COO^-), and 3340 (OH)] and the Al content it was aluminum dihydroxybenzoate. Found Al, %: 14.48. $C_7H_7AlO_4$. Calculated Al, %: 14.83. The residue was hydrolysed by boiling with dilute sulfuric acid. Benzoic acid, 0.05 g, was isolated from the hydrolyzate, mp 121°C.

The ethereal extract contained 0.02 g of *tert*-butylhydroperoxide, 1.00 g of *tert*-butanol, 1.08 g of tribenzylsilane, 0.03 g of benzyl alcohol, 0.04 g of benzoic acid (analyzed as methyl ether after treatment with diazomethane), and 0.27 g of tribenzylhydroxysilane.

For quantitative analysis for $(PhCH_2)_3SiH$, an aliquot of the ethereal solution was evaporated. The dry residue was dissolved in boiling hexane. After cooling, crystals of $(PhCH_2)_3SiH$, mp 85–86°C, formed and were filtered off. The filtrate was spiked with a small crystal of $(PhCH_2)_3SiH$. After 1 h, was filtered off, mp 102-103°C. Mixed sample gave no melting point depression.

Oxidation of triethylsilane with the $(t\text{-BuO})_4$Ti–*t*-BuOOH system (1 : 1 : 2) in benzene. During the reaction of 1.33 g of $(t\text{-BuO})_4)$Ti, 0.70 g of *t*-BuOOH, and 0.45 g of Et_3SiH in 13 ml of benzene, 36 ml of oxygen evolved (under normal conditions). The reaction mixture was orange. The condensate of the volatile fraction contained 0.91 g of *tert*-butanol, 0.22 g of triethylsilane, 0.05 g of hexaethylsiloxane, and traces of acetone. The residue was a viscous yellowish oil. The ethereal solution after hydrolysis contained 0.55 g of *tert*-butanol, 0.22 g of hexaethylsiloxane, and traces of triethylhydroxysilane. In the aqueous acidic solution, 0.23 g of *t*-BuOH and 0.18 g of titanium were found.

Reaction of triethylgermane with the $(t\text{-BuO})_3$Al–*t*-BuOOH system (1 : 1 : 2) in CCl_4. To a solution of 0.93 g of $(t\text{-BuO})_3$Al and 0.60 g of Et_3GeH in 15 ml of CCl_4, 0.68 g of *t*-BuOOH was added. After 30 min, oxygen evolution commenced (19 ml under normal conditions). The reaction solution got pink. In the condensed solvent, 0.77 g of *tert*-butanol, 0.40 g of (*tert*-butylperoxy)triethylgermane, 0.21 g of chlorotriethylgermane, 0.06 g of (*tert*-butoxy)triethylgermane, 0.04 g of hexaethylgermanoxane, and 0.01 g of acetone were found. No *t*-BuOOH was detected. The conversion of Et_3GeH was about 100%. Indirect evidence for the formation of Et_3GeCl was provided by the hydrolysis of the latter. After boiling of the condensate of the volatile products with a 5% NaOH solution for 30 min, hexaethylgermanoxane was found instead of chlorotriethylgermane. (*tert*-Butylperoxy)triethylgermane was determined by chromatography and iodometric titration. For qualitative identification of $Et_3GeOOBu$-*t*, an aliquot of the volatile fraction was treated with aqueous sulfuric acid; as a result, Et_6Ge_2O and t-BuOOH were found. It is known that (*tert*-butylperoxy)triethylgermane is easily hydrolyzed with regeneration of *tert*-butylhydroperoxide. The residue after removal of volatile products was a light pink solid. After treatment by the above-described procedure, the ethereal and aqueous acidic solutions contained 0.30 g of *tert*-butanol, 0.07 g of hexaethylgermanoxane, 0.10 g of aluminum, and 0.027 g of the chloride anion.

Phosgene was identified by qualitative reaction with benzidine and by the formation of 1,2-diphenylurea upon treatment of the volatile fraction with aqueous aniline [43].

Reaction of triphenylsilane with the $(t\text{-BuO})_3$Al–*t*-BuOOH system (1 : 1 : 2) in CCl_4. A mixture of 1.47 g of $(t\text{-BuO})_3$Al, 1.56 g of Ph_3SiH, and 1.08 g of *t*-BuOOH in 20 ml of carbon tetrachloride was kept at room temperature for 5 h. Over this period of time, 48 ml of O_2 evolved. The reaction solution got dark yellow. C_2Cl_6, 0.07 g, was chromatographically determined directly in the reaction mixture. The volatile fraction contained 1.31 g of *tert*-butanol, 0.05 g of tertbutyl hydroperoxide, and 0.01 g of acetone. Hydrolysis of the nonvolatile residue (light brown dry material) gave 0.67 g of *tert*-butanol, 1.40 g of hydroxytriphenylsilane, 0.17 g of Ph_3SiCl, 0.155 g of aluminum, and 0.082 g of the chloride anion.

Special experiments showed that Ph_3SiCl is not hydrolyzed by 10% H_2SO_4 in ether. For quantitative evaluation of this compound, an aliquot of the ethereal extract of the hydrolysis products, containing a mixture of Ph_3SiCl and Ph_3SiOH, was taken, the solvent was removed at reduced pressure, and the residue was refluxed for 5 h with 10% NaOH. After acidification of the aqueous phase, 0.022 g of the chloride anion was found, which corresponds to 0.17 g of Ph_3SiCl. The weight of the isolated hydroxytriphenylsilane was 1.56 g (mp 149°C) of which 0.16 g was formed from Ph_3SiCl and 1.40 g by hydrolysis of Ph_3SiO–Al bonds.

The reactions of the other element hydrides with alcoholate **I** (**II**)–hydroperoxide **III** systems and the analysis of the resulting products were carried out in a similar way.

Reaction of Ph_3SiH with Ph_3GeOOH and $Ti(OBu\text{-}t)_4$ (1 : 1 : 1) in benzene. To a solution of 0.31 g of Ph_3SiH and 0.42 g of $Ph_3 \cdot GeOOH$ in 15 ml of benzene, 0.42 g of $Ti(OBu\text{-}t)_4$ was added. Three min after component mixing, the reaction mixture got yellow and after 20 min, brown. Therewith, KJ test revealed no peroxide compounds. Simultaneously, a crystalline precipitate formed. After 20 h, the crystals were filtered off. Hexaphenylgermanoxane, 0.10 g, was isolated before hydrolysis. The melting points of the sample and mixed sample were 184°C. The volatile fraction contained 0.08 g of *t*-BuOH.

The residue was a solid yellow material. It was treated by the above-described procedure. *tert*-Butanol, 0.17 g, and 0.02 g of phenol were determined chromatographically in the ethereal solution. It also contained a mixture of Ph_3SiH, Ph_3SiOH, and Ph_6Ge_2O. For determination of unreacted Ph_3SiH, an aliquot of the ethereal hydrolyzate was evaporated. The residue was treated with a solution of KOH in *n*-butanol. The quantity of the evolved hydrogen was 7.07 ml under normal conditions, which corresponds to 0.08 g of triphenylsilane. From the rest ethereal solution, the solvent was removed, and the solid residue was treated with 5 ml of petroleum ether. Undissolved crystals of Ph_3SiOH (0.26 g, mp 149°C) were filtered off. Petroleum ether was evaporated, and triphenylsilane was dissolved in 10 ml of diethyl ether. The insoluble residue was Ph_6Ge_2O, 0.25 g, mp 185°C. The mixed sample of the isolated and authentic Ph_3SiOH and Ph_6Ge_2O gave no melting point depression. *t*-BuOH, 0.05 g, was found in the aqueous acidic hydrolyzate.

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