

Exchange Reactions in Alkoxy Derivatives of Silicon and Germanium

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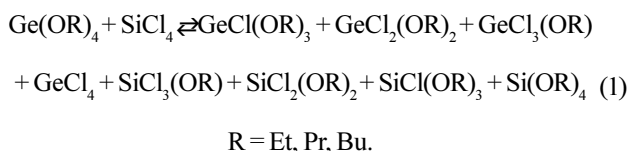
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Abstract—Reaction $\text{SiCl}_4 + \text{Ge}(\text{OR})_4 \rightarrow \text{GeCl}_4 + \text{Si}(\text{OR})_4$ was carried out for the first time. Triethoxysilane reduces tetraethoxygermane via intermediate formation of unstable $\text{GeH}(\text{OEt})_3$ that transforms into $\text{GeO} \cdot \text{Et}_2\text{O}$ or $\text{Ge}(\text{OH})_2$.

Exchange of alkyl substituents between silicon and germanium is known [1], and also a reduction of alkyltrichlorogermane with methylchlorosilane has been reported [2,3]. In attempt to reduce selectively germanium tetrahalides Me_2SiHCl , HSiCl_3 , $(\text{EtO})_3\text{SiH}$ were tried, but these compounds failed to react with GeCl_4 in ether [4].

This study was aimed at elucidation of the possibility of exchange by substituents H, OR between silicon and germanium compounds in the following systems:



The thermodynamic parameters of the reagents and products of these reactions were subjected to quantum-chemical calculations using software package Gaussian 98 in the *ab initio* approximation with the 6-31G(d,p) basis accounting for the correlation corrections by DFT procedure in B3LYP approximation. As initial parameters for calculation of the thermodynamic functions H , S , and G were chosen temperatures 298.15, 473, 573, and 673 K at a pressure of 1 at. The analysis of frequencies carried out on completing the calculations showed that imaginary vibrations with the negative frequency values were lacking for the molecules of all reagents and products. This fact evidences the calculation of stationary points corresponding to the minimum of potential energy for the molecules in question. The calculation results for the total energy, enthalpy, entropy, and free energy of

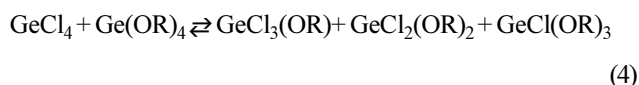
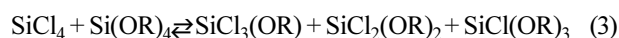
reactions under study obtained as difference between the respective parameters of products and reagents are compiled in Tables 1 and 2.

The results obtained evidence the possibility of reactions going in the direction of products for the difference between free energy of products and reagents has a negative value.

We actually found experimentally that reaction (1) occurred at room temperature without catalyst for $\text{R} = \text{Et, Pr}$. The reaction went to completion practically in 2 h. The reaction mixture contained GeCl_4 (44–48%) and $\text{Si}(\text{OR})_4$ (48–53%).

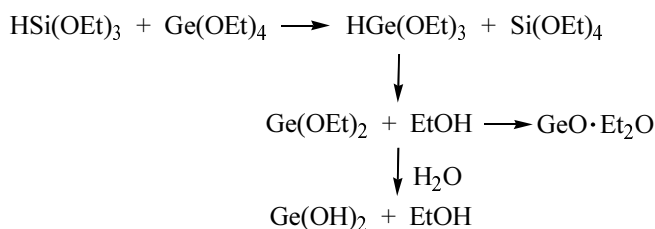
At $\text{R} = \text{Bu}$ in 2 h the content of GeCl_4 was 30%, $\text{Si}(\text{OBu})_4$ 34%. In 3 h the reaction mixture contained GeCl_4 (40%) and $\text{Si}(\text{OBu})_4$ (58%).

The systems composed exclusively of germanium or silicon compounds react in the presence of alcohol in catalytical amounts similarly to alkyltrichlorosilane and tetraethoxysilane described before [5].



The hydrogen transition from triethoxysilane to tetraethoxygermane (reaction 2, reduction of tetraethoxygermane with triethoxysilane) is also thermodynamically allowed according to the calculations. The changes in the reaction mixture were observed experimentally already at room temperature. In 2 h in the reaction mixture were found alongside the initial compounds also ethanol,

tetraethoxysilane, and a substance that was eluted a little later than tetraethoxysilane (poorly resolved peak). At standing for several days (from 2 to 14) an orange substance [probably a complex of germanium(II) oxide and ethyl ether or germanium(II) hydroxide] precipitated, and in the liquid phase remained tetraethoxysilane and ethanol. The following reactions occur apparently under these conditions:



The arising unstable triethoxygermane loses an ethanol molecule affording diethoxygermane that apparently converts into germanium(II) oxide coordinated with a liberated molecule of ethyl ether, or it reacts with air moisture to give germanium(II) hydroxide.

EXPERIMENTAL

Reactions simulation, structure optimization, and calculation of thermodynamic functions for molecules of reagents and reaction products was carried out on a PC Pentium Intel IV/1.9 GHz/RIMM 1 Gb/HDD 80 Gb with the use of software packages Gaussian 98 [6] and HyperChem. The designing, modeling, and preliminary optimization of structures for reagents and reaction products was performed in the framework of the software package HyperChem in molecular mechanics approximation with the use of force field MM+ till attaining the potential energy minimum with accuracy with respect to gradient no less than 10^{-5} kcal \AA^{-1} mol $^{-1}$.

The following initial settings and parameters were introduced into Gaussian 98 for calculation of all molecules under investigation:

Route Section: # B3LYP/6-31G** Opt=Tight IOp(2/16=3.2/17=3.2/18=3) Freq,

Charge and Multiplicity: 0 1,

Molecule Specification: atomic coordinates calculated by HyperChem.

The calculation of thermodynamic parameters at different temperatures was performed by including into the calculation of additional steps setting the necessary characteristics in the window Molecule Specification: 473.0 1.0; 573.0 1.0; 573.0 1.0. Into the field Route

Table 1. Calculation results (Gaussian 98, B3LYP/6-31G**) of thermodynamic parameters for reaction $\text{Ge(OEt)}_4 + \text{SiCl}_4 = \text{GeCl}_4 + \text{Si(OEt)}_4$

Total energy ΔE , kcal mol $^{-1}$	-27.47			
Thermodynamic parameters	Temperature, °C			
	25	200	300	400
Enthalpy ΔH , kcal mol $^{-1}$	-26.82	-26.90	-26.95	-26.99
Entropy ΔS , cal mol $^{-1}$ K $^{-1}$	1.04	0.83	0.73	0.66
Free energy ΔG , kcal mol $^{-1}$	-27.13	-27.29	-27.37	-27.44
$\ln K = -\Delta G/RT$	45.75	29.00	24.00	20.49
K	3.73×10^{16}	3.18×10^{10}	4.94×10^8	2.63×10^7
% GeCl $_4$	100	100	100	100

Table 2. Calculation results (Gaussian 98, B3LYP/6-31G**) of thermodynamic parameters for reaction (2)

Total energy ΔE , kcal mol $^{-1}$	-11.62			
Thermodynamic parameters	Temperature, °C			
	25	200	300	400
Enthalpy ΔH , kcal mol $^{-1}$	-11.56	-11.58	-11.58	-11.58
Entropy ΔS , cal mol $^{-1}$ K	-5.39	-5.43	-5.43	-5.44
Free energy ΔG , kcal mol $^{-1}$	-9.95	-9.01	-8.46	-7.92
$\ln K = -\Delta G/RT$	16.79	9.57	7.42	5.91
K	1.2×10^6	2.9×10^3	4.9×10^2	2.4×10^2
% GeH(OEt) $_3$	100	99.96	99.80	99.28

Section simultaneously commands were introduced for reading structural and frequency characteristics from the chk-file: # B3LYP/6-31G** Freq (ReadIso, ReadFC) Geom=Check Guess=Read Test.

All calculations of molecules under study were continued till normal completion.

Data from the out-files were read-out and processed in MS Excel.

The analysis of initial and final products was carried out on a chromatograph LKhM-80 equipped with a katharometer, column 2000 \times 2 mm charged with Chromaton N-AW-DMCS covered with 5% of methylsilicone SE-30, carrier gas helium, flow rate 20 ml min $^{-1}$. Oven temperature programmed from 20(50) to 300°C at a rate 16°C/min.

Table 3. Reaction of MCl_4 with $M(OR)_4$

M	R	$MCl_4:M(OR)_4$, (mol/mol)	Reaction time, h	Content in the mixture, %				
				MCl_4	MCl_3OR	$MCl_2(OR)_2$	$MCl(OR)_3$	$M(OR)_4$
Si	Et	1:3	2	–	5.4	25.8	66.7	2.1
Si	Bu	1:2	120	11.4	8.7	6.7	7.0	66.2
Ge	Bu	1:1.5	2	13.5	17.7	5.8	–	–
		1:1.2	2	17.9	20.5	2.5	0.5	59.3
		1:1	2	29.8	5.8	5.0	10.3	49.1
		1:0.5	2	42.0	8.2	7.0	14.5	28.4
Ge	Et	1:1	2	22.4	9.5	7.8	41.2	20.1
Ge	Pr	1:1	2	28.6	–	–	43.4	28.0

Table 4. Reaction of $SiCl_4$ with $Ge(OR)_4$

R	Reaction time, h	Content in the mixture, %				
		$GeCl_4$	$GeCl_3OR$	$GeCl_2(OR)_2$	$GeCl(OR)_3$	$Ge(OR)_4$
Bu	2	30.2	–	14.1	21.8	33.9
Bu	3	39.9	2.4	–	–	57.7
Et	2	48.1	–	–	–	48.2
Pr	2	53.2	–	–	–	44.0

Reagent mixtures were charged into a flask with a ground-glass stopper. A catalyst was added when necessary. The reaction mixture was maintained at room temperature, and samples were intermittently analysed. The results are presented in Tables 3 and 4.

The identification was performed by retention time of individual compounds.

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