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Abstract

Full Text

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Radiation-Chemical Synthesis of Organosilicon and Silicon-Fluoroorganic Compounds

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The use of radiation-chemical processes for the synthesis of substances is of scientific and practical interest, especially in carrying out complex chemical reactions. Thus, the synthesis of organosilicon and silicon-fluoroorganic compounds of the chlorosilane type:
$R_{(1,2)}SiCl_3$ and $R_{(1,2)}R_{(1,2)}SiCl_2$ ($R_1 = \dot{C}_nH_{2n+1}$ or $\dot{C}_6H_5$ and $R_2 = \dot{C}_nH_{2n+1-m}F_m$), which are starting products in the manufacture of various materials (rubbers, heat-transfer agents, oils, lubricants, varnishes, etc.), is very complex. A large number of studies have been devoted to the synthesis of organosilicon and silicon-fluoroorganic compounds ([1–4]), but practically no attention has been paid to radiation-chemical synthesis ([5,6]). The aim of our work was to study the conditions for obtaining derivatives of chlorosilanes by the method of radiation-chemical synthesis, which we carried out as follows: a metal ampoule was connected to two measuring ampoules, one of which contained (C_nH_{2n} or $C_nH_{2n-m}F_m$ or C_6H_6 or C_6H_5Cl), and the second ($HSiCl_3$ or H_2SiCl_2 or CH_3SiHCl_2 or $C_2H_5SiCl_2H$).

The gases were then evacuated from the system. After this, the metal ampoule was cooled with liquid oxygen and the required amounts of the starting components were recondensed into it. For more complete removal of gases (O_2, HCl, H_2, etc.), two- or threefold freezing, evacuation, and thawing of the mixture were carried out.

The mixtures were irradiated with γ-radiation from Co^{60} at temperatures of $+20^\circ$ and $+70^\circ$. After irradiation was completed, the mixtures were separated into narrow fractions by repeated recondensation in vacuum. Depending on the volatility of the initial and final substances, the temperature of the mixture during recondensation was varied from -40° to 250°.

To determine the nature of the substances obtained, the following analytical methods were used: elemental microanalysis for C, H, Cl, F, and Si (by difference) ([7]); determination of the amount of hydrolyzable chlorine and fluorine; determination of molecular weight, density, refractive index, and molar refraction. Using the synthesis of known substances ($(C_2H_5)_2SiCl_2, C_6H_5SiHCl_2$, etc.)

as examples, it was shown that the analytical methods used make it possible to establish the chemical composition and molecular structure of new substances.

Thus, the radiation-chemical method is suitable for the synthesis of organosilicon and silicon-fluoroorganic compounds. It should be noted that this synthesis is possible in those cases where, upon irradiation of the system, the rate of polymerization of olefins (fluorinated and nonfluorinated) is lower than the rate of their addition to chlorosilanes. The radiation-chemical yield (G), like the quantitative yield of the target product, depends on the molar ratio of the starting components. At a molar ratio of one olefin molecule per one hydrogen atom of the chlorosilane molecule, the highest yield (G) of the target product is obtained. Raising the temperature from +20° to +70° does not change the yield (G) of perfluoro-(alkyldialkyl)-chlorosilanes (G = 80–100 molecules/100 eV) and arylchlorosilanes.

Table 1

Compound formula	d^{20}	n_D^{20}	Molecular weight, found	Molecular weight, calculated	Molar refraction, found	Molar refraction, calculated	b.p., °C/mm Hg	Hydrolyzable Cl, %	C, %, found	C, %, calculated	H, %, found	H, %, calculated	F, %, found	F, %, calculated	Cl, %, found	Cl, %, calculated	Si, %, found	Si, %, calculated	Yield, % of starting product used	G, molecules/100 eV
$(C_3HF_6)SiCl_3$*	1.7086	1.3610	—	285.5	39.06	39.78	84/766	[illegible]	12.81	12.60	0.52	0.35	39.83	39.93	37.53	37.30	10.26	9.81	95	190
[illegible]	[illegible]	[illegible]	[illegible]	401	49.39	49.51	160	17.31	27.91	27.95	5.59	0.50	56.12	56.81	17.91	17.71	7.37	6.98	80	~100
[illegible]	1.4610	1.3383	265*	39.63	39.59	[illegible]	[illegible]	26.91	28.01	28.11	1.55	1.51	42.94	43.02	27.01	26.79	10.41	10.58	75	225
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	44.10	44.18	110–112/752	25.32	21.62	21.52	2.18	2.15	40.94	40.86	25.32	25.45	9.86	10.05	35	180
$C_2HF_4SiCl_3$*	1.5136	1.3645	—	235.5	34.73	34.88	[illegible]	44.30	10.51	10.19	0.51	0.42	32.06	32.24	45.04	45.21	11.81	11.89	91	1.6
$(C_6H_5)SiCl_3$	1.3212	1.5243	[illegible]	214	49.10	48.84	—	50.06	33.59	34.02	2.84	2.38	—	—	50.05	50.28	13.51	13.28	[illegible]	6
[illegible]	1.2156	[illegible]	[illegible]	[illegible]	45.14	44.64	—	—	41.00	40.68	3.80	3.39	—	—	40.08	40.11	15.11	15.85	[illegible]	6
[illegible]	[illegible] (20.5°)	[illegible] (20.5°)	—	—	34.09	34.18	88–94/753	49.42	25.09	25.15	5.69	5.53	—	—	49.75	49.65	19.47	19.59	70	165
[illegible]	[illegible] (25°)	[illegible] (25°)	—	—	48.10	48.11	140–146/746.8	38.33	38.93	38.97	7.98	7.57	—	—	38.13	38.31	14.97	15.13	[illegible]	160
[illegible]	[illegible]	[illegible]	—	—	38.36	38.82	127	45.03	30.73	30.57	7.14	6.37	—	—	45.30	45.21	17.86	17.85	[illegible]	165
[illegible]	[illegible]	[illegible]	—	—	38.38	38.43	—	59.32	20.02	20.23	3.95	3.94	—	—	60.16	60.00	15.81	15.77	70	150

Compound formula	d^{20}	n_D^{20}	Molecular weight, found	Molecular weight, calculated	Molar refraction, found	Molar refraction, calculated	b.p., °C/mm Hg	Hydrolyzable Cl, %	C, %, found	C, %, calculated	H, %, found	H, %, calculated	F, %, found	F, %, calculated	Cl, %, found	Cl, %, calculated	Si, %, found	Si, %, calculated	Yield, % of starting product used	G, molecules/100 eV
$(C_2H_5)SiHCl_2$	1.1041	1.4188	–	–	29.33	29.57	73–75/756	54.91	18.96	18.60	4.99	4.65	–	–	55.05	55.04	20.32	21.70	5	–
$(C_2H_5)_2SiCl_2$	1.0512 (25°)	1.4392 (25°)	–	–	38.59	38.82	114–115/751.5	45.23	30.43	30.57	6.29	6.37	–	–	45.49	45.21	17.80	17.88	80–85	210
$(C_2H_5)(CH_3)SiCl_2$	1.0712	1.4405	–	–	[[unclear: 34.72]]	34.18	100	49.50	24.98	25.15	5.79	5.59	–	–	50.04	49.61	19.21	19.58	50–60	200
$(CF_3)_2C_2H_5Si(CH_3)Cl_2$*	1.4326	1.3645	–	–	46.90	44.18**	–	[[unclear: 25.5]]	21.72	21.58	2.00	2.16	40.74	41.01	[[unclear: 25.24]]	25.54	[illegible]	10.03	70	50
$(C_6H_{11})_2SiCl_2$	0.9988	1.4673	–	–	[[unclear: 66.25]]	[[unclear: 66.55]]	–	29.74	49.94	49.79	9.57	9.73	–	–	29.13	29.46	11.38	11.63	28	10
$(C_6H_5)CH_3SiCl_2$	–	–	–	–	[[unclear: 44.11]]	49.36	–	37.54	43.98	43.99	4.24	4.22	–	–	37.03	37.10	14.71	14.69	9	4

* New substances.
** M_R calculated as the sum of atomic refractions.

(G = 6–10 molecules/100 eV), whereas the yield (G) of (alkyl-dialkyl)chlorosilanes increases from 8–10 molecules/100 eV at +20° to 160–210 molecules/100 eV at 70°. The high radiation-chemical yields (G), 50–225 molecules/100 eV, of the target product are due to the fact that the addition of olefins to chlorosilanes apparently proceeds by a chain reaction.

In the hydrolysis of fluorinated (alkyl-dialkyl)chlorosilanes, the total amount of hydrolyzable fluorine located in the β-, γ-, and α-positions relative to the silicon atom does not exceed 1–1.5%.

Physicochemical Institute
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Note: Figure translations are in progress. See original paper for figures.