Corresponding Member of the Academy of Sciences of the USSR R. Kh. FREIDLINA, E. Ts. CHUKOVSKAYA,

TsAO-I, and Academician A. N. NESMEYANOV

1961

SovietRxiv

Abstract

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CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR R. Kh. FREIDLINA, E. Ts. CHUKOVSKAYA,
TsAO-I, and Academician A. N. NESMEYANOV

TELOMERIZATION AND POLYMERIZATION OF ETHYLENE WITH SILICON HYDRIDES IN THE PRESENCE OF TITANIUM TETRACHLORIDE

In one of our preceding papers (^{1}) we briefly reported that titanium tetrachloride catalyzes (initiates) the telomerization reaction of ethylene and propylene with methyldichlorosilane according to the scheme:

$$CH_3SiCl_2H + nCH_2{=}CHR \rightarrow CH_3SiCl_2(CH_2CHR)_{nH}.$$

The reaction was carried out at a pressure of ~ 200 atm and a temperature of 190–200°. Tin chlorohydrogen acid hexahydrate acts similarly.

In the present work we have studied the reactions of ethylene with silicochloroform, methyldichlorosilane, and triethylsilane in the presence of $TiCl_4$. The reactions were carried out in a steel autoclave under pressure and with heating. It was found that, in the case of methyldichlorosilane and silicochloroform, telomerization of ethylene proceeds smoothly and with good conversion.

From the mixture of products of the telomerization of ethylene with silicochloroform in the presence of $TiCl_4$, we isolated individual products of the structure $SiCl_3C_{nH_{2n+1}}$, where $n = 2, 4, 6, 8$. The constants of these compounds, as well as of the products of their methylation, coincided with those previously described by us (^{2}). The normal structure of the alkyl groups of these products was confirmed by studying their IR spectra. A comparison of the yields of the individual telomer homologs obtained in thermal telomerization and in the presence of $TiCl_4$ is presented in Table 1.

Table 1

Experimental conditions	Conversion of $HSiCl_3$, %	Relative yield, % $n = 2$	Relative yield, % $n = 4$	Relative yield, % $n = 6$	Relative yield, % $n = 8$	Relative yield, % $n > 8$
Thermal reaction 280°, 200 atm. (^{2})	90	21.7	28	17.7	15	17.7
Reaction in the presence of $TiCl_4$ 180°, 190 atm. (experiment B)	87	25	35.5	21	11.8	6.6
Reaction in the presence of $TiCl_4$ 180°, 280 atm. (experiment A)	83	14.7	22.7	28.5	14.5	19.6

The reaction of methyldichlorosilane with ethylene, carried out in the presence of $TiCl_4$ at a temperature of 180-200° and a maximum pressure of 280 atm, led to the formation of a mixture of telomer homologs of the structure $CH_3SiCl_2C_{nH_{2n+1}}$. The reaction is complicated by the formation of liquid hydrocarbons as a result of the polymerization of ethylene.

Individual methylalkyldichlorosilanes were isolated from the reaction mixture, for which $n = 2, 4, 6, 8$ (see the experimental part, experiment II).

In the case of the reaction of triethylsilane with ethylene in the presence of $TiCl_4$ in an autoclave, under pressure, at 130°, polymerization of ethylene occurs with

Fig. 2

Figure 1: Fig. 2

the forma-

polyethylene. Telomeric products were not detected. This difference in the course of the reaction of the silicon hydrides under study with ethylene is apparently connected with the difference in their reducing ability.

Triethylsilane, which has electron-donor groups bonded to silicon, is a stronger reducing agent than trichlorosilane and methyldichlorosilane (3). Therefore, it is possible that these silicon hydrides give products of different degrees of reduction with $TiCl_4$.

The polyethylene obtained by us, according to X-ray structural investigation* (see Fig. 1), proved to be a crystalline substance with a high degree of ordering in the crystalline regions.

Fig. 2

A comparison of the X-ray diagrams of the polyethylene synthesized by us, low-pressure polyethylene, and polyethylene obtained in the decomposition of diazomethane**, showed their identity.

According to thermomechanical investigation (see Fig. 2), the polyethylene melts at a temperature of 135°, which also corresponds to the melting temperature of low-pressure polyethylene. The molecular weight, determined from the viscosity of a solution of polyethylene in tetrahydronaphthalene at 135°, is 26670.

Thus, the method described by us for obtaining polyethylene by polymerization of ethylene in the presence of triethylsilane and titanium tetrachloride leads to a product which practically does not differ from polyethylene obtained by the Ziegler method at low pressure. In a recently published report by Nitsche (4) it is also noted that, when ethylene reacts with methylpolysiloxane (obtained by hydrolysis of methyldichlorosilane) in the presence of titanium tetrachloride, polyethylene is formed.

Experimental Part

I. Telomerization of ethylene with silicochloroform

A. Into a half-liter stainless-steel autoclave were charged 80 g of $HSiCl_3$, 1 ml of $TiCl_4$; the air was displaced from the autoclave with nitrogen, and then ethylene was introduced to a pressure of 55 atm. The autoclave was heated to 200°. The maximum pressure was 280 atm. The reaction was carried out at this temperature for 3 hours, during which the pressure fell to 160 atm. The

Figure 1

Figure 2: Figure 1

Figure 1 panels a–d

Figure 3: Figure 1 panels a–d

experiment was repeated 4 times; the reaction products were combined and subjected to fractional distillation.

In all, 320 g of $HSiCl_3$ were charged. 394 g of reaction products were obtained. As a result of the distillation, the following fractions were isolated:

Fraction No.	1	2	3	4	5	6	7	8	Residue
Temperature, °C	30–40	95–100	101–145	145–150	60–87 (30 mm)	87–89 (30 mm)	70–96 (10 mm)	102 (10 mm)	
Weight, g	36	48	2	71	4	93	2	47	64

From fractions Nos. 2, 4, 6, 8, after repeated distillation, the corresponding individual alkyltrichlorosilanes were obtained. The constants of the compounds obtained, compared with the constants of these same substances previously obtained by us by thermal telomerization, are given in Table 2.

These alkyltrichlorosilanes were methylated with methylmagnesium iodide. The constants of the compounds obtained, compared with literature data ([5]), are given in Table 3.

* The X-ray diagram and thermomechanical curve were obtained in the laboratories of X-ray structural analysis and polymer physics of the Institute of Organoelement Compounds.
** The X-ray diagrams of these polymers were kindly provided for comparison of the results by V. A. Sergeev.

To the article by R. Kh. Freidlina, E. Ts. Chukovskaya, Tsao-i, and A. N. Nesmeyanov, p. 885

Fig. 1

To the article by A. M. Kuzina and L. M. Kryukova, p. 970

Fig. 1. *a* —double chromosomal bridge; *b* —chromatid bridge; *c* —chromatid bridge with fragments; *d* —micronuclei.

Table 2

Compound	B.p., °C found	B.p., °C literature data	n_D^{20} found	n_D^{20} literature data	d_4^{20} found	d_4^{20} literature data	MR found	MR calculated
$C_2H_5SiCl_3$	97	97—100	1.4248	—	1.2264	—	34.08	33.41
$C_4H_9SiCl_3$	146	146—151	1.4358	1.4352	1.1585	1.1577	42.92	42.71
$C_6H_{13}SiCl_3$	87 (30 mm)	87—89 (30 mm)	1.4435	1.4440	1.1092	1.1094	52.53	52.12
$C_8H_{17}SiCl_3$	102 (10 mm)	97 (10 mm)	1.4490	1.4490	1.0746	1.0744	61.81	61.41

Table 3

Compound	B.p., °C found	B.p., °C literature data	n_D^{20} found	n_D^{20} literature data	d_4^{20} found	d_4^{20} literature data	MR found	MR calculated
$C_2H_5Si(CH_3)_3$	62	62	1.3820	1.3828	0.6838	0.6849	34.78	34.83
$C_4H_9Si(CH_3)_3$	113	115	1.4035	1.4030 (at 25°)	0.7167	0.7181	44.42	44.12
$C_6H_{13}Si(CH_3)_3$	161—163	163	1.4162	1.4154	0.7418	0.7422	53.57	53.41
$C_8H_{17}Si(CH_3)_3$	82 (10 mm)	82.3 (10 mm)	1.4235	1.4242	0.7571	0.7581	62.76	62.70

B. The experiment was carried out as experiment A, but the maximum pressure reached 190 atm and fell during the reaction to 100 atm. From 80 g of $HSiCl_3$, 103 g of reaction products were obtained. As a result of distillation, the following fractions were isolated:

Fraction No.	1	2	3	4	5	6	7	Residue
Temperature, °C	30–90	98–100	100–145	145	56–79 (30 mm)	80 (30 mm)	87 (7 mm)	–
Weight, g	12	19	3	26	6	16	9	5

II. Reaction of ethylene with methyldichlorosilane. The experiment was carried out as experiment I A. The autoclave was charged with 60 g of CH_3SiCl_2H and 1 ml of $TiCl_4$. At a temperature of 190–200°, the maximum pressure reached 270–280 atm, and during the reaction it fell to 150 atm. A total of 94 g of reaction products was obtained. The experiment was repeated 3 times; the products were combined and distilled on a column. As a result of distillation of 259 g of the reaction mixture, individual methylalkyldichlorosilanes were isolated. The relative yields and constants of the compounds obtained, compared with the constants of these same substances previously obtained by us by thermal telomerization, are given in Table 4.

Table 4

Compound	Yield, %	B.p., °C found	B.p., °C literature data	n_D^{20} found	n_D^{20} literature data	d_4^{20} found	d_4^{20} literature data	MR found	MR calculated
$C_2H_5SiCl_2CH_3$	18	100.5	100	1.4190	1.4240	1.0644	1.0655	33.94	33.87
$C_4H_9SiCl_2CH_3$	18	149	147–148	1.4320	1.4312	1.0212	1.0190	43.46	43.26
$C_6H_{13}SiCl_2CH_3$	25	90 (31 mm)	91 (32 mm)	1.4390	1.4390	0.9892	0.9931	52.95	52.59
$C_8H_{17}SiCl_2CH_3$	13	90 (6 mm)	94 (6 mm)	1.4450	1.4440	0.9684	0.9761	62.32	61.88

In addition, intermediate fractions were obtained with b.p. 70–90° at 31 mm and 60–89° at 6 mm, containing an admixture of hydrocarbons (elevated carbon and hydrogen content and reduced specific gravities).

III. Reaction of triethylsilane with ethylene (preparation of polyethylene). The autoclave was charged with 40 g of $(C_2H_5)_3SiH$, 2.5 ml of $TiCl_4$. Air

nitrogen was forced out of the autoclave, and ethylene was introduced to a pressure of 50 atm. The reaction was carried out at 130°. The maximum pressure was 95 atm. As a result of 2 hours of heating, the pressure fell to atmospheric. The reaction product, a dirty-gray solid mass that turned white in air, was removed from the autoclave and purified by recrystallization from toluene.

Found, %: C 84.98; 85.04; H 14.14; 14.15
$(CH_2)_x$. Calculated, %: C 85.63; H 14.37

The molecular weight was determined in an Ostwald viscometer with a suspended level at 135° in tetralin at a concentration of the substance being determined of 0.1 g/100 ml. Since η_{reduced} at $C = 0.1$ g/100 ml $\simeq [\eta]$, formula (6) was used for calculating the molecular weight:

$$[\eta] = 2.4 \cdot 10^{-4} \cdot M_w^{0.78},$$

where $[\eta]$ is the intrinsic viscosity and M_w is the weight-average molecular weight. The molecular weight found was 26670.

Received
8 XII 1960

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