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Abstract

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On the Structure and Thermal Destruction of Cyclic and Linear Polymers of Dimethylsilylene and Dimethylgermylene

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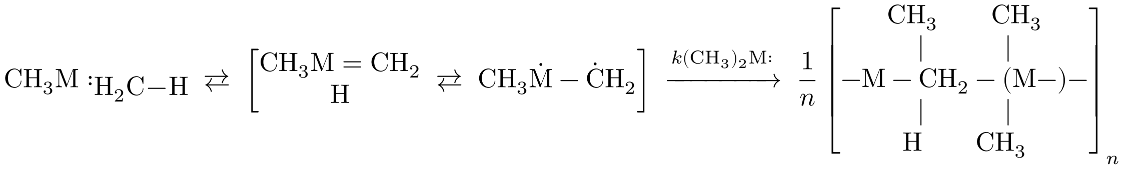
As we showed previously ($^{1-4}$), $(CH_3)_2SiCl_2$ and $(CH_3)_2GeCl_2$ readily react in tetrahydrofuran (THF) with metallic lithium, evidently leading to the intermediate formation of the corresponding carbenoids and then to products of their polymerization of the general formula $[(CH_3)_2M\langle]_n$, where M = Si or Ge and $n > 3$. The low-molecular cyclic polymers (cyclooligomers) are high-melting crystals, readily soluble in most organic solvents, while the considerably higher-molecular, apparently linear, polymers are light amorphous powders with m.p. from 220 to 360° (decomp.), practically insoluble in ordinary solvents and possessing exceptional hydrophobicity. At the same time, the weight ratio between the low- and high-molecular compounds is determined mainly by the conditions under which the interaction is carried out and varies from $1:9$ to $3:1$. According to a series of preliminary experiments, pyrolysis of these polymers $[(CH_3)_2M\langle]_n$ ($n \sim 55$ or more) is accompanied by their destruction down to elementary units—dimethylsilylene and dimethylgermylene—which was proved by their addition at the multiple bonds of tolane (^{5}) and ethylene (^{6}), with formation of the corresponding heterocyclic and heterochain compounds. These results, confirming the structure of the indicated polymers and, moreover, making it possible to regard the pyrolysis of compounds of the type $[R_2M\langle]_n$ as one of the general methods for generating carbenoids $R_2M:$, prompted us to undertake a more detailed study of the thermal destruction of polymers of dimethylsilylene and dimethylgermylene.

A study of the IR and NMR spectra of the low-molecular soluble products and of the IR spectra of the insoluble polymers showed the presence in them, along with CH_3 groups at silicon and germanium, also of 2-5% CH_2 groups bonded to Si or Ge atoms ($\nu \sim 2853$ and ~ 2925 cm^{-1}, τ 9.2–9.0 ppm). In turn, gas-chromatographic and spectral study of the initial $(CH_3)_2SiCl_2$ and $(CH_3)_2GeCl_2$ showed the complete absence of any impurities in them. This permits the assumption that the appearance of CH_2 groups in the indicated products is due to partial isomerization of the carbenoids $(CH_3)_2M:$ formed under the reaction conditions, proceeding according to the type of the known carbene-olefin isomerization (^{7,8}):



$$CH_3M\,{:}H_2C{-}H \rightleftarrows \left[\begin{matrix}CH_3M = CH_2\\ H\end{matrix} \rightleftarrows CH_3\dot{M} - \dot{C}H_2\right] \xrightarrow{k(CH_3)_2M:} \frac{1}{n}\left[\begin{matrix} & CH_3 & & CH_3 & \\ & | & & | & \\ -M- & CH_2 & - & (M-) & - \\ & | & & | & \\ & H & & CH_3 & \end{matrix}\right]_n$$

The failure to detect M − H bonds in the products formed is probably explained by their subsequent interaction with lithium and then with $(CH_3)_2MCl_2$, which readily proceeds in the highly polar THF medium (^{1}).

A more detailed investigation of the composition of the soluble portion of the products of the reaction of $(CH_3)_2SiCl_2$ with lithium in THF showed that, irrespective of the conditions under which this interaction is carried out, it consists mainly (95-97%) of crystals with m.p. 228-231° (after 3-4 recrystallizations from 96%

ethanol or from acetone with the addition of petroleum ether*, which, according to elemental and spectral (IR and NMR) analysis (^{3,8}), are a cyclopolymer $[(CH_3)_2Si <]_m$ (τ 9.89 m.u.). Attempts to establish the exact molecular weight of the latter by the usual methods (cryoscopy, ebullioscopy, isopiestic and distillation methods) were unsuccessful—the molecular-weight values ranged from 207 to 340, which corresponds to values of m from 4 to 6. Its true molecular weight was found by mass spectrometry, which gave a value of 348 ± 2 (for Si^{28}), exactly corresponding to dodecamethylcyclohexasilane $[(CH_3)_2Si <]_6$ (calculated 348.4). The same molecular-weight value (348 ± 2) was obtained for a similar cyclopolymer (m.p. 233-235°), prepared in 75% yield by the method (^{9}) from $(CH_3)_2SiCl_2$ and Li in THF at 50° in the presence of small amounts of $(C_6H_5)_3SiLi$ [from $(C_6H_5)_3SiCl$ and lithium]. Moreover, both of these samples of $[(CH_3)_2Si <]_6$ showed no depression of the melting point when mixed and had identical IR and NMR spectra and chromatograms (V_R and R_F).

Similarly, by mass spectrometry it was confirmed that the germanium cyclopolymer with m.p. 207-209° (after 5-7 recrystallizations from 96% ethanol) (τ 9.66 m.u.), of which the soluble products of the reaction of $(CH_3)_2GeCl_2$ and lithium in THF consist to 95-97%, also represents, as was noted earlier (^{3}), cyclohexamer $[(CH_3)_2Ge <]_6$ (molecular weight found 615 ± 15 (for Ge^{74}), calculated 624.4).

The investigation of the thermal stability of the cyclic (soluble) and linear (insoluble) polymers of the general type $[(CH_3)_2M <]_n$ was carried out by us by the method of microreactor gas-liquid chromatography, widely used for establishing the structure and thermal stability of sparingly volatile (mainly polymeric) compounds (see, for example, (^{10})). For this purpose an argon chromatograph from the firm "W. G. Pye" was used, with a glass column 1.2 m long, packed with Celite 545 (80-120 mesh) containing 5% polyvinylated silicone rubber "Wacker HV," the column temperature being 150°, and the carrier-gas flow rate 30-50 ml/min. The column was connected to the microreactor described previously (10), having inside it a tantalum boat to which electric heating and a thermocouple for recording the heating temperature (in the range from 20 to 800°) were connected. By means of a three-way stopcock the carrier gas (argon) could be directed either through the microreactor or bypassing it. A weighed portion of the substance under investigation (1-3 mg) was placed in the tantalum boat, which was heated to the required temperature. Sampling for analysis from the microreactor was carried out by opening the above-mentioned three-way stopcock for 1-10 sec after the necessary time intervals.

Since, after the use of the usual purification methods (washing and extraction or recrystallization), the compounds under investigation almost always still contained chromatographically detectable impurities of more volatile substances, the weighed samples were first freed from these impurities by purging them in the microreactor with the carrier gas at temperatures that did not cause decomposition of the samples (50-150°) (see Table 1). Slight decomposition of insoluble $[(CH_3)_2Si <]_n$ began at 125° and became very noticeable at 160°. Similar temperature limits for insoluble $[(CH_3)_2Ge <]_n$ were higher—respectively 170 and 220°. The characteristic decomposition products of the insoluble polymers $[(CH_3)_2M <]_n$ and the changes in their relative amounts with temperature are presented in Table 1. As can be seen from the data given in it, the principal decomposition products in the case of $[(CH_3)_2Si <]_n$ are the compounds with assigned numbers 3, 5, 8 and 11, and in the case of $[(CH_3)_2Ge <]_n$—compounds Nos. 3, 4, 7, 10 and 12. In this comparison

* Determinations of melting temperatures were carried out in a block preheated to 200°.

Table 1

Peak heights of characteristic pyrolysis products* (in % of the potentiometer scale)

Starting polymer and pyrolysis temp., °C	No. 1	No. 3	No. 5	No. 6	No. 8	No. 9	No. 11
$[(CH_3)_2Si <]_n$, 20	None	None	None	None	Traces	None	Traces
50	»	Traces	»	Traces	3	Traces	0.5
80	»	5	»	None	Traces	None	3
120	»	None	»	»	None	»	None
160	»	25	10	Traces	4	Traces	0.5

Starting polymer and pyrolysis temp., °C	No. 1	No. 3	No. 5	No. 6	No. 8	No. 9	No. 11
260	»	>100	100	None	100	None	15
400	>100	100	100	»	100	»	3

(continued)

	No. 1	No. 2	No. 3	No. 4	No. 6	No. 7	No. 10	No. 12
$[(CH_3)_2Ge <]_n$, 40	None	None	5	5	None	2	None	None
80	»	»	6	4	»	Traces	»	»
120	»	»	Traces	Traces	»	None	»	»
170	»	Traces	5	5	Traces	Traces	Traces	»
220	»	15	10	26	4	4	17	1
400	>100	>100	>100	>100	None	23	13	2

* The arbitrary numbers of the pyrolysis products are given in the order of increasing V_R.

Comparison of the retained volumes (V_R) of compounds Nos. 11 and 12 with the V_R of reference cyclopolymers $[(CH_3)_2M <]_6$ shows that the first is $[(CH_3)_2Si <]_6$, and the second is $[(CH_3)_2Ge <]_6$. The formation of these cyclohexamers from the corresponding linear polymers was also demonstrated by the results of experiments on the pyrolysis of $[(CH_3)_2M <]_n$, carried out on a macroscale at 300–400° in an atmosphere of dry N_2.

Other characteristic products of the pyrolysis of $[(CH_3)_2M <]_n$, and above all compounds Nos. 5 and 8 for M = Si and Nos. 7 and 10 for M = Ge, apparently are also cyclopolymers of dimethylsilylene and dimethylgermylene, respectively, $[(CH_3)_2M <]_m$ with m equal to 4 (Nos. 5 and 7) and 5 (Nos. 8 and 10). This assumption is confirmed by the linear dependence of $\lg V_R$ for compounds Nos. 5, 8, and 11, on the one hand, and Nos. 7, 10, and 12, on the other, on the assumed degree of polymerization m (respectively Nos. 4, 5, and 6). In addition, in favor of this are the preliminary results of chromatographic and mass-spectrometric analyses of low-molecular impurities in the soluble fraction of the reaction products of $(CH_3)_2MCl_2$ with lithium, the demonstrated fact of formation of $(CH_3)_2M:$ particles during pyrolysis of $[(CH_3)_2M <]_n$ (5, 6), and also the known data (11) on the possible existence of four- and five-membered silicon and germanium rings, for example $[(C_6H_5)_2M<]_m$, where $m = 4$ or 5.

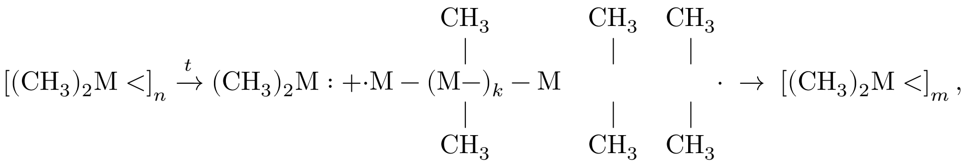
In contrast to compounds Nos. 5, 8, 11 and 7, 10, 12, which are evidently individual substances, peaks Nos. 1, 2, and 3 (Table 1) correspond to mixtures of light pyrolysis products, most of which nevertheless are organoelement compounds. The percentage ratio of the pyrolysis products of $[(CH_3)_2Si<]_n$ at 210° and $[(CH_3)_2Ge<]_n$ at 240° is given in Table 2.

Table 2

Ratio of pyrolysis products (in percent)

Starting polymer and pyrolysis temp., °C	No. 2	No. 3	No. 5	No. 7	No. 8	No. 10	No. 11	No. 12
$[(CH_3)_2Si<]_n$, 210	20	–	33.5	–	33.5	–	13	–
$[(CH_3)_2Ge<]_n$, 240	–	20	–	5	–	50	–	25

Thus, on the basis of the data obtained in the present work and earlier (6), it may be assumed that pyrolysis of polymeric dimethylsilylene and dimethylgermylene at moderate temperatures (up to 350-400°) leads mainly to rupture of M–M bonds and to the formation of monomeric, dimeric, and polymeric biradicals:



$$[(CH_3)_2M<]_n \xrightarrow{t} (CH_3)_2M: + \cdot\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{M}} - (\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{M}}-)_k - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{M}}\cdot \rightarrow [(CH_3)_2M<]_m,$$

where M = Si or Ge; k = 0-4 and higher; m = 3(?), 4-6 and higher. In the absence of special acceptors, these biradicals mainly recombine with one another, leading to cyclopolymers $[(CH_3)_2M<]_m$.

An additional thermogravimetric study of the pyrolysis process of insoluble $[(CH_3)_2Si<]_n$, carried out with a Stanton thermobalance in the range from

20 to 700° with temperature programming, showed that this process has two distinct maxima corresponding to temperatures of 310 and 420° (at a heating rate of $\sim 4°$ per minute), or 400 and 450° (at a heating rate of $\sim 6°$ per minute). The presence of these two maxima evidently corresponds to two different stages of pyrolysis of this polymer. The first of them, occurring in the range from 200 to 350° (at Δt 4 deg/min) or from 220 to 435° (at Δt 6 deg/min) and leading to a loss of 30-40 wt.% of the original sample, most likely consists in the formation of volatile cyclic compounds of composition Si_4-Si_6. At the same time, higher-molecular-weight organosilicon compounds are evidently formed as the nonvolatile residue, for example macrocycles of the same general type $[(CH_3)_2Si <]_m$, the decomposition of which proceeds upon further increase of the temperature (in the range from 350 to 470° at Δt 4 deg/min, or from 435 to 550° at Δt 6 deg/min) and therefore already leads mainly to products of deeper pyrolysis, of probable composition Si_1-Si_3 (sample weight loss 35-50%).

Consequently, the data obtained in the present work confirm the previously indicated [(1–4)] structure of the compounds formed from $(CH_3)_2MCl_2$ and lithium, and at the same time indicate the possibility of using pyrolysis of polymers $[(CH_3)_2M <]_n$, where $M = Si, Ge, Sn$, or Pb, as a general method for generating the corresponding carbenoids $(CH_3)_2M :$.

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