THE PYROLYSIS OF DIGERMANE.

BY H. J. EMELÉUS AND H. H. GUNTER JELLINEK.

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Although the formation of free radicals of short life in the pyrolysis of hydrocarbons and certain of their derivatives is well established, it has not yet been shown directly that they occur in the decomposition of silicon and germanium hydrides. There is evidence consistent with the existence of silicon free radicals in experiments on the pyrolysis of disilane at 314-360° 1 in which it was established that the addition of hydrogen during the pyrolysis increased the proportion of monosilane in the reaction product. Also, when the silicon hydrides were pyrolysed in presence of ethylene, polymerisation of the latter was induced. The second of these observations is probably analogous to the polymerisation of ethylene induced by free methyl radicals formed by decomposition of lead tetramethyl.² The experiments described in this paper provide similar evidence as to the mechanism of the decomposition of digermane. The kinetics of the thermal decomposition of this compound at 195-222° have been studied, and it has been shown that when digermane is decomposed in presence of propylene, polymerisation of the latter is similarly induced.

Experimental.

Crude GeO₂, obtained by the alkaline extraction of germanite,³ was suspended in 30% HCl and distilled at 80-85° in a stream of chlorine. The distillate containing GeCl₄ was hydrolysed, and the precipitate of oxide dried for 4 hours at 650° in a current of air. The oxide was then reduced in hydrogen at 650°, and the resulting germanium converted to magnesium germanide, Mg₂Ge; this was done by grinding the elements together and heating the mixture in porcelain boats to a red heat in a current of hydrogen. The Mg₂Ge was decomposed by dilute HCl, and digermane isolated from the resultant mixture of hydrogen and germanium hydrides by vacuum fractionation. The vapour pressure of purified digermane was re-measured between -50° and 11.4° , using a SO₂ vapour pressure thermometer in the lower temperature range. The data were in accordance with those of Dennis, Corey and Moore,4 the extrapolated boiling-point being 29°. The latent heat of evaporation was found to be 6400 cal./g. mol., and the melting-point of the hydride – 109°.

The investigation of the pyrolysis of Ge₂H₆ was made in an all-glass apparatus, connected to a mercury diffusion pump backed by an oil pump. A Töpler pump was also included in the apparatus to enable gas samples to be withdrawn for measurement and analysis.

The reaction bulb was made of soft glass, and was 15 cm. long and 3 cm. It was connected with one arm of a capillary U-tube manoin diameter. meter, the other being evacuated. The reaction bulb had a dead space of not more than 3%, and was heated in the vapour of one of several organic compounds. It was connected to an auxiliary bulb which was attached in turn to a manometer with a millimetre scale. All pressure readings could be related to the volume $(233.9 \text{ c.c. at } 27^\circ)$ of the auxiliary bulb. In

 ¹ Emeléus and Reid, J. Chem. Soc., 1939, 1021.
 ² Taylor and Jones, J. Am. Chem. Soc., 1930, **52**, 1111.
 ³ Sebba and Pugh, J. Chem. Soc., 1937, 1371.
 ⁴ Dennis, Corey and Moore, J. Am. Chem. Soc., 1924, 46, 663.

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starting an experiment a certain amount of digermane was introduced into the auxiliary bulb and the tap to the reaction bulb, heated to the desired temperature, was opened for about 10 seconds. Knowing the volume and pressure of the gas in the auxiliary bulb before and after opening of the tap, the amount of digermane introduced into the reaction bulb could be ascertained. The amounts of gases in the reaction mixture are expressed in cm. Hg when occupying a volume of 233.9 c.c. at 27°. Lastly, all values were expressed as molecular proportions.

Decomposition of Digermane.—A series of experiments were first made to determine the reaction in the decomposition of Ge_2H_6 . For this purpose the reaction was allowed to go almost to completion and the hydrogen, monogermane and digermane remaining at the end of the experiments were measured. The two hydrides were separated readily by vacuum distillation, since their vapour pressures are sufficiently different. Table I, given below, shows the analytical results at three temperatures.

Temp. t°C.	Ge ₂ H ₆ taken (cm. Hg.).	Ge ₂ H ₆ undecomp. (cm. Hg.).	GeH ₄ formed (cm. Hg.).	H ₂ formed (cm. Hg.).	GeH₄ Ge₂H ₆	$\frac{H_2}{Ge_2H_6}$
222 222 222 217 217 210 210	3.62 3.0 4.02 3.15 5.2 2.89 4.27	0.15 0.295 0.196 0.588 	4.05 3.63 4.19 3.53 5.09 3.59 5.30	1.69 1.60 1.46 2.22 1.45 1.98	I·17 I·21 I·125 I·195 I·105 I·24 I·24	0.487 0.535 0.453 0.496 0.483 0.502 0.465

TABLE I.

Over the limited temperature range of these experiments the reaction may be represented by the equation

$$Ge_{2}H_{6} = 1.18 GeH_{4} + 0.49 H_{2} + 0.82 GeH_{0.3}$$

These analytical results justify the use of changes in pressure as a measure of the extent of reaction. Some hydrogen is present in the dark solid deposit which separates on the wall of the reaction vessel during pyrolysis and, since Sieverts and Hagen ⁵ have shown that Ge does not absorb hydrogen, it is probably bound chemically. A similar solid hydride forms in the pyrolysis of disilane, when the empirical composition is SiH₀₋₇; only at considerably higher temperatures is the decomposition of silicon and germanium hydrides into the elements complete. The experiments discussed in this paper were made without removing the "germanium" mirror formed in earlier experiments from the reaction bulb, but before each run the bulb was heated to the reaction temperature and evacuated for at least 30 min. The "germanium" mirror was blue-black in colour, with a silver sheen. Thin sheets appeared red-brown by transmitted light.

Kinetics of the Decomposition of Digermane.—Measurements of the reaction rate were made at 222°, 217°, 210° and 195°. In this temperature range the reaction was of the first order over a large part of its course. This is shown in Fig. 1, in which $\log \frac{p_f - p_o}{p_f - p_i}$ is plotted as a function of time $(p_f, p_o \text{ and } p_i \text{ are respectively the final and initial pressure and the pressure at time <math>t$).

Each of the four curves represents experiments made at several initial pressures, and the various sets of data at any one temperature fall closely on the curve, which is linear except in the early stage of the reaction.

⁵ Hagen and Sieverts, Z. anorg. Chem., 1930, 185, 225.

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The measurements in curves I, II and III extended over 100 minutes, those in curve IV over 240 minutes. The reaction was retarded as it neared completion, probably because of the accumulation of reaction products, this retardation increasing with the initial pressure of digermane.



FIG. 1.—Decomposition of pure digermane:

I. 222° $\times p_0 = 20.95$ cm.II. 217° $\times p_0 = 13.05$ cm. $\bigcirc p_0 = 15.90$ cm. $\bigcirc p_0 = 16.30$ cm. $\bigcirc p_0 = 27.70$ cm.III. 210° $\times p_0 = 14.9$ cm. $\bigcirc p_0 = 21.8$ cm.

Derived values of the velocity constants for the stage of the reaction which was of the first order are given in Table II.

The temperature dependence of the velocity constant is given by the expression $k = 2.44 \times 10^{13} \times e^{\frac{-33700}{RT}}$ min.⁻¹. The activation energy of

expression $k = 2.44 \times 10^{13} \times e^{RT}$ min.⁻¹. The activation energy of the process is thus 33.7 kg.-cal., and is believed to be subject to an error of \pm 1 kg.-cal.

Decomposition in Presence of Propylene.—Attempts to study the decomposition of $Ge_{2}H_{6}$ in presence of $C_{2}H_{4}$ were abandoned because of the difficulty of analysing the

resulting mixture of GeH₄ and unchanged C_2H_4 . Various methods of analysis were tested, but complete separation by vacuum fractionation was

TΔ	RI	F	TT
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$ \begin{array}{c c} I. \ (abs.) \\ k \ (min.^{-1}) \end{array} \begin{array}{c c} 495 \\ \circ \cdot \circ_{313} \end{array} \begin{array}{c c} 490 \\ \circ \cdot \circ_{238} \end{array} \begin{array}{c c} 483 \\ \circ \cdot \circ_{155} \end{array} $	468 0·0457
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impracticable and reagents which absorbed C_2H_4 also reacted with GeH₄. Substitution of propylene for ethylene solved this difficulty, since it was found to be separable from GeH₄ by vacuum fractionation.

Propylene was prepared by dropping propyl alcohol on to P_2O_5 . The gas was passed through weak NaOH solution and water and dried by granular CaCl₂. It was then condensed in a trap cooled in liquid nitrogen, distilled in vacuum at -110° and stored. It was found that when mixtures of C_3H_6 and GeH₄ were distilled in the vacuum apparatus through two traps, the first of which was cooled to -145° and the second in liquid nitrogen, propylene, and propane if present, condensed completely in the

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first trap, whereas GeH_4 passed into the second. The volumes of these two condensates were then separately determined.

In studying the decomposition of Ge_2H_6 in the presence of C_3H_6 , a measured quantity of a $\text{C}_3\text{H}_6\text{-}\text{Ge}_2\text{H}_6$ mixture of known composition was introduced into the reaction bulb and heated for 14 hours at 210-220° (a time sufficient for the decomposition of all the Ge_2H_6). At the conclusion of the reaction the condensable products were frozen by liquid nitrogen and hydrogen was pumped off with the Töpler pump and measured. The residual gases were then fractionated at -145° as already described; the condensate of C_3H_6 and C_3H_8 was measured and transferred to a Bone and Wheeler apparatus, in which C_3H_6 was determined by absorption in concentrated H_2SO_4 . The results of four experiments are given in Table III. The gas quantities are expressed as molecular proportions.

Ge ₂ H ₈ .	С зН 6.	GeH₄ formed.	H ₂ formed.	C ₃ H ₈ formed.	C ₈ H ₆ polymerised.	
I	2	0·425	0·585	0.09	I·44	
I	2	0·476	0·71	< 0.1	I·10	
I	3	0·323	0·82	< 0.1	I·47	
I	5	0·306	1·68	0.29	I·60	

TABLE III.

Blank experiments at 210-220° showed that C_3H_6 when heated alone did not polymerise on a Ge surface, nor was it hydrogenated on such a surface. The deposit produced in runs with $Ge_3H_6-C_3H_6$ mixtures was slightly darker in colour than the "germanium" mirror obtained in the decomposition of pure Ge_2H_6 , and was insoluble in alcohol, ether, acetone, petrol ether and benzene.

With C_3H_6 present, the amounts of GeH_4 produced were less than when pure Ge_2H_6 was used; increasing the C_3H_6 pressure decreased the amount of GeH_4 formed, but at the same time the amount of hydrogen formed was increased. These data show that about 1.5 moles of propylene were converted to polymer for each mole of digermane decomposed.

Effect of Packing and of the Addition of Hydrogen.—Experiments were next made on the pyrolysis of Ge_2H_6 in a packed reaction vessel

Ge ₂ H ₆ (cm. Hg.).	GeH ₄ produced (cm. Hg.).	H _s produced (cm. Hg.).	$\frac{\text{GeH}_4}{\text{Ge}_2\text{H}_6}$	$\frac{H_2}{Ge_2H_6}$
2·28	2·76	1.06	1·21	0·465
1·77	2·15	0.95	1·215	0·536

TABLE IV.

in which there was approximately an eightfold increase in the surface. Runs at 210° in the packed reaction vessel showed that the various reaction

products were similar to those in experiments with unpacked bulbs (Table I). Data are given in Table IV. In the first of these experiments the glass surface was initially clean. In the second run the deposit from the first experiment was present at the start.

The reaction was slightly retarded by packing; the first order velocity constants at 210° for the unpacked and packed reaction vessels are as follows: $k_{unpacked} = 0.0155$; $k_{packed} = 0.0134$ min.⁻¹. The kinetic measurement with the packed reaction vessel extended over 120 minutes.

Two runs were made with digermane-hydrogen mixtures, the results of which are shown in Fig. 2.

It is seen from the graphs that the addition of hydrogen shortens the induction period (i.e. the period of negligible reaction), though the time elapsing before the reaction obeys the first-order law is about the same. The amounts of the reaction products formed in the presence of added



FIG. 2.—Decomposition of digermane-hydrogen mixtures at 210° C.

I. Pure Ge_2H_6 : $p_0 = 14.9$ cm. II. $H_2 + Ge_2H_6$: $p_0 = 17$ cm., 50 mol.-% H_2 . III. $H_2 + Ge_2H_6$: $p_0 = 9$ cm., 56.4 mol.-% H_2 .

hydrogen are similar to those in runs without hydrogen. Thus in the two sets of data for a temperature of 210° given in Table V, in which the figures refer to molecular proportions, the amounts of GeH4 and H2 produced are about the same as in the experiments recorded in Table I.

TABLE V.

Ge ₂ H ₆	H ₂	GeH ₄ H ₂ produced		GeH ₄	$\frac{H_2}{Ge_2H_6}$	
taken.	taken.	produced. by decomp.		Ge ₂ H ₆		
1	I	1·18	0•485	1.18	0·485	
0·7	0·9	0·78	0•36	1.11	0·515	

In the decomposition of disilane and trisilane the effect of adding hydrogen is to increase markedly the proportion of monosilane in the reaction product.1

Discussion.

The decomposition of digermane is similar kinetically to the decomposition of ethane 6 and of disilane.¹ The three reactions are apparently homogeneous and of the first order. It is reasonable to assume that the initial reaction is the rupture of the Ge-Ge bond, a process with which

⁶ Rice and Herzfeld, J. Am. Chem. Soc., 1934, 56, 288; Kassel and Storch, ibid., 1937, 59, 1245.

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the observed activation energy of the reaction (33.7 kg.-cal.) is to be associated. The corresponding value for the Si—Si bond, based on a similar assumption as to the mechanism of the decomposition of disilane, is 51.3 kg.-cal,¹ whilst the dissociation energy of the Si-H bond is 80.5 kg.-cal.⁷ The mechanism of the subsequent reaction in the decomposition of Ge₂H₆ is largely speculative. Following a mechanism suggested by Rice and Herzfeld \circ for ethane, we may suppose that the GeH₃ radical produced initially reacts with Ge₂H₆ according to the equation

$$\operatorname{GeH}_3 + \operatorname{Ge}_2\operatorname{H}_6 = \operatorname{GeH}_4 \times \operatorname{Ge}_2\operatorname{H}_5.$$

The Ge_2H_5 radical may decompose into Ge_2H_4 and H or, more probably, into GeH₂ and GeH₃, the latter acting as chain propagator. The production of a polymerised solid germanium hydride is indicated by the analytical results (Table I), which show that there is chemically combined hydrogen in the "germanium" mirror. Royen and Schwarz 8 have described a polymerised hydride $(GeH_2)_n$ which is formed in the reaction between calcium germanide and HCl and which decomposes above 135° into a mixture of germanium, hydrogen and germanium hydrides.

The above reaction mechanism involving the GeH₃ radical would explain the induced polymerisation of C_3H_6 , but an alternative explanation of this induced polymerisation is that at some stage in the complex reaction mechanism atomic hydrogen is produced. Reactions producing atomic hydrogen are known to be capable of inducing the polymerisation of ole-The addition of molecular hydrogen during the decomposition does fines. not increase the relative amount of GeH₄ in the reaction product, though such an effect is well marked in the decomposition of disilane. This implies that the reaction $GeH_3 + H_2 = GeH_4 + H$ is more endothermic than $SiH_3 + H_2 = SiH_4 + H$, which is a direct consequence of the relative strengths of the Ge—H and Si—H bonds. The small retardation of the reaction by packing accords with a chain mechanism. The marked induction period, which is apparent in the curves of Fig. 1, must be associated with some reaction in which hydrogen participates. Normally this hydrogen is produced in the initial stage by the reaction, and when hydrogen is added at the outset, the induction period is considerably shortened (Fig. 2).

We may, therefore, represent the main course of the pyrolysis of digermane as follows :

$Ge_2H_6 = 2 GeH_3$.				(1)
$\mathrm{GeH}_3 + \mathrm{Ge}_2\mathrm{H}_6 = \mathrm{GeH}_4 + \mathrm{Ge}_2\mathrm{H}_5$		•		(2)
$\mathrm{Ge}_{2}\mathrm{H}_{5}=\mathrm{GeH}_{2}+\mathrm{GeH}_{3}$			•	(3)
$GeH_2 = Ge + H_2$.	•	•	•	(4a)
$2 \text{ GeH}_2 = \text{GeH}_4 + \text{Ge}$	•		•	(4b)
$n \operatorname{GeH}_2 = (\operatorname{GeH}_2)_n$.	•	•	•	(4C)

A study of the kinetics of the decomposition of monogermane ⁹ shows the latter reaction to be heterogeneous, the rate of decomposition being proportional to the pressure of undecomposed monogermane to the one-third power. The thermal decomposition of monosilane, 10 however, was shown to be homogeneous and of the first order. There is no apparent reason why the decomposition of monogermane should differ from that of monosilane.

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- ⁷ Emeléus, Maddock and Reid, J. Chem. Soc., 1941, 357.
 ⁸ Royen and Schwarz, Z. anorg. Chem., 1933, 211, 412; 215, 288.
 ⁹ Hogness and Johnson, J. Am. Chem. Soc., 1932, 54, 3583.
 ¹⁰ Hogness, Johnson and Wilson, J. Am. Chem. Soc., 1936, 58, 108.

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Summary.

The thermal decomposition of digermane was studied over the temperature range $195-222^{\circ}$ C. The reaction is, in its middle stages, of the first order and homogeneous, has an induction period, and is retarded in its later stages. The activation energy was found to be 33.7 kg.-cal. Digermane was also decomposed in the presence of propylene and hydrogen to elucidate the mechanism of the reaction more fully. The observed facts are discussed and a chain mechanism is proposed.

Imperial College, London, S.W.7.