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358. *The Oxidation of Monogermane and Digermane.*

By H. J. Emeléus and E. R. Gardner.

The slow oxidation of monogermane at 160—183° has been studied analytically. The proportions of the reactants used at all stages of the reaction may be represented by the equation $GeH_4 + 2O_2 = GeO_2 + 2H_2O$, but the pressure decrease in the reaction is greater than would be expected from this equation. This has been traced to the retention by the solid oxidation product of part of the water formed in the oxidation. The oxidation is catalysed by the solid product, which forms a white deposit on the walls of the reaction vessel, and in the presence of such a deposit the slow oxidation occurs at a temperature about 100° lower than on a clean glass surface. The slow reaction in the presence of the oxide deposit within the temperature range 160—183° is approximately of zero order with respect to oxygen and of second order with respect to monogermane. It is slightly retarded by packing the reaction vessel so as to give a 3·6-fold increase in the oxide-coated surface.

The ignition of monogermane–oxygen mixtures in clean glass reaction vessels is preceded by an induction period. The lower explosion limit curve has been studied, and the ignition has been shown to occur at lower temperatures with higher proportions of monogermane in the reaction mixture. The ignition temperature is lowered and the induction period almost eliminated by the presence of the oxide deposit, or by irradiation of the heated reaction mixture with the unfiltered light of a mercury arc. The photochemical oxidation of monogermane, unlike the thermal oxidation, takes place with the formation of free hydrogen. Ignition of digermane–oxygen mixtures takes place at lower temperatures than in the case of monogermane. The reaction may be represented by the equation $2Ge_2H_6 + 7O_2 = 4GeO_2 + 6H_2O$.

The oxidation of the germanium hydrides has not hitherto been systematically investigated. Considerable interest attaches to this aspect of their chemistry, for the oxidation of the hydrides of carbon and of silicon has been fully investigated and the results have been interpreted in terms of the theory of chain reactions. The germanium hydrides have a moderate thermal stability, and it was possible to study the oxidation of monogermane at a temperature at which it did not decompose thermally. It proved to be less inflammable than monosilane, but much more so than methane. Evidence was obtained that the oxidation took place by a chain mechanism, but it was shown to differ from that of other hydrides in that the solid product formed in the oxidation, which is either germanium dioxide or a hydroxylated derivative of it, had a remarkable catalytic effect upon the reaction.

Experimental.

Preparation of Monogermane and Digermane.—Germanium was extracted from a quantity of germaniferous flue dust, the method of Morgan and Davies (J., 1935, 566) being modified for small-scale operation as follows. The finely ground dust was distilled in batches of 250 g. with 500 c.c. of 10·6N-hydrochloric acid. The first 25 c.c. of distillate were collected separately and consisted of an aqueous layer and a heavy oily layer of germanium tetrachloride. After

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most of the aqueous layer had been poured off, the oil was hydrolysed by the gradual addition of about 20 c.c. of cold water, and the hydrated germanium dioxide which separated was filtered off. The filtrate and the decanted liquid were added to the next 150 c.c. of distillate and worked up separately by co-precipitation of the germanium and arsenious sulphides with hydrogen sulphide. The sulphide which accumulated from a number of batches was dissolved in concentrated sodium hydroxide solution, an excess of concentrated hydrochloric acid added, and the resulting yellow suspension distilled in a current of chlorine. The oily liquid which separated from the distillate was hydrolysed as before.

The oxide recovered by the sulphide precipitation was combined with that obtained from the initial distillates, and the whole was distilled with concentrated hydrochloric acid (1 g. to 10 c.c. of acid) in a current of chlorine to remove arsenic. The latter is converted by the chlorine into the quinquevalent condition, in which it is almost completely non-volatile. The distillate was then hydrolysed as before. The precipitated oxide gave only a slight turbidity when dissolved in hydrochloric acid and treated with hydrogen sulphide in the presence of hydrofluoric acid (for details of the test see Müller, *J. Amer. Chem. Soc.*, 1921, **43**, 2549). This test showed the presence of only a trace of arsenic, which was removed at a later stage in the preparation of the hydrides. The oxide was finally ignited. 50 G. of purified germanium dioxide were prepared from 9 kg. of flue dust.

The oxide was reduced by heating a weighed amount in a porcelain boat in purified hydrogen. At 540—560°, the temperature used by Dennis, Tressler, and Hance (*ibid.*, 1923, **45**, 2033), the reduction of 4·2 g. of oxide was completed only after 7 hours, with a loss of 0·7% due to volatilisation. At 670°, the reduction of 3·0 g. of oxide was completed in 5 hours with a loss of 2·3%. The higher temperature was used throughout, as being likely to favour the removal of the trace of arsenic present (the vapour pressure of arsenic is 758 mm. at 615·5°).

Magnesium germanide was prepared by the method of Dennis, Corey, and Moore (*ibid.*, 1924, **46**, 657), the magnesium used being of 99·9% purity. The mixture of germanium hydrides was generated by the action of dilute hydrochloric acid on the germanide, and the subsequent purification by fractional distillation in a vacuum was carried out in an all-glass apparatus with mercury valves in place of taps. Monogermane was first separated from higher germanes by distillation at − 125°. The material so obtained was distilled at − 160°; a small head fraction was discarded, and the bulk of the material was distilled at − 150° with the rejection of a small tail fraction which would contain arsine. This process was repeated three times, and the vapour-pressure curve after the second distillation was identical with that after the third. In the course of this purification the volume of the main fraction of monogermane (250 c.c. from 10 g. of germanide) was reduced to about one-half. Ethylene and carbon dioxide vapour-pressure thermometers were used as temperature standards. Identical vapour-pressure values (see Table I) were obtained with monogermane made from a further batch of germanide. The accumulated residues from experiments on the oxidation of monogermane gave completely negative tests for arsenic.

TABLE I.

The Vapour Pressure of Monogermane.

Temp.......	−127°	−125°	−123°	−121°	−119°	−117°	−115°	−113°	−111°	−109°
V. p., mm.	53	62	74	87·5	104	122	142·5	165	190	218
Temp.......	−107°	−105°	−103°	−101°	− 99°	− 97°	− 95°	− 93°	− 91°	− 89°
V. p., mm.	248·5	282	321	363·5	410·5	464·5	523·5	585	651·5	727

The b. p. of monogermane extrapolated from the log p–$1/T$ graph is − 88·1°. The latent heat of vaporisation is 48·3 cals./g.

A small quantity of pure digermane was prepared from the mixture of the hydrides formed in the decomposition of magnesium germanide. It was distilled from the residue left after the removal of monogermane at − 65°, and purified by repeated distillation from a bath at − 75° with the rejection of head and tail fractions until the vapour pressure of the middle fraction was unchanged by further fractionation (see Table II). The b. p. found as above is 31°, and the latent heat is 39·6 cals./g.

TABLE II.

The Vapour Pressure of Digermane.

Temp.	−68·1°	−63·0°	−55·5°	−47·6°	−38·9°	−30·4°	−23·1°	−14·5°	−10·2°
V. p., mm.	6·4	8·5	14·5	23·3	38·6	60·8	86·5	128·2	152·7
Temp.	− 6·8°	− 3·4°	0·0°	3·8°	6·7°	9·9°	12·9°	16·2°	18·8°
V. p., mm.	181·2	208·3	239·0	286·9	320·4	361·1	403·1	454·5	503·5

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Comparison of these vapour-pressure data with those of other workers shows a marked discrepancy: for monogermane, Dennis, Corey, and Laubengayer (*J. Amer. Chem. Soc.*, 1925, **47**, 112) gave b. p. – 90°, Schenck and Imker (*Ber.*, 1925, **58**, 271) b. p. – 90·5°, and Paneth and Rabinowitsch (*ibid.*, p. 1138) b. p. – 88·5° for material prepared by electrolytic reduction. Our data agree best with the last value. The only other recorded b. p. of digermane is 29° (Dennis, Corey, and Moore, *loc. cit.*).

The Oxidation of Monogermane.

This oxidation was studied in a static system. The hydride was stored in a 2-l. glass reservoir, closed by a mercury valve. Oxygen, prepared by heating potassium permanganate in a vacuum, was freed from carbon dioxide and water by passage through a trap cooled in liquid oxygen, and stored in a glass globe. The two reservoirs were connected to a mixing bulb immersed in water, in which any required mixture of the reactants could be prepared manometrically. The reaction vessel was connected to the mixing bulb, a constant-volume capillary manometer, a small McLeod gauge, a Töpler pump, and a three-stage mercury-diffusion pump backed by a Cenco " Hyvac " pump. All connections in the reaction system were of capillary tubing of approximately 1 mm. bore, and were heated by a winding of nichrome wire in order to avoid the condensation of water formed in the oxidation. The dead space of the apparatus was less than 4% of the total volume of the reaction system in the experiments in which the 80-c.c. reaction bulb was used. A furnace (10 cm. diam.), the temperature of which was constant to ± 0·5°, was used. In a clean glass bulb a slow oxidation became perceptible at a temperature of 230—330°, depending on the pressure and mixture composition. During the slow reaction a white deposit formed on the glass and the pressure decreased. At somewhat higher temperatures explosions took place, with the formation of a brownish-white deposit. On a surface which was coated either with the white oxide deposit formed in the slow reaction or with the brownish deposit from an explosion, the slow reaction took place at a considerably lower temperature (150—190°), the product in this case also being white.

Reproducible reaction rates could be obtained on the oxide-coated surface by first admitting a mixture at a pressure of about 10 cm. into the reaction vessel which had been rinsed with 10% hydrofluoric acid, and heating until explosion took place. The vessel was then evacuated, and a further mixture admitted and allowed to react without explosion at about 180°. After this treatment a series of about 8 measurements of the reaction rate which were usually reproducible to within ±5% could be carried out. In subsequent experiments on the same surface the reaction rate tended to increase and become erratic. Between each experiment the reaction vessel was evacuated, filled with dry air, heated at 170—190° for 15 mins., and finally evacuated for 30 mins. at 170—190°. In the course of these preliminary observations it was established that monogermane undergoes no measurable decomposition when heated for 2½ hours at 183—196°, either in a clean glass bulb or in a bulb coated with the oxide deposit. This accords with the observations of Hogness and Johnson (*J. Amer. Chem. Soc.*, 1932, **54**, 3583).

Ratio of Reactants in Reaction on an Oxide-coated Surface.—The reaction bulb was spherical and had a volume of 80 c.c. The volatile products and unchanged reactants could be pumped off for analysis at any stage by means of the Töpler pump. A trap cooled in liquid nitrogen was inserted between the reaction system and the Töpler pump to condense out excess monogermane and the water formed in the reaction, while allowing excess oxygen to pass. The oxygen was measured in a Bone and Wheeler apparatus, and shown to be completely absorbed by sodium hyposulphite. In none of the experiments on the slow oxidation was any hydrogen produced, nor was any volatile germanium compound other than monogermane present. After complete removal of the oxygen, the temperature of the trap containing the monogermane and water was raised to – 80°, and the monogermane was pumped off and measured in the Bone and Wheeler apparatus. The water formed in the reaction was not measured directly.

Table III contains the results of a series of runs at 180° in the first three of which the reaction was carried practically to completion by heating for 15—20 hours, while in the remainder only a part of the monogermane was oxidised. These figures show that at this temperature monogermane and oxygen react in a 1 : 2 volume ratio. Similar data were obtained at 160°, 168°, 173° and 178°. The most probable equation representing the reaction is $GeH_4 + 2O_2 = GeO_2 + 2H_2O$. The amount of oxygen used should be proportional to twice the pressure decrease in the reaction, provided the water formed is prevented from condensing. Actually, it was invariably found that the pressure decrease was greater than would have been expected from the

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oxygen consumption. That this was not due to fortuitous condensation of water was proved by varying the temperature of the heated capillaries, and by carrying an experiment to a stage at which the pressure of water vapour present did not exceed the saturation pressure at room temperature. The ratio of the pressure of oxygen used to twice the pressure decrease in the reaction varied at random from 0·72 to 0·81 in a number of experiments (Table IV) in which the reaction was allowed to proceed to various degrees of completeness at a series of temperatures between 160° and 183°.

TABLE III.

Ratio of Reactants in the Slow Oxidation of Monogermane.

GeH_4 oxidised, %.	Initial mixture.		Reactants used.	
	p_{GeH_4}, mm.	p_{O_2}, mm.	p_{GeH_4}, mm.	p_{O_2}, mm.
96	76	303	73	140
96	76	228	73	144
94	52	147·5	49	98·5
35	73	218	25·5	49
40	81	243	32	60
56	63	190	35	73
58	80	239	46	92
65	62	186	40·5	80·5

TABLE IV.

Relationship between Pressure Decrease and Oxygen Consumption.

Temp.	Initial press., mm.		GeH_4 oxidised, %.	Press. of O_2 used, p_{O_2}, mm.	Press. decrease, Δp, mm.	$p_{O_2}/2\Delta p$.
	GeH_4.	O_2.				
183°	62	185·5	15	18	12·5	0·72
183	75	226	20	30	19	0·79
183	56·5	227	26	30	20	0·75
183	73	218	34	49	32	0·77
183	80	239	58	92	57·5	0·80
183	62	186	65	80·5	50·5	0·80
160	63·5	191	31	39·5	25·5	0·77
168	62	186	40	49·5	30·5	0·81
173	63	189	44	55	35·5	0·77
178	62	187	44	54·5	35	0·78

These measurements show that the pressure decrease in the reaction in the presence of an oxide surface is proportional to the amount of oxygen used at all stages of the slow reaction in the temperature range 160—183°. Therefore, observations of the pressure decrease in the reaction may legitimately be used as a measure of the reaction rate. It was also proved directly as follows that the discrepancy is due to the retention of part of the water formed in the reaction by the oxide deposit, or to the presence of a hydroxy-derivative. After the reaction had proceeded to a convenient stage, the reaction bulb was allowed to cool to room temperature and then evacuated; when the bulb was subsequently heated to 300°, water was evolved from the deposit, and the pressure which it developed was in good agreement with that calculated from the observed discrepancy between the pressure decrease in the reaction and the oxygen consumption.

Kinetics of the Slow Oxidation with an Oxide-coated Surface.—In the following experiments in which the reaction rate was measured, the furnace was first adjusted to the required temperature and pressure readings were taken at intervals, the experiments being timed from the instant of admitting the gases into the heated reaction vessel. The pressure decrease–time curves for the slow oxidation of monogermane in an oxide-coated bulb have the general form illustrated in Fig. 1. The curves shown are essentially different from the S-shaped curves which have been observed in studies on the slow oxidation of hydrocarbons, and show no induction period.

The method employed in obtaining a measure of the rate of reaction was to calculate from the pressures of the reactants in the initial mixture the total change in pressure (Δp) corresponding to the equation $GeH_4 + 2O_2 = GeO_2 + 2H_2O$, and to measure the time for a given fraction (10—30%) of this pressure change to take place. Experiments were first carried out with a gas mixture containing 20% of monogermane. The temperature was maintained at 183°, and the initial pressure of the reaction mixture was varied. The reaction vessel was cylindrical and had a length of 10 cm. and a diameter of 2·3 cm. The data obtained are given in Table V. The apparent order of reaction calculated from these results is approximately 2.

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TABLE V.

Variation of the Reaction Rate with Initial Pressure in a 1 : 4 GeH_4–O_2 *Mixture.*

Initial press., mm.	197	248	346	411
Time, mins., for 10—30% change	27·8	20·0	17·1	15·8

In the following series of experiments a number of different gas mixtures were used, the monogermane content of which varied from 14 to 33%. The temperature was again maintained at 183°, and the reaction vessel was spherical, having a diameter of 5·5 cm. and a capacity of 80 c.c. From the results of experiments with mixtures B and C (Table VI) it appears that the reaction rate is almost independent of the oxygen concentration, although a slight retardation due to increase in oxygen concentration is indicated. Also from B, D, and E it is shown that increase in the monogermane concentration has a considerable accelerating influence on the reaction. The order of reaction with respect to monogermane concentration is approximately 2. On combining the separate effects of the two reactants, a total apparent order of two is obtained, this being in agreement with the value calculated from the results in Table V.

TABLE VI.

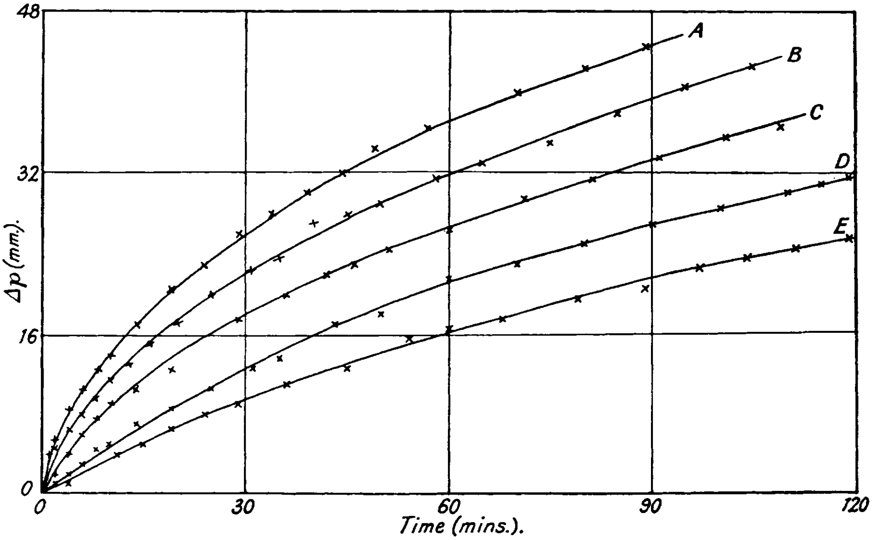
Variation of the Reaction Rate with Mixture Composition.

	Initial mixture. GeH_4 press., mm.	Initial mixture. O_2 press., mm.	Time, mins., for 10—30% change.	
A	78	156	Explosion	
B	77	230	14·2	mean 13·1
	75	225	12·2	
	73	218	13·0	
C	77	309	13·8	mean 13·8
	76	303	13·8	
D	56·5	227	17·8	mean 18·1
	56·5	226	18·3	
E	38	229	25·8	

The effect of temperature on the reaction rate was investigated with a mixture containing 23% of monogermane. The reaction vessel as before was a spherical bulb (diam. 5·5 cm.). The data for six different temperatures are recorded in Table VII, and some of the pressure decrease–time curves are given in Fig. 1. On plotting the logarithm of the time for 10—30% change against the reciprocal of the absolute temperature, the resulting points lie approximately on a straight line. The apparent energy of activation for the reaction was 24,000 cals.

FIG. 1.

Effect of temperature on the rate of oxidation of monogermane.



A, 183°, 253 *mm.* B, 180°, 247 *mm.* C, 173°, 247 *mm.* D, 168°, 249·5 *mm.* E, 160°, 254·5 *mm.*

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TABLE VII.

Effect of Temperature on the Reaction Rate.

Temp.	Initial press., mm.	Time, mins., for 10—30% change.	Temp.	Initial press., mm.	Time, mins., for 10—30% change.
160°	254	62·5} mean 60·4	177·5°	248	22·6
160	254·5	58·3	180	247	19·7
168	249·5	37·7} mean 39·8	183	253	14·7} mean 14·1
168	248	42·0	183	248	13·6
173	247	25·3			

The influence of the extent of the surface on the reaction rate in an oxide-coated glass vessel was studied by means of parallel experiments in two reaction vessels 10 cm. long and of 2·3 cm. diameter, one of which was packed with short lengths of glass tubing so as to give a 3·6-fold increase in the surface. The surfaces were coated with a deposit of oxide in the manner already described. The results of experiments carried out at 183° with a mixture containing 20% of monogermane are given below. Packing the reaction vessel retards the reaction slightly, but the magnitude of the effect is very much smaller than would be expected from a reaction propagated by reaction chains which are initiated in the gas phase and terminated on the walls.

The Influence of the Extent of the Surface on the Rate.

Bulb.	Initial press., mm.	Time, mins., for 10—30% change.	Bulb.	Initial press., mm.	Time, mins., for 10—30% change.
Unpacked	346	17·1	Packed	339	17·5
Unpacked	248	20·0	Packed	252	23·3
Unpacked	197	27·8	Packed	203	31·7

Finally, some experiments were conducted in which a small amount of benzene was added to mixtures of monogermane and oxygen. This addition caused a considerable retardation of the reaction, which has been shown to be due, at least in part, to a diminution in the catalytic effect of the oxide deposit.

The Ignition of Monogermane–Oxygen Mixtures.—The ignition of monogermane–oxygen mixtures was studied by introducing an auxiliary bulb of 80 c.c. capacity, connected to a manometer, between the mixing bulb and the reaction vessel in the apparatus already described. This auxiliary bulb was filled with the reaction mixture at a measured pressure and then connected momentarily with the heated reaction vessel (2·3 cm. diam.). The pressure of the mixture in the hot bulb was deduced from the residual pressure in the auxiliary bulb after connecting the two. It was possible in this way to determine by trial for each of a series of temperatures two pressures, below the first of which the mixture in the hot bulb did not explode, and above the second of which an explosion occurred. The reaction vessel was connected to the apparatus by a ground joint, and was washed with 10% hydrofluoric acid and water after each trial (whether explosion occurred or not) and dried by evacuation at the reaction temperature for 30 mins.

Ignition in clean glass vessels differed from that in the presence of an oxide deposit in that it was preceded by a pronounced induction period. Table VIII contains values of the critical explosion pressure of a 20% monogermane–oxygen mixture at 240—346°. The induction periods recorded are those observed at the explosion pressures.

These data may be plotted as a section of the lower explosion limit curve, and the result is similar to that obtained for many other explosive reactions. The observations could not be extended to higher pressures owing to shortage of material, so it is not possible to say if the upper explosion limit curve was also normal. The absolute values of the pressures on the lower-limit curve are much greater than those on the corresponding curve for monosilane–oxygen mixtures, and the explosions are also different from those obtained with silane in that they occur after an induction period, whereas, in the case of silane, ignition takes place much more abruptly as the limiting pressure is reached.

The data in Table VIII may be used in plotting the relationship between log p/T (where p

TABLE VIII.

Temp.	346°	322°	293°	265°	237°
Explosion, mm.	31·0	35·3	41·0	54·0	73·5
No explosion, mm.	29·8	32·7	39·3	51·4	70·7
Induction period	40 secs.	2·5 mins.	5 mins.	23 mins.	77 mins.

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is the critical pressure for explosion) and $1/T$, and a straight line is obtained for temperatures up to about 280°. At higher temperatures the limiting pressures are somewhat higher than values corresponding to points on the line.

The explosive oxidation of monogermane follows the same course as the slow oxidation, as is shown in the following table. The solid product formed in the explosion was brown, but this may be due to the thermal decomposition of a small amount of the monogermane. No free hydrogen was formed in the explosions.

Ratio of Reactants in the Explosive Oxidation of Monogermane.

GeH_4 in mixture, %.	Temp.	Press., mm.	Induction period.	GeH_4 used, mm.	O_2 used, mm.
20	322°	42·5	48 secs.	7·5	14·5
20	293·5	42·5	29 mins.	8	15
20	265	61·5	21 mins.	11·5	22·5
20	265	70	36 mins.	13·5	26
33	322	42	32 secs.	12	23·5
33	322	52·5	25 secs,	16·5	31

A series of experiments was next carried out at 322° to determine the effect of the monogermane concentration on the explosion limit. Decrease in the proportion of monogermane results in an increase in the lower critical explosion pressure at a fixed temperature. This result is similar to observations made with monosilane, which, in its mixtures with oxygen, becomes more inflammable the greater the proportion of the hydride in the mixture.

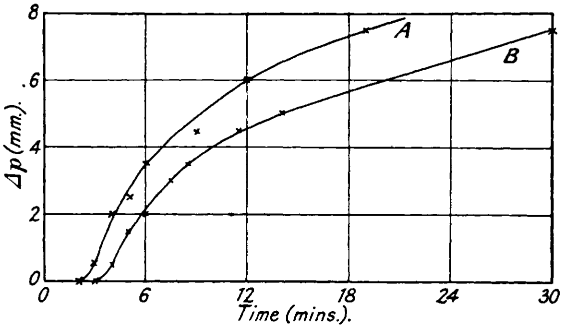
Effect of Monogermane Concentration on the Explosion Limit.

GeH_4 in mixture, %.	Press. (mm.).		Induction period, mins.	GeH_4 in mixture, %.	Press. (mm.).		Induction period, mins.
	Ignition.	No ignition.			Ignition.	No ignition.	
33	21·8	19·9	34	20	35·3	32·7	2·5
25	28·6	26·9	6·5	14	47·1	44·6	0·75

Slow Reaction on a Clean Glass Surface.—When gas mixtures were heated in a clean bulb at pressures below the explosion limit, an induction period followed by a period of slow reaction was observed. This slow reaction is of considerable interest because, unlike the reaction in the presence of an oxide deposit, it was auto-accelerating and was also retarded by packing the reaction vessel with clean glass. The first of these points is illustrated by Fig. 2. The acceleration of the reaction may be attributed to catalysis by the oxide deposited on the initially clean glass surface. It is unnecessary to postulate degenerate branching. This view is supported by the fact that in comparable experiments in clean and in oxide-coated bulbs the induction period was almost eliminated in the latter case, while at the same time the ignition pressure was slightly lowered.

FIG. 2.

Oxidation of monogermane in clean glass vessel.



A. 322°, 20% *mixture at* 33 *mm. initial pressure.*
B. 322°, 14% *mixture at* 42 *mm. initial pressure.*

Packing of the reaction vessel with clean glass retarded the reaction. For instance, in an unpacked bulb (20% monogermane, temp. 346°, initial pressure 30 mm.) the pressure de-

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crease in 14 mins. was 5 mm., but with the same conditions in a bulb packed to give a 3·6-fold increase in the surface, the pressure decrease in the same time was 2 mm. In a second experiment in an unpacked bulb (20% monogermane, temp. 322°, initial pressure 33 mm.) the pressure decrease in 19 mins. was 7·5 mm.; in the packed bulb under similar conditions it was 2·5 mm. The retarding effect caused by increasing the surface must be interpreted as evidence of a homogeneous chain reaction, the active centres of which are deactivated at the glass walls. As the oxide deposit is built up by deposition of the products of the slow reaction the catalytic activity of the walls increases, and in the case of a bulb coated with oxide from a previous reaction, this catalytic effect is the controlling factor in the oxidation.

Effect of the Oxide Deposit on the Induction Period.

		Pressure (mm.).		
Bulb.	Temp.	Ignition.	No ignition.	Induction period before ignition.
Clean glass	322°	35·3	32·7	2·5 mins.
Oxide deposit	322	29·5	22·9	1 sec.
Clean glass	293·5	41·0	39·3	5 mins.
Oxide deposit	293·5	36·7	33·1	5 secs.
Clean glass	265	54·0	51·4	23 mins.
Oxide deposit	265	51·5	46·0	8 secs.

Effect of Irradiation on the Explosion Limit.—The ignition of monosilane–oxygen mixtures has been shown to be facilitated by irradiation with light from a quartz mercury arc (Emeléus and Stewart, *Trans. Faraday Soc.*, 1936, **32**, 1577), and a number of experiments were carried out to determine if a similar effect is to be observed with monogermane. This compound exhibits no banded absorption at wave-lengths greater than 1550 A., and continuous absorption extends from about 1700 A. to shorter wave-lengths (Mahncke and Noyes, *J. Amer. Chem Soc.*, 1935, **57**, 456). If, therefore, ignition is influenced by ultra-violet light from the mercury arc, the spectrum of which after passage through quartz extends to about 1850 A., the effect must be due to absorption of energy by oxygen.

The apparatus employed in these experiments was similar to that used in studying the slow and the explosive oxidation, except that a transparent silica reaction vessel was substituted for the glass bulb. The silica vessel was 12 cm. long and had a diameter of 2·8 cm. A hot mercury arc, which had been allowed to run for at least 15 minutes before use, served as the source of illumination. The reaction vessel was heated by means of a transparent silica jacket wound with nichrome wire. The experimental procedure was to determine the explosion limit with the arc at a measured distance from the bulb. A mixture containing 20% of monogermane was employed. The results obtained are given below, the values of the ordinary thermal ignition limit given being taken from the curve based on the data in Table VIII.

Effect of Irradiation on the Explosion Limit.

			Pressure, mm.		
Temp.	Thermal ignition limit, mm.	Distance of arc from bulb, cm.	Ignition.	No ignition.	Induction period, secs.
244°	67	12	58·8	56·5	40
244	67	5	55·5	55·2	16
230	80	5	69·0	67·5	12

As in the explosion experiments in the presence of the oxide deposit, the observed effect is two-fold. The critical explosion pressure is lowered by irradiation, and at the same time the induction period in the reaction is considerably reduced. The latter, for example, would have been of the order of 100 mins. in the experiment at 230°, but under the influence of the light it was reduced to 12 secs. This effect was increased by increasing the intensity of irradiation of the gas mixture by decreasing its distance from the arc.

A further series of experiments was carried out to determine the nature of the slow reaction which takes place on irradiating a monogermane–oxygen mixture with ultra-violet light. Experiments were performed with a mixture containing 25% of monogermane. The hot mercury arc was placed 2 cm. from the reaction vessel, which was not otherwise heated, and irradiation was continued for 4—5 hours, after which the reaction products were analysed in the manner already described. The temperature of the reaction bulb during irradiation was estimated as 50—70°. During the course of the reaction a white solid accumulated on the walls

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and gradually rendered the vessel opaque to the light. The results of the analysis are given below.

Initial press., mm.	191	181	141	115·5	90
GeH_4 used, mm.	20·5	17·5	16	15·5	12
O_2 used, mm.	29·5	25·5	24	25·5	20
Pressure decrease, mm.	19·5	18	15·5	17	11
H_2 formed, mm.	10	9	8·5	7·5	6

Mixed with the excess oxygen there was a gas which was not absorbed by sodium hyposulphite, and it was proved by sparking with oxygen to consist of pure hydrogen. The pressures of monogermane and oxygen reacting in the photo-oxidation, the hydrogen formed, and the pressure decrease in the reaction are in the ratio 1 : 1·4—1·7 : 0·5 : 0·9—1·1, and the reaction may be represented by the equation $2GeH_4 + 3O_2 = H_2 + 2H_2O + Ge_2O_4H_2$. The experimental evidence is too slight for a discussion of the mechanism of the reaction. The solid product, if indeed it is homogeneous, would have a formula analogous to that of oxalic acid, but when dissolved in dilute sulphuric acid it did not reduce potassium permanganate. Hydrogen is found in the photo-oxidation, but is definitely absent from the products of the thermal oxidation. The action of ultra-violet light in facilitating the explosion of monogermane–oxygen mixtures is believed to be primarily the acceleration of the homogeneous reaction by increasing the supply of active centres in the gas phase. The products of the homogeneous reaction appear to render the walls of the reaction vessel catalytically active and so initiate the explosion.

Some Observations with Digermane.

Preliminary observations on the ignition of digermane–oxygen mixtures were made with the small quantity of pure hydride isolated in the course of the preparation of monogermane. Two experiments were carried out in which a mixture containing 20% of digermane was ignited by admitting it to a bulb heated at 116°. The excess of the reactants was then determined, the excess oxygen being determined in the usual manner, and the excess digermane being distilled back into the reaction vessel and measured under the conditions of the reaction. The results were as follows :

	Expt. 1.	Expt. 2.
Pressure of gas mixture, mm.	90	99
Pressure of Ge_2H_6 used, mm.	15	17
Pressure of O_2 used, mm.	53	57

The ratio of oxygen to digermane is 3·5 in the first experiment and 3·4 in the second, and these figures are consistent with the equation $2Ge_2H_6 + 7O_2 = 4GeO_2 + 6H_2O$. The solid deposit formed in these explosions was brown, owing probably to thermal decomposition of a small proportion of the digermane during the explosion. The amount of material available was insufficient for a detailed study of the ignition phenomena of this hydride, but it was found that the ignition temperature is about 150° lower than that for monogermane. This is parallel to the behaviour of the homologous series of silicon hydrides, in which the inflammability of a given mixture increases with the molecular weight of the hydride. A similar effect is observed with the paraffins, although the ignition temperatures of methane and ethane are very much higher.

DISCUSSION.

The nature of the reaction taking place in the oxidation of monogermane has been definitely established, apart from the question of whether the solid oxidation product is a hydroxylated intermediate or merely germanium dioxide which has adsorbed water vapour. The first of these alternatives is the more probable because of the comparatively high temperature at which the water is held. By analogy with the oxidation of methane and monosilane, it is reasonable to postulate intermediates such as GeH_2O and $GeO(OH)_2$ in this reaction, and if the dehydration of the second of these compounds were incomplete and approximately constant in amount over the limited temperature range employed in studying the slow oxidation (160—183°), the experimental results could be explained satisfactorily. If this were the case, the main reaction taking place in the oxidation would be $GeH_4 + 2O_2 = GeO(OH)_2 + H_2O$.

The mechanism of the slow oxidation in the presence of the oxide deposit is complex. That the reaction is not purely heterogeneous is shown by the fact that the rate is not in-

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creased by an increase in the oxide-coated surface. Von Elbe and Lewis have shown recently (*J. Amer. Chem. Soc.*, 1937, **59**, 970) that the rate of a reaction which is partly heterogeneous may be independent of the diameter of the reaction vessel in the case of a chain reaction in which the chains are both initiated and broken mainly on the walls, and in which branching occurs only to a small extent. The evidence bearing on this point in the case of the oxidation of monogermane is fairly complete, for the reaction is catalysed by the oxide deposit. The latter also has the effect of eliminating the induction period which is observed when the reaction is carried out in a clean reaction vessel. It is reasonable to suppose that a heterogeneous reaction on the oxide surface will provide active centres for a chain reaction in the gas phase. A reaction such as $GeH_2O + O_2 = GeH_2O_2 + O$ would, for example, serve this purpose. To initiate the reaction in a clean glass vessel requires a considerably higher temperature, and this may represent a homogeneous production of active centres. The effect of packing a clean glass vessel is to retard the reaction, and under such conditions (*i.e.*, in the absence of the oxide deposit) the behaviour of monogermane is analogous to that observed in the oxidation of methane and other hydrocarbons. In further support of the applicability of von Elbe and Lewis's treatment to the oxidation of monogermane in an oxide-coated bulb, the reaction rate shows no auto-acceleration (Fig. 1), indicating that there is no appreciable branching.

The observations on the kinetics of the slow oxidation cannot be interpreted unambiguously. The non-dependence of the reaction rate on the oxygen concentration finds a parallel in Thompson and Hinshelwood's experiments on the oxidation of ethylene (*Proc. Roy. Soc.*, 1929, *A*, **125**, 277). These authors found that under certain conditions the rate was of zero order with respect to oxygen, and suggested that the function of the oxygen was to break chains. The same might be true in the oxidation of monogermane. Alternatively, if the oxygen were taking part in a heterogeneous reaction, it would again be possible for the rate to be of zero order if oxygen were strongly adsorbed on the catalytic surface. A parallel is furnished by the combination of hydrogen and oxygen in contact with silver (Benton and Elgin, *J. Amer. Chem. Soc.*, 1926, **48**, 3027), in which the rate is independent of the oxygen pressure but proportional to that of hydrogen.

The autocatalytic effect observed in reactions in a clean glass vessel is explained by the catalytic activity of the oxide product. The latter is formed from the homogeneous reaction of monogermane and oxygen, and its presence causes the reaction rate to accelerate gradually until much of the material is used up, and then to fall gradually to zero rate. The result is an **S**-shaped pressure decrease–time curve. In interpreting reactions which show such an autocatalytic effect, resort is usually made to the theory of degenerate branching chains, but it seems possible that some of the reactions which have been interpreted in this way may be more simply explained in a manner similar to the above, *i.e.*, by consideration of the catalytic effect of the products.

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