502. *Gas-phase Reactions of Halogenoalkylsilanes. Part I. 2-Chloroethyltrichlorosilane.*

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The kinetics of the gas-phase thermal decomposition of 2-chloroethyltrichlorosilane have been studied in a static system between 356 and 417°. The products are mainly ethylene and silicon tetrachloride, with some hydrogen chloride, vinyltrichlorosilane, vinyl chloride, trichlorosilane, and ethyltrichlorosilane. A reaction scheme involving three concurrent unimolecular β-eliminations is proposed.

THE unusual reactivity of 2-chloroethylsilanes has been extensively studied in solution,[1-3] but little work has been done on the gas-phase reactions of these interesting compounds. It is known that 2-chloroethylsilanes with three alkyl groups attached to silicon decompose readily when heated, to give ethylene and a chlorosilane, and that replacement of the alkyl groups by halogen increases the thermal stability.[1,4] 2-Chloroethyltrichlorosilane has been pyrolysed in a flow tube at 610°, to give ethylene, silicon tetrachloride, and vinyltrichlorosilane;[5] ethylene and silicon tetrachloride were the main products, except in the presence of quinoline, in which case vinyltrichlorosilane predominated. A preliminary kinetic study of the thermal decomposition of 2-chloroethyltrichlorosilane in a static system at 394° indicated that the elimination to form ethylene predominated, and that the overall decomposition was first-order and apparently unimolecular.[6] We have since confirmed that the formation of ethylene and a chlorosilane is a characteristic reaction of

[1] Sommer and Whitmore, *J. Amer. Chem. Soc.*, 1946, **68**, 485.
[2] Sommer and Baughman, *J. Amer. Chem. Soc.*, 1961, **83**, 3346.
[3] Sommer, Dorfman, Goldberg, and Whitmore, *J. Amer. Chem. Soc.*, 1946, **68**, 488; Sommer, Goldberg, Dorfman, and Whitmore, *ibid.*, p. 1083; Sommer, Bailey, and Whitmore, *ibid.*, 1948, **70**, 2869; Sommer, Bailey, Goldberg, Buck, Bye, Evans, and Whitmore, *ibid.*, 1954, **76**, 1613.
[4] Batuev, Petrov, Ponomarenko, and Matveeva, *J. Gen. Chem. (U.S.S.R.)*, 1956, **26**, 2613.
[5] Agre and Hilling, *J. Amer. Chem. Soc.*, 1952, **74**, 3895.
[6] Davidson, *Chem. and Ind.*, 1960, 1107.

2-chloroethylsilanes, accounting for 90% of the pyrolysis products of 2-chloroethylethyldi-chlorosilane,[7] and for virtually all the pyrolysis products of 2-chloroethyltrimethylsilane [8] and 2-chloroethylphenyldimethylsilane.[9] Transition states with appreciable charge separation may be involved, as they are in many dehydrohalogenations of alkyl halides,[10] and we now report detailed results of the decomposition of 2-chloroethyltrichlorosilane as the first part of an investigation of this possibility.

EXPERIMENTAL AND RESULTS

2-Chloroethyltrichlorosilane was prepared by the free-radical chlorination of ethyltrichloro-silane,[1] vinyl chloride by the action of methanolic potassium hydroxide on 1,2-dichloroethane, and nitric oxide by the reaction between sodium nitrite and ferrous sulphate solutions.[11]

Silicon tetrachloride, trichlorosilane, ethyltrichlorosilane, vinyltrichlorosilane, hydrogen chloride, ethylene, and cyclohexene were obtained commercially and fractionated where necessary.

All compounds were finally purified by trap-to-trap distillation in a high-vacuum system, and their purity checked by gas chromatography. The chlorosilanes were stored under a vacuum in break-seal containers, to avoid hydrolysis.

The kinetic experiments were done in a static system; the reaction vessel was usually a 1·5-l. Pyrex bulb housed in an electric furnace, but reaction vessels of different size were used for some experiments. The furnace temperature was controlled by a Sunvic RT 2 proportional controller and measured by a chromel–alumel thermocouple in a glass pocket reaching to the centre of the vessel; the thermocouple was checked periodically against an N.P.L. standard platinum/platinum–rhodium thermocouple. The pressure in the reaction vessel was measured by a glass spiral manometer (G. Springham Ltd.) which reflected a light spot on to a calibrated curved scale. All parts of the apparatus connected to the reaction vessel were heated electrically to prevent condensation, and stopcocks in these parts were lubricated with silicone high-vacuum grease. The apparatus was arranged so that the dead-space was small, and only a small part of one greased stopcock was in contact with the reaction mixture during a run.

The reaction products were analysed by gas chromatography on a vapour-jacketed glass column approximately 6·5 m. × 3 mm., packed with 10% silicone oil on 60 mesh Embacell kieselguhr. The products were ethylene, silicon tetrachloride, vinyltrichlorosilane, hydrogen chloride, vinyl chloride, trichlorosilane, and ethyltrichlorosilane. No other products were detected at any stage in a run (our limit of detection was about 0·05 mm. Hg). Samples were transferred directly from reaction vessel to column through a sampling valve.[12] The sample volume was small (to minimise pressure drop in the reaction vessel), and in order to detect the organic products satisfactorily a flame ionisation detector was used. This was insensitive to the inorganic products, so a simple thermistor (thermal conductivity) detector [13] was included, which gave adequate analyses for silicon tetrachloride but not for hydrogen chloride or trichloro-silane, both of which gave a small and irreproducible response. A mass spectrometer suitable for compounds with molecular weights up to 100 (MS 10, A.E.I. Ltd.) was used to determine hydrogen chloride at the end of a run, but we were unable to improve on the approximate gas chromatographic analysis for trichlorosilane. The gas chromatography sampling system fractionated a sample, giving high results for the volatile products and low results for the less volatile; from analyses of known mixtures a correction was applied which gave an uncertainty of about 5% for analyses at the end of a run and slightly more for analyses during a run.

Manometric Results.—2-Chloroethyltrichlorosilane was pyrolysed between 356 and 417° at initial pressures from 12·15 to 138·4 mm. Hg. Plots of log $(2P_0 - P)$ against time were linear up to about 70% decomposition; the rate then decreased. No induction period was observed. Typical plots are given in Fig. 1. The ratio of final to initial pressure was $1·93 \pm 0·02$. The overall rate was insensitive to condition and age of surface, and to variations

[7] Part II, Davidson and Metcalfe, following Paper.
[8] Davidson and Pett, unpublished results.
[9] Lilly, unpublished results.
[10] Maccoll, in " Theoretical Organic Chemistry," Butterworths, London, 1959, p. 230.
[11] Blanchard, *Inorg. Synth.*, 1946, **2**, 126.
[12] Pratt and Purnell, *Analyt. Chem.*, 1960, **32**, 1213.
[13] Davis and Howard, *J. Appl. Chem.*, 1958, **8**, 183.

in surface-to-volume ratio from 0·28 to 2·39 cm.$^{-1}$. Neither nitric oxide nor cyclohexene inhibited the reaction, but each increased the overall rate slightly. First-order rate constants,

TABLE 1.

Manometric results.

Temp.	P_0 (mm.)	P_∞ (mm.)	10^4k (sec.$^{-1}$)	Surface/Vol. (cm.$^{-1}$)	Temp.	P_0 (mm.)	P_∞ (mm.)	10^4k (sec.$^{-1}$)	Surface/Vol. (cm.$^{-1}$)
379·7°	32·25	61·10	1·38	0·41	385°	39·80	81·65	1·875	0·28
380·6	38·60	75·00	1·42	,,	,,	31·30	62·40	1·79	,,
,,	40·10	78·90	1·43	,,	,,	27·40	52·60	1·77	0·41
,,	22·50	43·50	1·45	2·39	398	30·20	60·00	3·56	,,
,,	39·60	76·30	1·49	,,	,,	43·00	89·15	3·65	,,
385	12·15	24·50	1·79	0·38	,,	31·25	63·40	3·71	,,
,,	138·4	279·4	1·84	0·28	407·3	28·85	—	5·75	0·38
,,	29·85	58·70	1·86	,,					

k, calculated from the pressure increase, are given in Table 1, which contains manometric results only, and in Tables 2—5, which have gas-chromatographic results as well. The Arrhenius equation, k (sec.$^{-1}$) $= 10^{11\cdot40\pm0\cdot16}$ exp $- (45{,}500 \pm 500)/\boldsymbol{R}T$, was calculated from all values of k in Tables 1—5.

Gas-chromatographic Results.—Pressures of ethylene, vinyltrichlorosilane, and vinyl chloride were measured by the flame-ionisation detector during runs, and plotted against $(1 - e^{-kt})$.
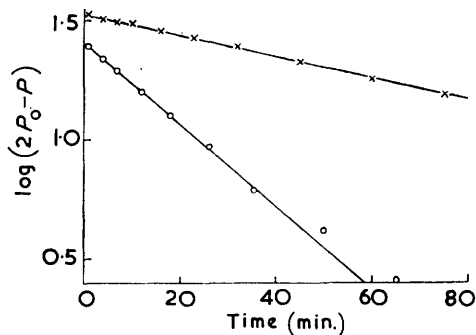

FIG. 1. Typical plots of log $(2P_0 - P)$ against time.

These measurements were made during the first 40 min. of reaction, and within this period the plots for ethylene and vinyltrichlorosilane were linear; the plot for vinyl chloride was linear initially, but the pressure of vinyl chloride then declined to a low final value. The pressure of trichlorosilane followed a similar pattern, but fell to zero; the pressure of ethyltrichlorosilane was too small for kinetic measurements to be made.

Fig. 2. Plot of ethylene peak height against silicon tetrachloride peak height during a run. The numbers on the axes represent arbitrary units.
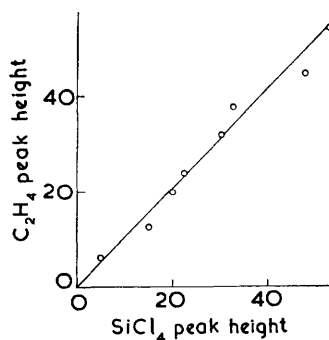
Ratios of rate constants, calculated from the linear plots, are given in Tables 2—4. The rate of formation of silicon tetrachloride was measured by the thermistor detector, and equalled the rate of formation of ethylene (Fig. 2). Equal pressures of vinyltrichlorosilane and hydrogen chloride were found at the end of a run.

We also analysed some runs when reaction was complete, and these results are in Table 5.

TABLE 2.

Initial rate of formation of ethylene (E) at 408·5°.

Time	P_E	Time	P_E	Time	P_E	Time	P_E	Time	P_E
6	1·8	2	0·5	6	5·8	3	0·4	3	0·5
17	4·9	14	9·0	17	16·9	16	5·6	16	6·3
29	7·2	26	16·0	29	22·0	32	10·8	29	11·4
40	8·2	36	19·5	40	26·4	44	13·6	42	15·0
P_0	13·5		37·5		53·7		21·5		23·4
$P_{cyclohexene}$	0		0		0		9·7		21·2
$10^4 k$	5·75		6·03		5·64		6·00		6·30
k_E/k	0·73		0·69		0·70		0·70		0·71

Pressures are in mm. Hg, rate constants in sec.$^{-1}$, and time in minutes.

TABLE 3.

Initial rate of formation of vinyltrichlorosilane (S) at 408·5°.

Time	P_S	Time	P_S	Time	P_S	Time	P_S	Time	P_S
6	0·3	6	—	6	0·2	2	—	6	—
17	0·8	17	1·0	17	1·3	14	1·0	17	2·0
29	1·2	29	1·7	29	1·8	26	1·7	29	2·6
40	1·4	40	2·1	40	2·3	36	2·5	40	3·2
P_0	13·5		21·5		28·9		37·5		53·7
$10^4 k$	5·75		5·65		5·75		6·03		5·64
k_S/k	0·12		0·13		0·12		0·11		0·10

Pressures are in mm. Hg, rate constants in sec.$^{-1}$, and time in minutes.

TABLE 4.

Initial rate of formation of vinyl chloride (V).

Time	P_V	Time	P_V	Time	P_V	Time	P_V
5	0·25	5	0·20	6	0·21	5	0·35
10	0·74	10	0·62	10	0·47	10	0·66
16	0·85	16	0·77	16	0·57	16	1·20
Temp.	383°		383°		383°		383°
P_0	26·0		27·0		28·6		33·4
$P_{cyclohexene}$	0		0		0		0
$10^4 k$	1·55		1·60		1·49		1·60
k_V/k	0·11		0·19		0·15		0·13

Time	P_V	Time	P_V	Time	P_V	Time	P_V
5	0·75	5	0·24	5	0·20	12	2·0
10	1·20	10	0·66	10	0·71	20	2·5
16	1·21	16	0·92	17	1·02	35	3·5
Temp.	383°		383°		383°		378°
P_0	38·7		42·2		42·3		45·2
$P_{cyclohexene}$	0		0		0		31·2
$10^4 k$	1·49		1·58		1·56		1·46
k_V/k	0·14		0·15		0·16		0·18

Pressures are in mm. Hg, rate constants in sec.$^{-1}$, and time in minutes.

TABLE 5.

Final product composition.

Temp.	356°	385°	417°	356°	356°	356°
P_0	37·5	46·6	49·4	36·2	39·2	43·0
P_{NO}	0	0	0	4·4	18·8	20·4
$10^4 k$	0·371	1·69	9·22	0·371	0·397	0·416
P_E	26·7	33·2	34·0	25·9	27·6	30·9
P_S	9·7	11·5	13·0	7·2	6·4	6·0
P_V	1·2	2·0	1·5	4·0	6·0	5·0
P_T	0·7	0·5	0·5	0	0	0
% C$_2$ balance	102	101	99	103	102	98
P_E/P_0	0·71	0·71	0·69	0·72	0·71	0·72
P_S/P_0	0·26	0·25	0·26	0·20	0·16	0·14
P_V/P_0	0·03	0·04	0·03	0·11	0·15	0·12
P_T/P_0	0·02	0·01	0·01	0	0	0

E, S, V, and T denote ethylene, vinyltrichlorosilane, vinyl chloride, and ethyltrichlorosilane, respectively. A flame-ionisation detector was used in these analyses.
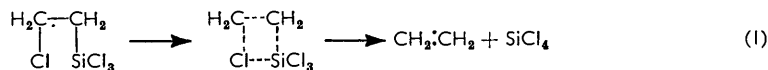
The pressures of silicon tetrachloride equalled the pressures of ethylene, and in runs without added nitric oxide the pressures of hydrogen chloride and vinyltrichlorosilane were equal.

Reactions Between Products.—All products were stable individually, but we found that vinyl chloride and trichlorosilane reacted together to give vinyltrichlorosilane and hydrogen chloride, but no ethylene. The reaction was first-order in each reactant, had a rate constant of about 10^{-5} mm.$^{-1}$ sec.$^{-1}$ at $405°$, and was completely inhibited by nitric oxide. Trichloro-silane also reacted with ethylene to give ethyltrichlorosilane about 10 times more slowly than it reacted with vinyl chloride. This reaction was also inhibited by nitric oxide.

No other reaction between products occurred, but trichlorosilane reacted with nitric oxide. This reaction was studied by Mr. C. J. Wood, using the MS 10 mass spectrometer; hydrogen chloride was formed, and the rate constant was about 10^{-3} mm.$^{-1}$ sec.$^{-1}$ at $420°$. Trichloro-silane also reacted with cyclohexene at about one third of the rate of the reaction with nitric oxide; hydrogen chloride was again formed. Because of the formation of hydrogen chloride in these reactions we did not analyse for it in runs with added nitric oxide or cyclohexene.

DISCUSSION

Formation of Ethylene and Silicon Tetrachloride.—These products are formed at equal rates (Fig. 2) by a first-order reaction which is neither inhibited nor accelerated by cyclo-hexene (Table 2). The ratio k_E/k agrees with the final analysis ratio P_E/P of Table 5, whether or not nitric oxide is present. The reaction is therefore kinetically simple, and insensitive to both cyclohexene and nitric oxide. Although Wojciechowski and Laidler [14] have shown that in some special cases " inhibitors " need not reduce the rate of a chain reaction, large " inhibitor " pressures should increase the rate. The reaction is also insensitive to surface effects and has no induction period (the initiation step of a chain reaction would have a rate constant of about 10^{-12} sec.$^{-1}$ at $417°$, since the weakest bond in 2-chloroethyltrichlorosilane is carbon–chlorine, with a dissociation energy of about 80 kcal./mole [15]). The simplest mechanism consistent with the results is the unimolecular β-elimination (1). (We make no assumptions at this stage about the electron distribution

$$\begin{array}{ccc} H_2C\text{---}CH_2 & H_2C\text{---}CH_2 & \\ | \quad\; | & \vdots \quad\; \vdots & \longrightarrow CH_2{:}CH_2 + SiCl_4 \qquad (1)\\ Cl \quad SiCl_3 & Cl\text{---}SiCl_3 & \end{array}$$

or bond-breaking sequence in the transition state.) We detected no variation in P_E/P with temperature (Table 5), and so we put E_1 equal to the overall activation energy. Since the reaction between ethylene and trichlorosilane is suppressed by nitric oxide, we use the value of P_E/P with nitric oxide present, *i.e.*, 0.72; this gives

$$k_1 \text{ (sec.}^{-1}) = 10^{11.26 \pm 0.16} \exp - (45{,}500 \pm 500)/RT.$$

The low pre-exponential term corresponds to $\Delta S_1 = -8.0 \pm 0.7$ e.u., which is reasonable for a unimolecular reaction involving a cyclic transition state.[16]

Formation of Other Products.—Tables 3 and 4 show that vinyltrichlorosilane and vinyl chloride are initially formed by first-order reactions, with rates unaffected by cyclohexene. The ratios k_S/k and k_V/k agree reasonably well with the corresponding product ratios P_S/P and P_V/P when large pressures of nitric oxide are present (Table 5). This indicates that there are primary reactions, one forming vinyltrichlorosilane and hydrogen chloride, and one forming vinyl chloride and trichlorosilane, which are, like (1), simple first-order reactions unaffected by surface and " inhibitors." We therefore suggest that they are also unimolecular β-eliminations, (2) and (3). Our results are not accurate enough for an evaluation of E_2 and E_3, but they will be 40—50 kcal./mole. Unimolecular dehydrochlorin-ations are well known,[17] but reaction (3) may be the first reported example of a gas-phase dehydrosilylation.

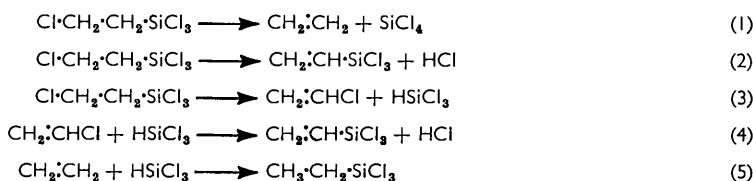[14] Wojciechowski and Laidler, *Trans. Faraday Soc.*, 1963, **59**, 369.
[15] Steele, Nichols, and Stone, *J. Amer. Chem. Soc.*, 1962, **84**, 4441.
[16] Benson, " Foundations of Chemical Kinetics," McGraw-Hill, New York, 1960, p. 254.
[17] Barton and Howlett, *J.*, 1949, 165; Barton and Onyon, *Trans. Faraday Soc.*, 1949, **45**, 725.

$$\xrightarrow{\quad} CH_2\text{:}CH\cdot SiCl_3 + HCl \qquad (2)$$

$$\xrightarrow{\quad} CH_2\text{:}CHCl + HSiCl_3 \qquad (3)$$
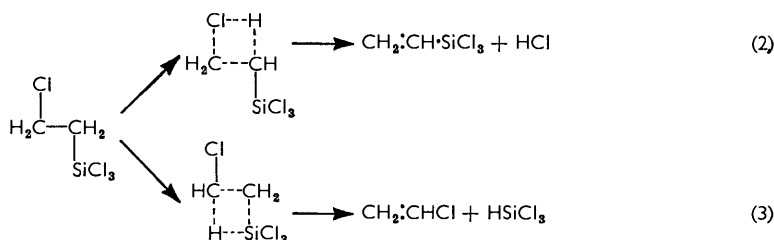
When nitric oxide is not present, other reactions occur (Table 5), forming more vinyl-trichlorosilane and hydrogen chloride (still in equivalent amounts) and some ethyltri-chlorosilane, while using up most of the vinyl chloride and all the trichlorosilane. The reactions which we found to occur between trichlorosilane and vinyl chloride and ethylene account for these observations, and we may represent the overall decomposition by the reactions (1)—(5).

$$Cl\cdot CH_2\cdot CH_2\cdot SiCl_3 \xrightarrow{\quad} CH_2\text{:}CH_2 + SiCl_4 \qquad (1)$$

$$Cl\cdot CH_2\cdot CH_2\cdot SiCl_3 \xrightarrow{\quad} CH_2\text{:}CH\cdot SiCl_3 + HCl \qquad (2)$$

$$Cl\cdot CH_2\cdot CH_2\cdot SiCl_3 \xrightarrow{\quad} CH_2\text{:}CHCl + HSiCl_3 \qquad (3)$$

$$CH_2\text{:}CHCl + HSiCl_3 \xrightarrow{\quad} CH_2\text{:}CH\cdot SiCl_3 + HCl \qquad (4)$$

$$CH_2\text{:}CH_2 + HSiCl_3 \xrightarrow{\quad} CH_3\cdot CH_2\cdot SiCl_3 \qquad (5)$$

Reactions (1)—(3) are the unimolecular β-eliminations, unaffected by nitric oxide and cyclohexene, while (4) and (5) are the secondary reactions, suppressed by nitric oxide; the occurrence of reactions (4) and (5) accounts for the fact that the pressures of vinyl chloride and trichlorosilane pass through a maximum, and that some vinyl chloride is present at the end. Reaction (5) also accounts for the decrease in the manometrically measured rate and for the fact that the ratio of final to initial pressure is less than 2; this ratio can be calculated, from the results in Table 5, to be 1·93, in agreement with experiment. The discrepancy between the final pressures of vinyl chloride and ethyltrichlorosilane in " uninhibited " runs (Table 5) is less than experimental error, and the ratio of extra vinyl-trichlorosilane [formed by reaction (4)] to ethyltrichlorosilane [formed by reaction (5)] is 10 : 1, in agreement with the rate ratio found for these reactions. The small accelerating effect of nitric oxide and cyclohexene on the overall manometrically measured rate is readily explained by the suppression of reactions (4) and (5) and the formation of hydrogen chloride from trichlorosilane.

Reactions (4) and (5) are known to occur at high temperature and pressure,[18] and (5) also occurs in the presence of free-radical initiators.[19] Free-radical mechanisms have been suggested, and the inhibition by nitric oxide, which we have observed, might be taken to confirm these, but it is noteworthy that large pressures of nitric oxide are necessary (Table 5 shows that 4·4 mm. of nitric oxide caused only partial inhibition), and it may be that the action of nitric oxide is simply to remove the trichlorosilane. Consequently, our work does not throw any light on the mechanisms of the minor reactions (4) and (5), except that if (4) proceeds by addition followed by elimination it cannot be through 2-chloroethyltrichlorosilane, since no ethylene is formed in this reaction.

We have noted that the reaction of type (1) is characteristic of 2-chloroethylsilanes in the gas phase, and elimination of ethylene can also be brought about in solution by nucleo-philic and electrophilic reagents.[1-3] 2-Chloroethyltrimethylsilane gives ethylene when dissolved in polar solvents at 30°, and the rate of this reaction in solution increases with the polarity of the medium in much the same way as does solvolysis of t-butyl chloride;[2]

[18] Mackenzie, Spialter, and Schoffman, U.S.P. 2,721,873/1955 (*Chem. Abs.*, 1956, **50**, 7844); B.P. 782,700/1956 (*Chem. Abs.*, 1957, **51**, 7402); Nesmeyanov, Friedlina, and Chukovskaya, *Doklady Akad. Nauk S.S.S.R.*, 1957, **113**, 120.
[19] Pietrusza, Sommer, and Whitmore, *J. Amer. Chem. Soc.*, 1948, **70**, 484.

in 50% ethanol it is not increased by the presence of potassium hydroxide. Furthermore, 2-chloroethylphenyldimethylsilane reacts more rapidly than its *m*-trifluoromethyl derivative. These facts have been reasonably interpreted by Sommer and Baughman [2] as implying a rate-determining heterolysis of the 2-chloroethyl–silicon bond, but they are also consistent with a cyclic transition state, such as we propose for the gas-phase eliminations, if this involves substantial separation of charge. Even if the process were fully concerted, the change from a silicon–carbon to a silicon–chlorine bond would involve a significant increase in the fractional positive charge on the silicon atom.