**503.** *Gas-phase Reactions of Halogenoalkylsilanes. Part II.*[1]
2-Chloroethylethyldichlorosilane.

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The kinetics of the gas-phase thermal decomposition of 2-chloroethyl-ethyldichlorosilane have been studied in a static system between 356 and 397°. The products were mainly ethylene and ethyltrichlorosilane, with some hydrogen chloride and ethylvinyldichlorosilane. A reaction scheme involving two unimolecular β-eliminations is suggested, and the factors influencing the rate are discussed briefly.

IN Part I[1] we described the gas-phase thermal decomposition of 2-chloroethyltrichloro-silane. We found that the main reaction was elimination of ethylene

$$\text{ClCH}_2\cdot\text{CH}_2\cdot\text{SiCl}_3 \longrightarrow \text{C}_2\text{H}_4 + \text{SiCl}_4$$
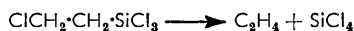
but that dehydrochlorination and dehydrosilylation also occurred, together with two secondary reactions. We are investigating the thermal decomposition of other 2-chloro-ethylsilanes, with particular reference to the kinetics of ethylene elimination, and now report the results of a study of 2-chloroethylethyldichlorosilane. No previous pyrolyses of this compound have been reported.

EXPERIMENTAL

2-Chloroethylethyldichlorosilane was prepared by the free-radical chlorination of diethyl-dichlorosilane.[2] Ethylvinyldichlorosilane was prepared by the addition of ethylmagnesium bromide to vinyltrichlorosilane. Ethylene and ethyltrichlorosilane were obtained commercially.

All compounds, after fractionation where necessary, were purified by trap-to-trap distill-ation in a high-vacuum system, and their purity was checked by gas chromatography (g.l.c.).

The chlorosilanes were stored under vacuum in break-seal containers to avoid hydrolysis.

The static system used for the kinetic experiments, and the g.l.c. apparatus, resembled those previously described.[1] A run was started by distilling 2-chloroethylethyldichlorosilane into a 500-ml. bulb (about the same volume as the reaction vessel) which was connected to the reaction vessel by a stopcock. The bulb was then heated electrically to 120° and the stopcock opened briefly, so that the vapour expanded into the evacuated reaction vessel. The g.l.c.
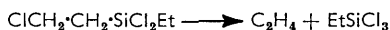
[1] Part I, Davidson, Eaborn, and Lilly, preceding Paper.
[2] Sommer and Whitmore, *J. Amer. Chem. Soc.*, 1946, **68**, 485.

sampling valve [3] was arranged so that samples could be taken either from the reaction vessel or from the bulb.

RESULTS

As before,[1] the main reaction was elimination of ethylene:

$$ClCH_2 \cdot CH_2 \cdot SiCl_2Et \longrightarrow C_2H_4 + EtSiCl_3$$

However, ethylene was also formed at the pre-injection stage in the bulb at 120°. G.l.c. analysis showed that no ethyltrichlorosilane was produced there, but there was an unidentified peak with retention time of 57 min. (ethyltrichlorosilane had a retention time of $15\frac{1}{2}$ min. and 2-chloroethylethyldichlorosilane of 92 min.). In the usual time taken to start a run, about 5% decomposed in this way. If the vapour was left in the bulb at 120°, decomposition continued; but this reaction did not occur in the reaction vessel at higher temperature, since ethylene and ethyltrichlorosilane were formed in equal amounts there. We found that the reaction in the bulb could be suppressed by propene, and since our objective was to study the homogeneous gas-phase reactions, we adopted the procedure of doing runs with added propene to inhibit this undesired reaction. Neither propene nor ethyltrichlorosilane decomposed appreciably at the temperatures used. Rate constants for the gas-phase reaction were then obtained by plotting log $(P_\infty - P)$ against time, where P is total pressure, so that the pressure of propene cancelled out. The pre-injection reaction in the bulb was completely suppressed by propene, while variation of the [propene] : [reactant] ratio from 0 to 4·5 caused no inhibition or acceleration of the gas-phase reaction which was also insensitive to surface condition and surface-to-volume ratio.

The ratio of final to initial pressure was 2·00 ± 0·02. First-order rate constants are given by $k(\text{sec.}^{-1}) = 10^{12\cdot26\pm0\cdot50} \exp(-46,500 \pm 1,500/\mathbf{R}T)$.

The products were ethylene, ethyltrichlorosilane, hydrogen chloride, and ethylvinyldichlorosilane. Analysis for the three organic products was by g.l.c., a flame ionisation detector being used; the product composition did not vary detectably between 359 and 411° for initial pressures from 6 to 25 mm. Hg. The pressures of ethylene (corrected for the amount present initially) equalled the pressure of ethyltrichlorosilane, and these two compounds accounted for 90% of the products; half of the remainder was ethylvinyldichlorosilane, and the rest was assumed to be hydrogen chloride (it had been detected qualitatively by a thermal conductivity detector in preliminary runs). Very small amounts of vinyl chloride were also observed. Analyses during runs confirmed that this simple situation prevailed throughout.

DISCUSSION

The reaction in the bulb at 120° was of secondary importance to us and was not investigated fully. We did not identify the other product formed with the ethylene, other than to establish that it was not one of the products of the homogeneous decomposition in the reaction vessel. The ethylene may have come from the ethyl group (*i.e.*, $ClC_2H_4 \cdot SiCl_2 \cdot C_2H_5 \longrightarrow C_2H_4 + ClC_2H_4 \cdot SiCl_2 \cdot H$) or it may have been formed heterogeneously from the chloroethyl group while the other fragments combined on the surface to form a new product, such as 1,2-diethyltetrachlorodisilane. In any case the reaction was heterogeneous, possibly liquid-surface rather than gas-surface.

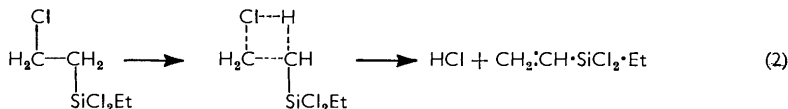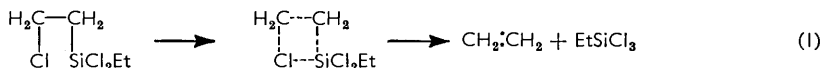The gas-phase decomposition can be represented by the reactions (1) and (2):

$$ClCH_2 \cdot CH_2 \cdot SiCl_2Et \longrightarrow C_2H_4 + EtSiCl_3 \qquad\qquad (1)$$

$$ClCH_2 \cdot CH_2 \cdot SiCl_2Et \longrightarrow HCl + CH_2 \colon CH \cdot SiCl_3 \qquad\qquad (2)$$

The mechanism which we suggested for 2-chloroethyltrichlorosilane [1] involves three unimolecular β-eliminations, two exactly analogous to reactions (1) and (2) and the third forming vinyl chloride and trichlorosilane; trichlorosilane then participates in secondary reactions with the ethylene and the vinyl chloride. The decomposition of 2-chloroethylethyldichlorosilane is therefore simpler because the third elimination does not occur to any extent and no reactive product like trichlorosilane is formed.

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[3] Pratt and Purnell, *Analyt. Chem.*, 1960, **32**, 1213.

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This strong similarity between reactions (1) and (2) and the corresponding unimolecular eliminations of 2-chloroethyltrichlorosilane, the lack of inhibition or acceleration by propene,[4] the insensitivity to surface conditions, and the ratio of final to initial pressure of 2·00, all support the conclusion that reactions (1) and (2) are homogeneous, unimolecular β-eliminations.

$$H_2C\text{—}CH_2 \quad\longrightarrow\quad H_2C\text{---}CH_2 \quad\longrightarrow\quad CH_2\text{:}CH_2 + EtSiCl_3 \qquad (1)$$
$$| \quad | \qquad\qquad\qquad | \quad\ \ |$$
$$Cl \ \ SiCl_2Et \qquad\qquad Cl\text{---}SiCl_2Et$$

$$Cl \qquad\qquad\qquad Cl\text{---}H$$
$$| \qquad\qquad\qquad\qquad | \quad\ |$$
$$H_2C\text{—}CH_2 \quad\longrightarrow\quad H_2C\text{----}CH \quad\longrightarrow\quad HCl + CH_2\text{:}CH\cdot SiCl_2\cdot Et \qquad (2)$$
$$| \qquad\qquad\qquad\qquad |$$
$$SiCl_2Et \qquad\qquad\quad SiCl_2Et$$

From the product composition, $k_1 = 9\,k_2$. Since we detected no variation of product composition with temperature,

$$k_1(\text{sec.}^{-1}) = 10^{12\cdot21\pm0\cdot50} \exp(-46{,}500 \pm 1{,}500/RT)$$

This gives $\Delta S_1^{\ddagger} = -3\cdot6 \pm 2\cdot0$ e.u. which is reasonable for a four-centre transition state.[5]

The amount of ethylvinyldichlorosilane formed was too small to permit satisfactory calculation of the Arrhenius parameters of reaction (2).

It is interesting to compare the results for 2-chloroethylethyldichlorosilane (*A*) with those for 2-chloroethyltrichlorosilane (*B*).

$$k_1(B) \ (\text{sec.}^{-1}) = 10^{11\cdot26\pm0\cdot16} \exp(-45{,}500 \pm 500/RT)$$

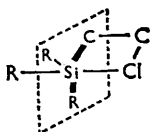$$\Delta S_1^{\ddagger}(B) = -8\cdot0 \pm 0\cdot7 \ \text{e.u.}$$

$$k_1(B) = 5k_2(B)$$

Hence
$$k_1(A) = 4\tfrac{1}{2}k_1(B) \quad\text{and}\quad k_2(A) = 2\tfrac{1}{2}k_2(B)$$

We cannot say whether the increase in the rate of dehydrochlorination is governed by the entropy or the energy of activation, but it is clear that the increase in the rate of elimination of ethylene is due to an increased entropy of activation.

If the elimination proceeds by a concerted, four-centre, homolytic process the replacement of a chlorine attached to silicon by an electron-supplying group would be expected to increase the rate; while if a quasiheterolytic process was involved, the rate would also be affected by such a replacement.[6] In either case, however, a decrease in activation energy would be expected. It follows that the rate increase caused by the replacement of one chlorine by ethyl is due mainly to a change in steric rather than electronic effects. The elimination may be likened to a flank substitution[7] with the configuration (*X*), and the ethyl group will have substantially free rotation in the transition state, whereas in the initial state there is some hindrance between the ethyl and chloroethyl groups. Hence the ethyl group would gain entropy in the transition state, thus counteracting the entropy decrease associated with cyclisation of the chloroethyl group sufficiently to give the observed difference between $\Delta S_1^{\ddagger}(A)$ and $\Delta S_1^{\ddagger}(B)$.

Although the in-plane R–Si–R angles are 120° in the transition state, the out-of-plane angles are only 90°. This would cause some compression of the ethyl group and hence a small increase in activation energy.

[4] Wojciechowski and Laidler, *Trans. Faraday Soc.*, 1963, **59**, 369.
[5] Benson, "Foundations of Chemical Kinetics," McGraw-Hill Book Co., New York, 1960, p. 254.
[6] Maccoll *J*, 1958, 3398.
[7] Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, pp. 103—109.