

1019. *Gas-phase Reactions of Halogenoalkylsilanes. Part III.*<sup>1</sup>  
*2-Chloroethyldiethylchlorosilane*

By I. M. T. DAVIDSON and M. R. JONES

The kinetics of the gas-phase thermal decomposition of 2-chloroethyldiethylchlorosilane have been studied in a static system between 298° and 352°. The only products were ethylene and diethyldichlorosilane, formed by a unimolecular mechanism. It is suggested that appreciable charge separation occurs in the transition state, forming an incipient siliconium ion.

In previous Papers<sup>1,2</sup> we have shown that the major gas-phase reaction in the pyrolysis of 2-chloroethylsilanes is elimination of ethylene by a homogeneous, unimolecular mechanism:  $R_3Si \cdot CH_2 \cdot CH_2Cl \longrightarrow C_2H_4 + R_3SiCl$ . The decomposition of 2,2-difluoroethyltrifluorosilane to silicon tetrafluoride and vinyl fluoride occurs by a similar mechanism,<sup>3</sup> which thus appears to be a general one for 2-halogenoalkylsilanes. Our previous studies were of 2-chloroethyltrichlorosilane<sup>2</sup> and 2-chloroethylethyldichlorosilane,<sup>1</sup> and we now report the results of a study of 2-chloroethyldiethylchlorosilane. This investigation casts some light on the possibility that appreciable charge separation may develop in the transition state of the elimination; this is believed to occur in several molecular decompositions of polar compounds,<sup>4-6</sup> and is of particular interest in our case because of the uncertainty about the role of the siliconium ion in the reactions of organosilicon compounds.<sup>7</sup>

<sup>1</sup> Part II, I. M. T. Davidson and C. J. L. Metcalfe, *J.*, 1964, 2630.

<sup>2</sup> I. M. T. Davidson, C. Eaborn, and M. N. Lilly, *J.*, 1964, 2624.

<sup>3</sup> R. N. Haszeldine, P. J. Robinson, and R. F. Simmons, *J.*, 1964, 1890.

<sup>4</sup> A. Maccoll in "Theoretical Organic Chemistry," Butterworths, London, 1959, p. 230.

<sup>5</sup> E. S. Lewis and W. C. Herndon, *J. Amer. Chem. Soc.*, 1961, **83**, 1955.

<sup>6</sup> G. G. Smith and B. L. Yates, *J. Org. Chem.*, 1965, **30**, 434.

<sup>7</sup> C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, pp. 114—116; L. H. Sommer and G. A. Baughman, *J. Amer. Chem. Soc.*, 1961, **83**, 3346.

## EXPERIMENTAL AND RESULTS

2-Chloroethyldiethylchlorosilane was prepared by the free-radical chlorination of triethylchlorosilane,<sup>8</sup> and fractionated under reduced pressure. It was characterised by n.m.r. and i.r. spectra, and by refractive index.

Diethylchlorosilane, ethylene, propene, and nitric oxide were obtained commercially. All compounds were purified by trap-to-trap high-vacuum distillation and their purity checked

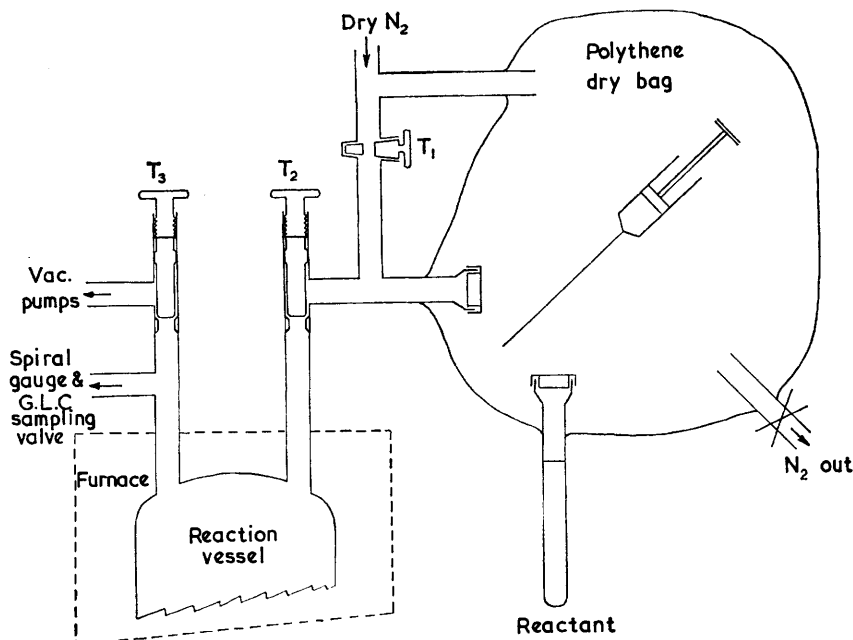


FIGURE 1. Reactant injection system

by gas chromatography (g.l.c.). 2-Chloroethyldiethylchlorosilane was stored under vacuum in a break-seal container to avoid hydrolysis and contamination by tap-grease.

The kinetic experiments were done in a static system fitted with a glass spiral manometer and with a sampling valve leading directly to the g.l.c. column; details have been given.<sup>2</sup>

The original method of starting a run,<sup>1</sup> by distilling reactant into a bulb, warming it, and expanding the vapour into the evacuated reaction vessel, could not be used because 2-chloroethyldiethylchlorosilane decomposed completely during this procedure. Instead, the arrangement shown in Figure 1 was devised. Taps 2 and 3 were "Lab-Crest" quick-opening valves, made of glass and polytetrafluoroethylene; the reaction vessel was made from new Pyrex tubing and was not cleaned or washed before use in case such treatment would make the surface active. When the reaction vessel had been evacuated and the dry bag and side-arm of tap 2 flushed with dry nitrogen, a run was started by closing tap 3, injecting the required amount of reactant round the base of the closed tap 2 by a Hamilton gas-tight syringe manipulated through the polythene dry bag, closing tap 1, and opening tap 2 briefly to allow the reactant and a small known volume of nitrogen to enter the reaction vessel. Tap 2 was mounted as close to the furnace as possible and heated electrically to about 120°.

*Manometric Results.*—At first the "Lab-Crest" valves were not available, and stopcocks lubricated with Kel-F grease were used for taps 2 and 3. The apparatus in this form gave results of poor reproducibility, and the integrated first-order plots from pressure measurement gave two lines, an initial steep line lasting for about 20 minutes and showing little temperature-dependence of slope, followed by a less steep line, rate constants from which gave an energy of

<sup>8</sup> L. H. Sommer, D. L. Bailey, W. A. Strong, and F. C. Whitmore, *J. Amer. Chem. Soc.*, 1946, **68**, 1881.

activation of about 20 kcal. mole<sup>-1</sup>. "Seasoning" by repeated runs and by pyrolysis of allyl bromide produced no improvement, nor did addition of propene. Clearly, the decomposition was mainly heterogeneous. When the greaseless system shown in Figure 1 was used, reproducible manometric results were obtained after one or two runs, and plots of  $\log(P_\infty - P)$  against time gave excellent straight lines. The ratio of final to initial pressure after allowance for the added nitrogen was 2, and runs between 298 and 352° with initial pressures of from 6 to 50 mm. Hg gave the Arrhenius equation:

$$k(\text{sec.}^{-1}) = 10^{11.88 \pm 0.26} \exp. (-41,100 \pm 1000/RT)$$

(95% confidence limits).

The rate was insensitive to surface : volume ratio (altered by adding Pyrex tubes with fire-polished ends to the reaction vessel) and to added nitric oxide or propene. These results are collected in Table 1.

TABLE 1  
Manometric results

Temp.	$P_0$ (mm.)	$10^4 k$ (sec. <sup>-1</sup> )	Surface : vol. (cm. <sup>-1</sup> )	Temp.	$P_0$ (mm.)	$10^4 k$ (sec. <sup>-1</sup> )	Surface : vol. (cm. <sup>-1</sup> )	Added gases
298°	20	1.23	0.5	320°	28	4.92	2.25	C <sub>3</sub> H <sub>8</sub> 10 mm.
298.5	15	1.56	2.25	324	17	7.50	0.5	NO 10 mm.
300	20	1.66	0.5	324	20	8.00	0.5	NO 4 mm.
308	10	2.50	0.5	333	25	11.5	2.25	C <sub>3</sub> H <sub>8</sub> 5 mm.
310.5	23	3.18	0.5	333.5	21	12.0	2.25	
312.5	25	3.43	2.25	342.5	38	20.0	0.5	
321	50	5.05	2.25	343	18	20.5	0.5	
326	10	7.56	0.5	343	30	20.3	2.25	
326	15	7.38	0.5	343	32	20.1	2.25	
327.5	6	8.43	0.5	352	12	31.0	0.5	
333	35	12.3	2.25					

*Product Analysis.*—G.l.c. analysis (flame ionisation detector) during runs and when reaction was complete showed that equimolecular quantities of ethylene and diethyldichlorosilane were produced throughout, and accounted for all the reaction products to within 1%. Plots of pressure increase measured by the glass spiral manometer against the pressure of either product gave straight lines of unit slope. One other very small peak was observed by g.l.c., and analysis by MS.10 mass spectrometer showed this to be vinyl chloride, which made up not more than 0.7% of the products when reaction was complete. The corresponding product, diethylchlorosilane, was probably also present, but could not be distinguished with certainty by the MS.10 from the diethylchlorosilyl fragment ion from diethyldichlorosilane. The mass spectrometric analysis also showed that no hydrogen chloride (undetectable by flame ionisation detector) was present.

The rate of formation of the products, and the product composition, were unaffected by large or small amounts of nitric oxide or propene.

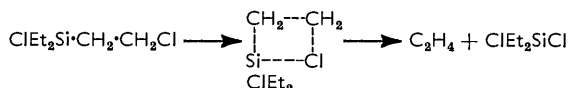
## DISCUSSION

The decomposition in the greaseless system gave good first-order results and Arrhenius parameters, and was unaffected by surface age and surface : volume ratio; we conclude that it is homogeneous. No treatment of the surface was necessary, and no appreciable deposit developed on the walls with use. The heterogeneous behaviour in the earlier apparatus therefore seems to be due to the presence of tap grease rather than to "unseasoned" glass walls. From our experience with this apparatus and with the preparation of 2-chloroethyldiethylchlorosilane we believe that initiation is by reaction between tap grease and the liquid rather than the vapour. This has some relevance to be supposed thermal stability of 2-chloroethylsilanes; it has been reported<sup>9</sup> that 2-chloroethyltriethylsilane decomposes on distillation under reduced pressure at 80°, but it is likely that this was a heterogeneous decomposition of the compound while still liquid, since in preliminary

<sup>9</sup> L. H. Sommer and F. C. Whitmore, *J. Amer. Chem. Soc.*, 1946, **68**, 485.

experiments we have found that this compound has to be heated above 250° in the gas phase in our greaseless apparatus before measurable decomposition occurs.<sup>10</sup>

In the homogeneous gas-phase decomposition, the elimination of ethylene accounts for more than 99% of the total reaction. It is a homogeneous, first-order reaction, completely insensitive to added nitric oxide or propene, and analogous in every respect to the elimination of ethylene from the related compounds we have studied previously.<sup>1,2</sup> We conclude that it is unimolecular (the test for fall-off in first-order rate constant at low pressure would not be feasible with a molecular of this complexity) and represent it thus:



The covalent radius of silicon<sup>11</sup> is sufficiently large for the four-membered ring to be relatively strainless, and the configuration is obviously electrostatically reasonable. We shall speculate below about the electron distribution and bond breaking and forming sequence in the transition state.

Since the above reaction accounts for more than 99% of the total reaction, the manometric results refer directly to it, and we have collected the kinetic data for the elimination of ethylene from 2-chloroethyl-trichlorosilane, -ethyl-dichlorosilane, and -diethylchlorosilane in Table 2.

TABLE 2  
Kinetic data for elimination of ethylene

Compound	log $A_1$	$\Delta S_1^\ddagger$ (e.u.)	$E_1$ (kcal. mole <sup>-1</sup> )	Relative rates at 350°	% Elimination total reaction
$\text{ClC}_2\text{H}_4\text{SiCl}_3$ .....	$11.08 \pm 0.23$	-8.5	$45.0 \pm 0.80$	1	72
$\text{ClC}_2\text{H}_4\text{SiCl}_2\text{Et}$ ...	$12.12 \pm 0.56$	-4.0	$46.2 \pm 2.00$	3	90
$\text{ClC}_2\text{H}_4\text{SiClEt}_2$ ...	$11.88 \pm 0.26$	-5.0	$41.1 \pm 1.00$	160	>99

[All Arrhenius parameters were obtained by least squares, using a computer which was not available earlier; the figures for the first two compounds therefore differ slightly, but not significantly, from those given previously.<sup>1,2</sup>]

The small difference in rate between 2-chloroethyltrichlorosilane and 2-chloroethyl-ethyl-dichlorosilane is best accounted for by the greater steric hindrance in the latter causing a smaller decrease in entropy in going to the transition state,<sup>1</sup> apparently the electronic effect of  $\text{SiCl}_2$  is little different from that of  $\cdot\text{SiCl}_3$ . But when there are two ethyl groups and only one chlorine on the silicon, there is a substantial increase in rate, mainly due to a decrease in activation energy. The elimination may be thought of as a flank substitution at silicon (Figure 2),<sup>12</sup> and while we do not suggest that the hypothetical pentavalent intermediate shown in Figure 2 is actually formed, it is likely to resemble the

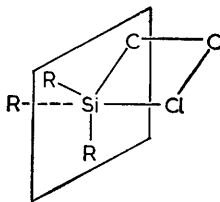


FIGURE 2. Flank substitution

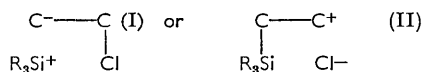
transition state (geometrically at least) more closely than do the initial or final states of the elimination. The rate increase caused by replacement of two chlorines attached to silicon by electron-supplying ethyl groups indicates that appreciable charge separation does

<sup>10</sup> I. M. T. Davidson and M. R. Jones, unpublished results.

<sup>11</sup> L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, 2nd edition, 1944, pp. 167 and 228; C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, p. 490.

<sup>12</sup> C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, p. 107.

develop in the transition state, and that the substituents on silicon are stabilising a positive charge;<sup>13</sup> limiting structures could be



It follows that the pentacovalent intermediate (Figure 2) is not formed, since silicon would then be more negative in the transition state, and electron-supplying substituents would decrease the rate, as they do in all  $S_N2$  reactions at silicon.<sup>12</sup>

Most work on the effect of substituents on the rates of gas-phase molecular reactions has been concerned with the dehydrohalogenation of alkyl halides,<sup>4</sup> where  $\alpha\text{C-X}$  bond breaking has been shown to exceed  $\text{H-X}$  bond formation in the transition state, although there are some complicating features.<sup>14</sup> There has also been a recent quantitative study of the pyrolysis of esters.<sup>6</sup> Although these investigations are not closely analogous to ours, they do indicate that the 160-fold increase in rate which we have observed is substantial for gas-phase reactions and must be due to the effect of substituents at the reaction centre, rather than removed some way from it. Also, the inductive effect is sharply attenuated in the gas phase, and does not extend beyond the  $\beta$ -position from the reaction centre.<sup>15</sup> Accordingly, we reject structure (II), and conclude that in the elimination of ethylene from 2-chloroethyldiethylchlorosilane at least, a partial positive charge develops on the silicon in the transition state. It should be emphasised that the positive charge is partial, *i.e.*, the transition state also has four-centre character and not the complete charge separation of the limiting structure (I).

It has proved difficult to find evidence for the involvement of siliconium ions in reactions in solution. Eaborn<sup>7</sup> has suggested that this difficulty is due to the existence of favourable alternative reaction paths involving direct displacement on silicon, or involving the pentacovalent intermediate; siliconium ions are produced by electron impact in a mass spectrometer, and it has been shown that the trimethylsiliconium ion can be produced as readily as the *t*-butyl cation from analogous precursors.<sup>16</sup> It thus appears that siliconium ion mechanisms should be observed in favourable circumstances. The problem has also been discussed by Sommer and Baughman,<sup>7</sup> who may have found evidence for siliconium ion formation being the rate-determining step in the decomposition of 2-chloroethyltrimethylsilane in polar solvents. In these circumstances our study of gas-phase reactions is of value, because the absence of solvent makes for a mechanistically simple situation in which the alternative reaction paths referred to above are no longer energetically favourable; it should then be possible to observe any trend towards siliconium ion formation, and our success in doing so confirms the view that siliconium ions can be formed.<sup>7</sup>

The smaller negative entropy of activation of 2-chloroethyldiethylchlorosilane compared with that of 2-chloroethyltrichlorosilane could be due to greater charge separation and therefore a less restricted transition state for the former compound, but it may simply reflect the greater restriction of rotation in the initial state of this compound.

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DEPARTMENT OF CHEMISTRY, THE UNIVERSITY, LEICESTER.

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<sup>13</sup> J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, 1956, pp. 150—153.

<sup>14</sup> W. C. Herndon, J. M. Sullivan, M. B. Henley, and J. M. Manion, *J. Amer. Chem. Soc.*, 1964, **86**, 5691.

<sup>15</sup> H. Singh and J. M. Tedder, *J.*, 1964, 4737; *Chem. Comm.*, 1965, 5.

<sup>16</sup> G. G. Hess, F. W. Lampe, and L. H. Sommer, *J. Amer. Chem. Soc.*, 1964, **86**, 3174.