Gas-phase Reactions of Halogenoalkylsilanes. Part IV.[1] 1-Chloroethyl-diethylchlorosilane and 2-Chloroethyltrialkylsilanes

By I. M. T. Davidson, M. R. Jones, and C. Pett, Department of Chemistry, The University, Leicester

The unimolecular elimination of ethylene from 2-chloroethyltrimethylsilane

$$k(\text{sec.}^{-1}) = 10^{10.98 \pm 0.20} \exp - (37{,}500 \pm 800)/RT$$

and from 2-chloroethyltriethylsilane

$$k(\text{sec.}^{-1}) = 10^{11.07 \pm 0.35} \exp - (39{,}200 \pm 1000)/RT$$

has been studied in the gas phase between 300 and 386°. The results, and earlier ones for similar compounds, are discussed in terms of a four-centre transition state with some charge separation. 1-Chloroethyldiethylchloro-silane has been found to undergo unimolecular dehydrochlorination

$$k(\text{sec.}^{-1}) = 10^{11.77 \pm 0.50} \exp - (45{,}400 \pm 1000)/RT$$

in the gas phase, and the kinetic results are compared with those for the dehydrochlorination of alkyl chlorides. Some general conclusions are drawn about electron distribution in the silicon–chlorine bond.

WE have shown [1,2] that 2-chloroethylsilanes decompose thermally in the gas phase by a homogenous, unimolecular elimination:

$$R_3SiCH_2 \cdot CH_2Cl \longrightarrow C_2H_4 + R_3SiCl$$
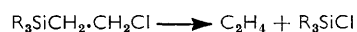
and that there is evidence for some charge separation in the transition state. To complete our study of these compounds we have now pyrolysed 2-chloroethyltri-methylsilane and 2-chloroethyltriethylsilane, and have also investigated the pyrolysis of 1-chloroethyldiethyl-chlorosilane. 1-Chloroethylsilanes are much less re-active in solution than their 2-chloroethyl isomers,[3] and would be expected to undergo dehydrochlorination in the gas phase, like other substituted ethyl chlorides,[4] rather than ethylene elimination.

[1] Part III, I. M. T. Davidson and M. R. Jones, J. Chem. Soc., 1965, 5481.

[2] (a) I. M. T. Davidson and C. J. L. Metcalfe, J. Chem. Soc., 1964, 2630; (b) I. M. T. Davidson, C. Eaborn, and M. N. Lilly, J. Chem. Soc., 1964, 2624.

[3] C. Eaborn, " Organosilicon Compounds," Butterworths, London, 1960, p. 133.

[4] A. Maccoll, " Advances in Physical Organic Chemistry," Academic Press, London and New York, 1965, vol. 3, p. 91.

EXPERIMENTAL AND RESULTS

The organosilicon compounds were prepared by standard methods, mostly from trimethylchlorosilane, and all other compounds were commercial. All were purified where necessary by trap-to-trap distillation, and their purity checked by physical methods (gas chromatography, n.m.r. and infrared spectra, mass spectrometry, and refractive index). The organosilicon compounds were stored under vacuum in greaseless containers.

The kinetic experiments were done in static systems, each fitted with a glass spiral manometer and sampling valve leading directly to a g.l.c. column (a gas density balance detector was used with 1-chloroethyldiethylchlorosilane and 2-chloroethyltriethylsilane, and a flame ionisation detector with the other compounds studied). Some early experiments with 2-chloroethyltrimethylsilane were done in apparatus with greased vacuum taps,[2a] but most of the results for this compound, and all results for the others, were obtained with the completely greaseless system described previously.[1]

1-Chloroethyldiethylchlorosilane.—This was pyrolysed between 372 and 437°, with initial pressures of 8—40 mm. Hg. The progress of the reaction was followed by frequent gas-chromatographic analysis and by the pressure increase during each run. The pressure at the end of a run was twice the initial pressure, and the pressure increase followed the first-order rate law

$$k \text{ (sec.}^{-1}) = 10^{11 \cdot 77 \pm 0 \cdot 50} \exp - (45,400 \pm 1000)/RT$$

(95% confidence limits). The only products were hydrogen chloride and vinyldiethylchlorosilane in equimolar amounts, and a plot of the partial pressure of either product (calculated from g.l.c. analyses) against the pressure increase gave a straight line of unit slope. The sole reaction is, therefore, dehydrochlorination: $ClEt_2Si \cdot CHClCH_3 \longrightarrow ClEt_2Si \cdot CH:CH_2 + HCl$. Prolonged seasoning of the reaction vessel surface was not necessary, and a six-fold increase in surface-to-volume ratio, achieved by packing the vessel with fire-polished Pyrex tubing, caused no change in rate. The rate was also unaffected by the addition of large or small amounts of nitric oxide.

2-Chloroethyltriethylsilane.—Pyrolysis between 316 and 330°, with initial pressure of 6—35 mm. Hg, gave the expected elimination of ethylene.[1] Early runs, however, gave some dehydrochlorination products as well, and the kinetic results were inconsistent; after repeated runs the dehydrochlorination products were no longer formed, and the reproducibility of the kinetic results improved. The stoicheiometry, order of reaction, and sensitivity to surface-to-volume ratio and added nitric oxide were then determined exactly as for 1-chloroethyldiethylchlorosilane and for the previous compound in this series.[1] Elimination of ethylene: $Et_3Si \cdot CH_2 \cdot CH_2Cl \longrightarrow C_2H_4 + Et_3SiCl$ accounted for more than 99% of the total reaction, and was of the first order,

$$k(\text{sec.}^{-1}) = 10^{11 \cdot 07 \pm 0 \cdot 35} \exp - (39,200 \pm 1000)/RT$$

(95% confidence limits). The rate was insensitive to surface-to-volume ratio and to added nitric oxide.

2-Chloroethyltrimethylsilane.—This pyrolysis was entirely analogous to that of 2-chloroethyltriethylsilane, except that the initial difficulties with irreproducible behaviour were not so severe. Between 300 and 340° and 12—32 mm. Hg the only products were ethylene and trimethylchlorosilane, and their rate of formation was insensitive to changes in surface-to-volume ratio and to added nitric oxide. First-order rate constants are given by

$$k(\text{sec.}^{-1}) = 10^{10 \cdot 98 \pm 0 \cdot 20} \exp - (37,500 \pm 800)/RT$$

(95% confidence limits).

The earlier results for 2-chloroethyltrimethylsilane in the apparatus with greased taps adjacent to the reaction vessel may be summarised thus:

(a) *Untreated reaction vessel, no added gas.* Manometric rate measurements gave

$$k(\text{sec.}^{-1}) = 10^{7 \cdot 4 \pm 1 \cdot 2} \exp - (29,600 \pm 3350)/RT$$

reproducibility being poor. The following equimolar pairs of products were found by g.l.c. and by mass spectrometry when reaction was complete: ethylene and trimethylchlorosilane, 96%; vinyl chloride and trimethylsilane, 2%; hydrogen chloride and vinyltrimethylsilane, 2%.

(b) *Untreated reaction vessel, with added propene.* In the presence of approximately equal pressures of propene, kinetic results were much more reproducible:

$$k(\text{sec.}^{-1}) = 10^{7 \cdot 4 \pm 0 \cdot 5} \exp - (29,600 \pm 1300)/RT$$

The final product analysis was unchanged.

(c) *Carbon-coated reaction vessel.* The vessel was given a heavy coating of carbon by pyrolysis of allyl bromide at 360°; manometric rate measurements were then made between 326 and 386°. Provided that the coating was regularly renewed, reproducible results were obtained:

$$k(\text{sec.}^{-1}) = 10^{10 \cdot 05 \pm 0 \cdot 14} \exp - (37,500 \pm 500)/RT$$

Again, the product analysis was the same as in (a). The rate was unaffected by increase in surface-to-volume ratio, once the packing had been coated by pyrolysis of allyl bromide, and the rate of formation of products was also unaffected by added nitric oxide.

2-Hydroxyethyltrimethylsilane.—This was pyrolysed in the greaseless apparatus used for the pyrolysis of 2-chloroethyltrimethylsilane, between 313 and 341° and 7—14 mm. Hg. The rate of increase in pressure was of the first order up to about 70% decomposition

$$k(\text{sec.}^{-1}) = 10^{8 \cdot 4} \exp - 29,200/RT$$

and the ratio of final to initial pressure was close to 2. At least 95% of the total reaction was dehydration: $Me_3SiCH_2CH_2OH \longrightarrow Me_3SiCH:CH_2 + H_2O$. The vinyltrimethylsilane was analysed by g.l.c. and the water by mass spectrometry. Minor products were not identified and no experiment was done with added gases or altered surface-to-volume ratio.

1,2-Dichloroethyltrimethylsilane.— This decomposed rapidly in the greaseless apparatus ($k = 3 \times 10^{-3}$ sec.$^{-1}$ at 250°), giving mainly trimethylchlorosilane and vinyl chloride (80%) with some hydrogen chloride and a chlorovinyltrimethylsilane. Consistent kinetic results could not be obtained.

DISCUSSION

1-Chloroethyldiethylchlorosilane.—Dehydrochlorination was of the first order, insensitive to surface and to added nitric oxide. It is, therefore, a homogeneous unimolecular reaction, entirely analogous to the well-known unimolecular dehydrochlorination of alkyl chlorides.[4]

These unimolecular dehydrohalogenations are be-

lieved to proceed by polar transition states and to show some similarities to heterolytic reactions in solution.[4,5] For instance, the rates of dehydrochlorination of alkyl chlorides have been successfully correlated[6] by the Taft equation,[7] giving $\rho^* = -23.5$. Rate data for these chlorides[4] and for 1-chloroethyldiethylchlorosilane are in Table 1. Interpolation in the

TABLE 1

Dehydrochlorination

Compound	$\log A$ (sec.$^{-1}$)	E (kcal. mole^{-1})	k_{rel} 400° c
EtCl	14·22	59·5	1·00
Pr^{n}Cl	13·45	55·5	3·38
Bu^{n}Cl	14·00	57·0	3·80
Pr^{i}Cl	13·40	50·5	129
Bu^{s}Cl	13·75	50·1	371
Bu^{t}Cl	12·40	41·4	12,000
Et$_2$ClSi·CH(CH$_3$)Cl	11·77	45·4	142

linear plot of $\log k_{rel.}$ against σ^* gives $\sigma^* = -0.21$ for Et$_2$ClSi·ĊHCH$_3$ close to the value for the isopropyl group, so that the ·SiClEt$_2$ group supplies electrons inductively to an adjacent carbon atom about as effectively as a methyl group. On the other hand, the corresponding group ·CClEt$_2$ is strongly electron-withdrawing, with $\sigma^* = +0.82$.

We also observed dehydrochlorination as a minor reaction in the pyrolysis of 2-chloroethyltrichlorosilane[2b] and 2-chloroethylethyldichlorosilane.[2a] Arrhenius parameters could not be obtained, but the values of $k_{rel.}$ at 400° (defined as in Table 1) are 8 and 17, respectively. It appears, therefore, that ·SiCl$_2$Et and even ·SiCl$_3$ may be electron-supplying groups, but we consider these results to be much less reliable than those for 1-chloroethyldiethylchlorosilane. We shall discuss the implications of these findings below.

2-*Chloroethyltrimethylsilane and 2-Chloroethyltriethylsilane.*—In apparatus fitted with greaseless stopcocks these compounds decomposed to ethylene and the trialkylchlorosilane only, in first-order reactions insensitive to surface and to nitric oxide; we infer that they, like the previous compounds in this series,[1,2] undergo homogenous unimolecular elimination of ethylene in the gas phase: R$_3$SiCH$_2$·CH$_2$Cl $\longrightarrow$ C$_2$H$_4$ + R$_3$SiCl. The initial difficulties with surface reactions are not surprising, in view of the thermal instability of 2-chloroethyltrialkylsilanes in the liquid phase.[8] Our accumulated results for the elimination of ethylene from 2-chloroethylsilanes are in Table 2. Clearly the overall trend is for the activation energy to decrease as chlorine attached to silicon is replaced by alkyl groups; this is evidence for some charge separation in the transition state, with the development of a partial positive charge on silicon (although the second compound in the series appears

TABLE 2

Elimination of ethylene

Compound	$\log A$ (sec.$^{-1}$)	E (kcal. mole^{-1})
ClC$_2$H$_4$·SiCl$_3$	11·08 ± 0·23	45·0 ± 0·80
ClC$_2$H$_4$·SiCl$_2$Et	12·12 ± 0·56	46·2 ± 2·00
ClC$_2$H$_4$·SiClEt$_2$	11·88 ± 0·26	41·1 ± 1·00
ClC$_2$H$_4$·SiEt$_3$	11·07 ± 0·35	39·2 ± 1·00
ClC$_2$H$_4$·SiMe$_3$	10·98 ± 0·20	37·5 ± 0·80

to deviate from this trend, the experimental errors were particularly large in that case, and we do not consider the deviation to be genuine).

The A factors (Table 2) are all in the range expected for unimolecular four-centre reactions,[9] and there is evidence from Raman spectra[10] that silicon–chlorine interactions are significant in these compounds. Hence, the transition state for the elimination has four-centre as well as polar character, and appears to be well described by the semi-ion pair model suggested by Benson and Bose,[5] which we depict for this reaction as (I)—(IV), with (II) as the semi-ion pair and (III) as the four-centre system. The feasibility of polar transition states
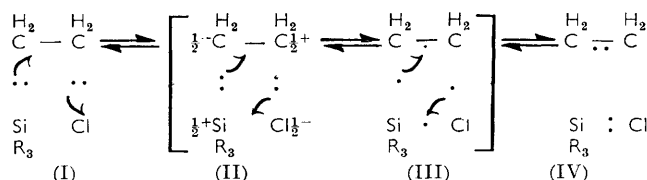
in alkyl halide decompositions has been evaluated;[3,5,11] the necessary data are not available for organosilicon compounds, but the above model accounts for the overall features of our kinetic results very well. It is possible that this type of transition state, with polar and four-centre character, could be postulated in the neutral solvolysis of 2-chloroethyltrialkylsilanes;[12] we have alluded to this point previously,[2b] and it has been discussed in detail recently.[13]

Our results cast little light on the reverse reaction, the molecular addition of ethylene to chlorosilanes. Addition is obviously much slower than elimination, since the latter invariably went " to completion " (probably >99%), but this does not necessarily mean that the activation energies for addition are much higher than those for elimination, because the rate difference could be entirely due to the A factors, as it is with the alkyl chlorides and bromides.[5] Indeed, from bond dissociation energies[14] we estimate that the elimination of ethylene from 2-chloroethylsilanes is approximately thermoneutral.

In the elimination reaction there will of course be a difference in electron distribution at silicon between states (I) and (IV) resulting from the change from a silicon–carbon to a silicon–chlorine bond, but it is not possible to estimate the size of this difference reliably.

[5] S. W. Benson and A. N. Bose, *J. Chem. Phys.*, 1963, **39**, 3463.

[6] M. Kraus, *Chem. and Ind.*, 1966, 1263.

[7] R. W. Taft, jun., *J. Amer. Chem. Soc.*, 1952, **74**, 2729.

[8] L. H. Sommer and F. C. Whitmore, *J. Amer. Chem. Soc.*, 1946, **68**, 485.

[9] S. W. Benson and W. B. DeMore, *Ann. Rev. Phys. Chem.*, 1965, **16**, 397.

[10] M. I. Batuev, A. D. Petrov, V. A. Ponomarenko, and A. D. Matveeva, *J. Gen. Chem. U.S.S.R.*, 1956, **26**, 2613.

[11] C. J. Harding, A. Maccoll, and R. A. Ross, *Chem. Comm.*, 1967, 289.

[12] L. H. Sommer and G. A. Baughman, *J. Amer. Chem. Soc.*, 1961, **83**, 3346.

[13] R. W. Bott, C. Eaborn, and B. M. Rushton, *J. Organometallic Chem.*, 1965, **3**, 455.

[14] I. M. T. Davidson and I. L. Stephenson, *Chem. Comm.*, 1966, 746.

The Pauling electronegativity scale [15] assigns 12% ionic character to the silicon–carbon bond and 30% to silicon–chlorine, but the scale is based on average bond energies, whereas the effective " electronegativity " of silicon will vary with environment; it is unlikely to be the same in trimethylchlorosilane and silicon tetrachloride, for instance. Also, Pauling's figure for the silicon–chlorine bond is derived from the extent to which E(Si–Cl) is greater than the mean of E(Si–Si) and E(Cl–Cl), and partial ionic character is not the only explanation for the strengthening of the silicon–chlorine bond. However, even if this bond has substantial ionic character, this will only appear after the four-centre stage (III), and will not affect our conclusion that a partial positive charge develops at silicon much earlier along the reaction co-ordinate, at stage (II) in the Benson–Bose scheme. The final step, to give a partially ionic silicon–chlorine bond would be intermediate between the original (III) $\rightleftharpoons$ (IV) sequence and (III) $\rightleftharpoons$ (IV [1]).
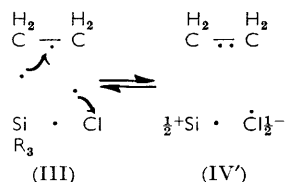
That the effect of substituents on reaction rate and activation energy is much less with the chloroethylsilanes than with the alkyl halides is easily seen by comparing the spread of activation energies in Tables 1 and 2. Also, a simple plot of log k against σ_p (R$_3$) for the 2-chloroethylsilanes, R$_3$SiCH$_2$·CH$_2$Cl, is reasonably linear, with $\rho = -2 \cdot 2$, in contrast to $\rho^* = -23 \cdot 5$ for the alkyl halides.[6] The negative sign is expected for reactions developing a positive charge in the transition state.[7]

We infer from these small substituent effects in 2-chloroethylsilanes that the electron distribution around silicon changes less in the series Cl$_3$SiCH$_2$·CH$_2$Cl to Alk$_3$SiCH$_2$·CH$_2$Cl than would be expected from inductive effects alone, i.e., that the inductive withdrawal of electrons from silicon in the silicon–chlorine bond is partially counteracted by delocalisation of electrons originally in the 3p atomic orbitals of chlorine (" p–d π-bonding "). Purely inductive effects are enhanced in silicon relative to carbon, cf. $\sigma^* = -0 \cdot 165$ for Me$_3$CCH$_2$· and $-0 \cdot 26$ for Me$_3$SiCH$_2$·. Further evidence in support of our inference comes from the dehydro-

chlorination experiments, discussed above, which showed that the ·SiClEt$_2$ group was electron-supplying. Thus, all our kinetic results are consistent with appreciable delocalisation in the silicon–chlorine bond, and may therefore be of some interest in the current debate about bonding in silicon compounds.[16]

In the early experiments with 2-chloroethyltrimethylsilane in apparatus fitted with greased taps, small amounts of vinyl chloride, trimethylsilane, hydrogen chloride, and vinyltrimethylsilane were formed as well as the main elimination products, ethylene and trimethylchlorosilane. These additional products were probably formed heterogeneously on a surface activated by traces of tap grease; a homogenous radical-chain mechanism is unlikely, because of the insensitivity to added propene. In the untreated reaction vessel the low Arrhenius parameters obtained for the main elimination reaction would indicate that it, too, was heterogeneous, but in the carbon-coated vessel the activation energy of 37·5 kcal. mole^{-1} was the same as in the grease-free vessel, and this lack of dependence of activation energy on surface is further evidence that the reaction was homogenous in these two vessels.

2-Hydroxyethyltrimethylsilane.—This was an intermediate compound in the preparation of 2-chloroethyltrimethylsilane, and we thought that the latter might be contaminated by a small amount of it. We were able to show that this was not so, because it decomposed much more quickly than 2-chloroethyltrimethylsilane, giving different products, and would therefore have been easily detected kinetically.

It is almost certain that 2-hydroxyethyltrimethylsilane decomposed heterogeneously under our experimental conditions; the activation energy of 29 kcal. mole^{-1} is about the same as for the heterogeneous decomposition of 2-chloroethyltrimethylsilane in the " greased " vessel, and probably relates to the same process in each case, adsorption and desorption on the surface via a silicon–oxygen bond. The predominance of dehydration is unexpected: we would have expected a free-radical chain reaction giving negligible amounts of dehydration products, by analogy with the decomposition of primary alcohols,[17] or the elimination of ethylene with formation of trimethylsilanol, and ultimately hexamethyldisiloxane, by analogy with 2-chloroethylsilanes. Perhaps one of these routes would be followed in the homogeneous decomposition.

1,2-Dichloroethyltrimethylsilane.—The few experiments on this compound indicate that the decomposition in our greaseless apparatus was heterogeneous, and probably involved a free-radical mechanism. We can, therefore, attach no significance to the rapid rate in relation to our unimolecular elimination mechanism.

[15] L. Pauling, " Nature of the Chemical Bond," Cornell University Press, New York, 1944, p. 58.

[16] P. G. Perkins, *Chem. Comm.*, 1967, 268; E. W. Randall and J. J. Zuckerman, *ibid.*, 1966, 732; E. A. V. Ebsworth, *ibid.*, 1966, 530; C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.*, 1967, **6**, 98; W. K. Musker and G. B. Savitsky, *J. Phys. Chem.*, 1967, **71**, 431; L. Goodman, A. H. Konstam, and L. H. Sommer, *J. Amer. Chem. Soc.*, 1965, **87**, 1012; B. G. Gowenlock and K. E. Thomas, *J. Chem. Soc.*, 1965, 5068; J. Hetfless, F. Mares, and V. Chvalovsky, *Coll. Czech. Chem. Comm.*, 1965, **30**, 1643; R. R. Hiatt, *Canad. J. Chem.*, 1964, **42**, 985; H. Schmidbauer, *J. Amer. Chem. Soc.*, 1963, **85**, 2336; D. E. Webster, *J. Chem. Soc.*, 1960, 5132.

[17] J. A. Barnard and H. W. D. Hughes, *Trans. Faraday Soc.*, 1960, **56**, 55, 64.