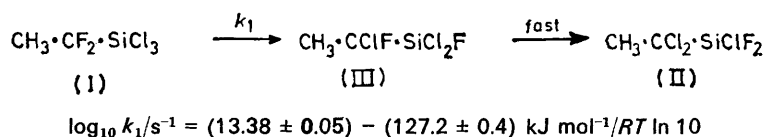


Kinetics of the Reactions of Silicon Compounds. Part 10.¹ Kinetics and Mechanism of the Gas-phase Thermal Reactions of Trichloro-(1,1-difluoroethyl)silane. An Intramolecular Halogen Exchange Reaction

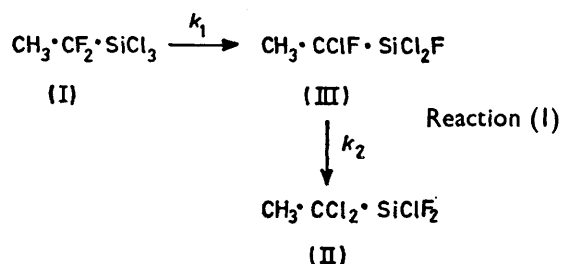
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The gas-phase thermal isomerisation of trichloro-(1,1-difluoroethyl)silane (I) to chloro-(1,1-dichloroethyl)-difluorosilane (II) is a first-order homogeneous process at 375–416 K and 11–67 mmHg initial pressure. The reaction is unaffected by the presence of the radical inhibitors 2,3-dimethylbut-2-ene and nitric oxide, and it is concluded that the rate-determining step is a unimolecular isomerisation of (I) to dichloro-(1-chloro-1-fluoroethyl)fluorosilane (III), which then undergoes a secondary fast isomerisation to the observed product (II). The



data suggest a transition state in which the fluorine atom transfer is more advanced than the chlorine atom transfer. The minor products vinyl chloride and dichlorodifluorosilane are shown to arise from thermal and chemically activated decomposition of the initially formed (II) and/or (III).

POLYHALOGENOALKYL silicon compounds have been shown to react thermally by a variety of mechanisms. Thus molecular β - and α -elimination of both chlorine and fluorine have been demonstrated by a series of mechanistic and kinetic investigations.^{1–8} A further type of reaction has been proposed and clearly characterised by the nature and distribution of products formed, but not subjected previously to kinetic study. This is the exchange of chlorine on silicon with α -fluorine,^{2,5,6,8} as



exemplified by the isomerisation of trichloro-(1,1-difluoroethyl)silane (I) to chloro-(1,1-dichloroethyl)-difluorosilane (II), which is reported to occur quantitatively in sealed tubes at 373–523 K.⁵ Reaction at 373 K in the presence of an excess of isobutene gave the same product, indicating that the reaction is molecular under these conditions. Approximate kinetic data from sealed-tube reactions suggested first order kinetics, and the proposed mechanism comprised two successive intramolecular halogen exchange reactions as shown in equation (1). At 453 K and above, vinyl fluoride and vinyl chloride were also produced, and the suggested

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routes to these products involved the well established mechanisms of α -fluorine elimination from (I) and from the intermediate isomerisation product (III), and possibly α -chlorine elimination from (II), to give carbenes which rearrange to the olefinic products.

The object of the present investigation was to conduct a full kinetic study of reaction (1) with a view to obtaining further evidence concerning its mechanism and those of the side-reactions noted above.

EXPERIMENTAL

The kinetic apparatus was similar to that described previously;³ the taps were Viton diaphragm type, the reaction vessels silica, the dead-space *ca.* 3%, pressure measurement by glass spiral gauge, and temperature variations $< \pm 0.2$ K. Reaction mixtures were analysed by condensing the whole contents of the reaction vessel into a mixing bulb along with a measured quantity of standard (carbon tetrachloride), allowing the mixture to evaporate and mix for several hours, then injecting by gas-sampling valve into a Pye 104 dual katharometer chromatograph with a Kent Chromalog Mark I integrator. Great difficulty was experienced in finding a suitable column. The main reaction product (II) was partially or completely absorbed by many column packings, and in addition had retention times similar to those of the reactant. The column eventually used for kinetic work was 10 m \times 5 mm i.d. glass containing 3 wt % DCQF-1 fluorosilicone oil on 80–120 mesh carefully silanised Celite. The hydrogen carrier gas was scrupulously dried and the column was resilanised *in situ* each day by injections of chlorotrimethylsilane before use.

Calibration plots for each component were constructed by plotting (pressure of component) *versus* (pressure of standard \times peak area for component/peak area for standard), where

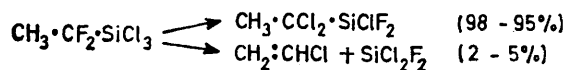
the pressures are those measured for both component and standard in the reaction vessel. Good linear plots were obtained, the slopes being independent of reasonable variations in the chromatographic conditions (in particular, the pressure of sample injected). The main reaction product (II) could not be obtained in a pure state, so an indirect calibration was obtained by allowing known pressures of (I) to react to completion (with allowance for decomposition; see later).

Thermolysis of (II).—The thermal decomposition of (II) was briefly investigated as a possible source of the minor products (vinyl chloride and dichlorodifluorosilane) in the isomerisation of (I) to (II). In fact, no observable reaction occurred in the kinetic system at 416 K ($k < 5 \times 10^{-7} \text{ s}^{-1}$). At higher temperatures, (II) decomposed to vinyl chloride and dichlorodifluorosilane with k ca. $5 \times 10^{-5} \text{ s}^{-1}$ at 513 K and $2 \times 10^{-3} \text{ s}^{-1}$ at 550 K. Assuming a probable A factor of 10^{13} s^{-1} , these rate constants require an activation energy for α -chlorine elimination of ca. 160 kJ mol^{-1} , but this can only be considered as a very approximate estimate.

Materials.—The reactant (I), prepared by the photochemical reduction⁵ of trichloro-(2-chloro-1,1-difluoroethyl)-silane with tributylsilane or (preferably) trimethylsilane, and purified by distillation through a 30 cm Fenske column, had b.p. 306 K at 100 mmHg (lit.,⁶ 353–355 K at 760 mmHg). G.l.c. revealed the presence of small amounts of isomerisation product (II) (*e.g.* 5%) and traces of unidentified impurities.

RESULTS AND DISCUSSION

Convenient rates of reaction were obtained at 375–416 K, and no ageing effect was observed. A slight pressure rise occurred during the reaction (typically 2% at 50 mmHg initial pressure and 5% at 5 mmHg). The observable products of the reaction were identified by i.r., n.m.r., and g.l.c.–mass spectrometry as predominantly chloro-(1,1-dichloroethyl)difluorosilane (II), with small amounts of vinyl chloride and dichlorodifluorosilane (2–5%). Other trace products were tentatively identified as vinyl fluoride and 1,1-dichloroethyltrifluorosilane. The partial pressures of vinyl chloride and dichlorodifluorosilane found by analysis were within experimental error equal to each other and to the pressure change which had occurred. The reaction stoichiometry is therefore represented by Scheme 1.



SCHEME 1

First-order plots for the major reaction were constructed from the reactant analyses for a series of runs at each temperature, after correction for the unreactive dead-space and for the small amount of (II) present in the initial reactant. Good linear plots were obtained, and the isomerisation rate constants thus obtained are summarised in Table 1. The Arrhenius plot was a good straight line corresponding to equation (2), in which the error limits are standard deviations.

Runs in a packed reaction vessel (S/V ca. 10.7 cm^{-1}) or in the presence of free-radical chain inhibitors (nitric

oxide or 2,3-dimethylbut-2-ene), gave rate constants for the disappearance of reactant which were within experimental error equal (Table 2) to those for uninhibited runs

$$\log_{10} k/\text{s}^{-1} = (13.38 \pm 0.05) - (127.2 \pm 0.4) \text{ kJ mol}^{-1}/RT \ln 10 \quad (2)$$

in the unpacked vessels (S/V ca. 1.2 cm^{-1}). It is concluded that there were no heterogeneous effects occurring, and that the main reaction does not involve either free-radical or carbene intermediates, *i.e.* only homogeneous molecular processes are involved.

TABLE 1

Mean first-order rate constants k and standard deviations $\sigma(k)$ for isomerisation of trichloro-(1,1-difluoroethyl)-silane

T/K	No. of runs	Reactant pressure/mmHg	$10^5 k/\text{s}^{-1}$	$10^5 \sigma(k)/\text{s}^{-1}$
375.0	4	20–65	4.63	0.23
380.4	4	23–66	8.20	0.23
389.2	5	37–62	19.9	0.2
396.4	6	31–67	41.1	0.5
404.0	5	20–43	85.9	0.9
410.8	7	11–53	160	3
415.9	5	23–47	254	2

Mechanism of Main Reaction.—The results thus show that reaction (1) obeys first-order kinetics during each run, and that the initial rate is also first-order over a six-fold variation of initial pressure, and involves only homogeneous molecular processes under the conditions used. The rate-determining process is thus considered to be a unimolecular reaction, which should indeed be in its high-pressure region at the relevant pressures for a molecule of this size.⁹ The rate constant at 373 K from the present gas-phase studies is considerably less than the approximate value determined by n.m.r. studies of neat

TABLE 2

Kinetic data for packed-vessel and inhibited runs

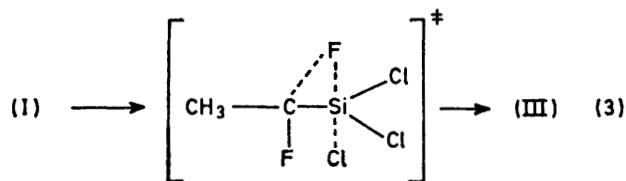
T/K	Type of run	No. of runs	Reactant pressure/mmHg	$10^5 k/\text{s}^{-1}$	$10^5 \sigma(k)/\text{s}^{-1}$
380.4	Packed vessel	4	12–66	8.8	0.5
380.4	Inhibited ^a	7	2–35 ^a	8.6	0.9
380.4	Standard	4	22–66	8.2	0.3
410.8	Packed vessel	5	12–66	154	6
410.8	Inhibited ^b	6	10–26 ^b	159	10
410.8	Standard	7	11–53	160	3

^a 50–100% 2,3-Dimethylbut-2-ene or 25–40% nitric oxide added. ^b 50–200% 2,3-Dimethylbut-2-ene or 40–100% nitric oxide added.

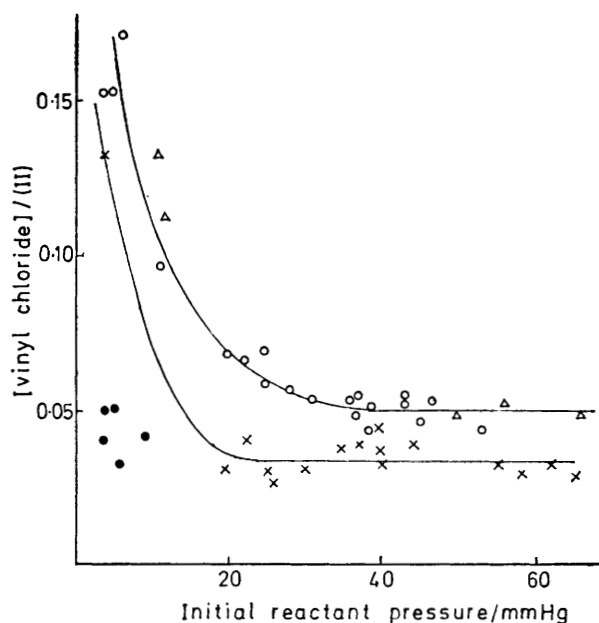
liquid in a sealed tube⁵ ($4 \times 10^{-5} \text{ s}^{-1}$, *cf.* $55 \times 10^{-5} \text{ s}^{-1}$). It can only be presumed that the liquid-phase reaction, although showing first-order kinetics, was accelerated by unidentified heterogeneous and/or catalytic effects.

The present results nevertheless support the mechanism suggested earlier,⁵ namely equation (1) in which the two reactions are unimolecular and $k_1 \gg k_2$. A concerted exchange of both pairs of halogen atoms would

involve an extremely tight transition state leading to a very low A factor. The Arrhenius parameters for the rate-determining first step are remarkably similar to those observed for α -fluorine elimination to give a carbene [e.g. $\log_{10}(A/s^{-1})$ 13.1 and $E/kJ\ mol^{-1}$ 138 for trifluoro-(1,1,2,2-tetrafluoroethyl)silane,⁴ cf. 13.4 and 127, respectively, for isomerisation of (I)], and the A factor is



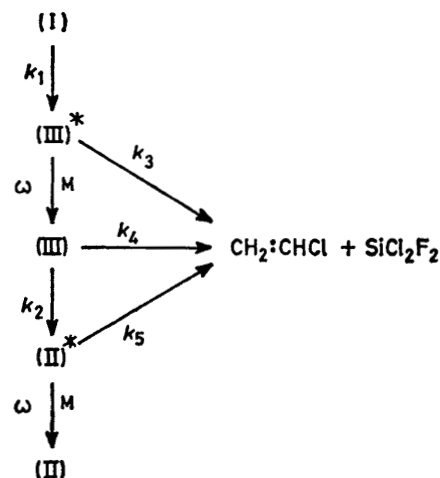
very close to the value predicted¹⁰ for three-centre transition states. These observations confirm the conclusion reached previously,⁵ that the reaction co-ordinate leading to the transition state is characterised predominantly by nucleophilic attack of α -fluorine on silicon [equation (3)] (a conclusion also reached for the α -fluorine elimination reactions^{1,5}). On this basis, the intermediate isomerisation product (III), having a more electropositive silicon atom and a more reactive α -fluorine atom than (I), would be expected to isomerise more rapidly than (I), as is required to account for the non-observation of (III) in the reaction products. A lowering



Relative formation of minor products as a function of reactant pressure: \circ , runs at 404–416 K; \triangle , runs at 411 K in packed vessel; \bullet , runs at 411 K with nitrogen, hexane, or 2,3-dimethylbut-2-ene added to give a total pressure of at least 55 mmHg; \times , runs at 375–390 K

of the activation energy by only 15 kJ mol^{-1} would reduce the steady-state concentration of (III) to $<1\%$ of the mixture, and it is also probable that chemical activation effects enhance the isomerisation of (III) (see next section).

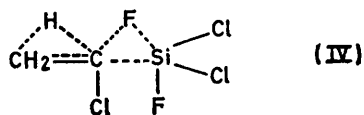
Formation of Minor Products.—As noted above, the partial pressures of vinyl chloride and dichlorodifluoro-silane were equal to the pressure increase at any time and the formation of these products was therefore conveniently followed by monitoring the pressure change. The nature of the minor products suggests their possible formation by secondary decomposition of the main product (II) and/or the presumed intermediate product (III). The thermal decomposition of (II) is too slow, however, (see Experimental section), and in addition the pressure increase occurred steadily throughout the reaction, being proportional to the extent of the main reaction at any time rather than showing a sigmoid appearance curve. Thus if secondary thermal decomposition is involved, it must be decomposition of the intermediate rearrangement product (III). The formation of minor products was essentially the same in the packed and unpacked reaction vessels (see Figure), so that heterogeneous effects can be ruled out. The Figure also shows, however, that the rate of formation of the minor products increased, relative to that of the main reaction, as the initial pressure of reactant decreased, and furthermore, that the addition of a non-reactive gas (nitrogen, hexane, or butene) to a low pressure of reactant reduced the relative rate to its limiting high-pressure value.



SCHEME 2 * Denotes chemical activation, ω = collision frequency, $k_2/k_1 \geq 10^2$, $k_2/k_4 \approx 10^2$, $k_3/k_5 \leq 1$ or $k_3/k_5 \geq 1$ or $k_3 \approx k_5 \leq \omega$

These effects suggest very strongly that chemical activation processes are involved, as might be expected from the significant exothermicities predicted for the two isomerisation reactions (20–30 kJ mol^{-1} on the basis of thermochemical bond energies). One such mechanism is shown in Scheme 2, in which the rate constant ratios have been chosen to give a semiquantitative fit to the data in the Figure. Other reactions could be included, e.g. direct conversion of (III)* to (II)*. Thermal decomposition of (III) has been included in Scheme 2 to account for the finite production of minor products even at high pressures, and the greater production of these products (relative to the isomerisation product) at

higher temperatures is consistent with the decomposition having the higher activation energy, as expected. The decomposition of (III) is envisaged as occurring pre-



dominantly by nucleophilic attack of fluorine on silicon as in (IV), and a corresponding less favoured nucleophilic attack by chlorine may account for the production of vinyl fluoride.

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