

367. *The Kinetics of the Reactions of Silicon Compounds. Part I. The Gas-phase Thermal Decomposition of 2,2-Difluoroethyltrifluoro-silane.*

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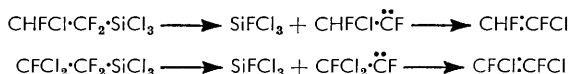
The gas-phase thermal decomposition of 2,2-difluoroethyltrifluorosilane into vinyl fluoride and silicon tetrafluoride, at temperatures from 151 to 221° and at pressures from 10 to 180 mm., is kinetically of the first order. The reaction is homogeneous and is unaffected by the addition of nitric oxide or cyclohexene. The first-order rate constant is independent of pressure, and is given by:

$$\log_{10} k \text{ (sec.}^{-1}\text{)} = (12.27 \pm 0.27) \exp [-(32,720 \pm 530)/4.576T]$$

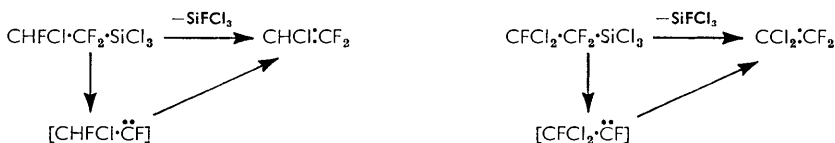
It is concluded that the reaction is unimolecular and proceeds through a four-centre transition state. This provides the first unambiguous demonstration of 2-fluorine elimination by a molecular process in a halogenoalkylsilane.

THE thermal stability of halogen-substituted alkylsilicon compounds depends markedly on the position of the halogen substituent in the alkyl group. This is well illustrated by the polysiloxanes $[\text{CHF}_2\text{-CH}_2\text{-SiO}_{1.5}]_n$, $[\text{CHF}_2\text{-CF}_2\text{-SiO}_{1.5}]_n$, and $[\text{CF}_3\text{-CH}_2\text{-CH}_2\text{-SiO}_{1.5}]_n$, which begin to decompose at about 160, 140, and 450°, respectively.¹ The striking difference between the decomposition temperatures of the 1- and 2-halogeno-compounds and the 3-halogeno-compounds strongly suggests that there are at least two distinct types of mechanism by which these polysiloxanes decompose.

There have been a number of reports² that the C-Si bond in 1- or 2-halogenoalkylsilanes is very easily broken thermally, with the elimination of one of the halogen atoms in the alkyl group to give an olefin, and two distinct types of mechanism have been suggested. Pyrolysis of trichloro-(2-chloro-1,1,2-trifluoroethyl)silane, $\text{CHFCl}\cdot\text{CF}_2\cdot\text{SiCl}_3$, and of trichloro-(2,2-dichloro-1,1,2-trifluoroethyl)silane, $\text{CFCl}_2\cdot\text{CF}_2\cdot\text{SiCl}_3$, at 250° gave 1-chloro-1,2-difluoroethylene and 1,2-dichlorodifluoroethylene, respectively.³ Elimination reactions involving the 1-fluorine were proposed:



Small (<10%) amounts of the olefins $\text{CF}_2\text{:CHCl}$ and $\text{CF}_2\text{:CCl}_2$, respectively, could be explained either by loss of fluorine from the 2-position, or by fluorine migration in the intermediate carbene:



It seems likely that the thermal decomposition of the 1- or 2-fluorinated polysiloxanes involves similar mechanisms. Where there are no 1- or 2-halogen atoms another mechanism must be operative, and this view is supported by the high decomposition temperature of the 3-fluorinated polysiloxane.

The aim of the present work was to study the kinetics of the thermal decomposition

¹ Haszeldine, Newlands, and Plumb, *Proc. Chem. Soc.*, 1960, 147.

² Eaborn, "Organosilicon Compounds," Butterworths, London, 1960.

³ Haszeldine and Young, *Proc. Chem. Soc.*, 1959, 394; Bevan, Haszeldine, and Young, *Chem. and Ind.*, 1961, 789.

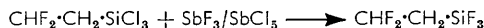
of selected model halogenoalkylsilicon compounds to determine more precisely the mechanisms by which these decompositions proceed. The first compound chosen for study was 2,2-difluoroethyltrifluorosilane, since earlier work⁴ had shown that the decomposition of the polysiloxane $[\text{CHF}_2\cdot\text{CH}_2\cdot\text{SiO}_{1.5}]_n$ involves the elimination of 2-fluorine to give vinyl fluoride.

EXPERIMENTAL

Apparatus.—The Pyrex reaction vessel (20×4.5 cm. i.d.) was enclosed in an electric furnace and connected to a conventional vacuum system by a ground-glass joint. Gases were admitted from a 1-l. expansion bulb, which was also used for the preparation of mixtures when the effect of additives was being studied. Samples of the reaction mixture for analysis were condensed into a 150-ml. bulb cooled to -196° . The pressure change during reaction was followed with a constant-volume mercury manometer fitted with a float valve⁵ and electrical contacts. The mercury level in the manometer was maintained at the required level by regulating the pressure in the mercury reservoir with a fine control.⁶ The dead-space between the reaction vessel and manometer (2.2%) was kept to a minimum by the use of capillary tubing. The furnace was controlled by a Sunvic RT2 temperature controller and platinum resistance thermometer, and the temperature was measured with calibrated chromel-alumel thermocouples. At 250° , the temperature of the furnace varied by $\pm 0.15^\circ$ over 80% of the length of the reaction vessel and by $\pm 0.3^\circ$ over the whole length. The temperature at a given point in the furnace did not vary by more than 0.2° during an experiment.

Analysis of reaction mixtures was carried out by a combination of fractional condensation and chemical absorption in a series of small traps and absorption tubes connected to a gas burette. The volumes of these traps were only a few ml., and gas samples of about 1 ml. at s.t.p. could thus be analysed. A sample was measured in the gas burette and separated into reactant and product fractions by distillation *in vacuo* through a trap cooled to -95° . The two fractions were individually measured after a second, precautionary, distillation. The silicon tetrafluoride in the product fraction was then absorbed by passing the gas several times through a tube containing solid sodium hydroxide. Finally, the residual gas, pure vinyl fluoride, was dried and measured. With mixtures of known composition this technique gave an accuracy of $\pm 1\%$ for each component.

Materials.—2,2-Difluoroethyltrifluorosilane was prepared by the following reaction:



Trichloro-2,2-difluoroethylsilane⁴ (47.2 g., 237 mmoles) was passed repeatedly, in the vapour phase, through a horizontal glass tube (30×2.5 cm. i.d.) packed with antimony trifluoride (50 g.) dispersed between glass-wool plugs and moistened with antimony pentachloride (1 ml.). Heat was evolved and some blackening of the solid occurred. After six passes the unreacted material, separated by fractional condensation, was passed six times through a second tube packed in the same way. The remaining unreacted material was again separated and passed six times through a third tube. Distillation of the combined liquid products through a packed column, followed by repeated trap-to-trap distillation in a conventional apparatus for the manipulation of volatile compounds, gave analytically and tensimetrically pure 2,2-difluoroethyltrifluorosilane (29.4 g., 196 mmoles, 83%) (Found: C, 16.0; H, 1.9%; *M*, 150. $\text{C}_2\text{H}_3\text{F}_5\text{Si}$ requires C, 16.0; H, 2.0%; *M*, 150). Its vapour pressure in the range $8\text{--}46^\circ$ is given by the equation $\log_{10} p$ (mm.) = $7.839 - 1581/T$, whence the b. p. is calculated as 45.7° , the latent heat of vaporisation as 7.20 kcal. mole⁻¹, and the Trouton constant as 22.5 cal. mole⁻¹ deg.⁻¹. Its infrared and nuclear magnetic resonance spectra were consistent with the proposed structure.

Cyclohexene, purified by fractionation from sodium wire, had b. p. 82.8° , n_D^{23} 1.4449 [lit.,⁷ b. p. $82.7\text{--}83.2^\circ$, n_D^{23} 1.4448 (interpolated)]. Impurities could not be detected by infrared spectroscopy.

⁴ Bell, Haszeldine, Newlands, and Plumb, unpublished results.

⁵ Dodd and Robinson, "Experimental Inorganic Chemistry," Elsevier, Amsterdam, 1954, p. 122.

⁶ Barr and Anhorn, *Instruments*, 1947, **20**, 716.

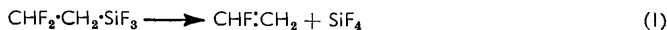
⁷ Timmermans, "Physicochemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950, p. 205.

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Nitric oxide,⁸ purified by repeated trap-to-trap distillation, showed no impurities on infrared spectroscopic examination.

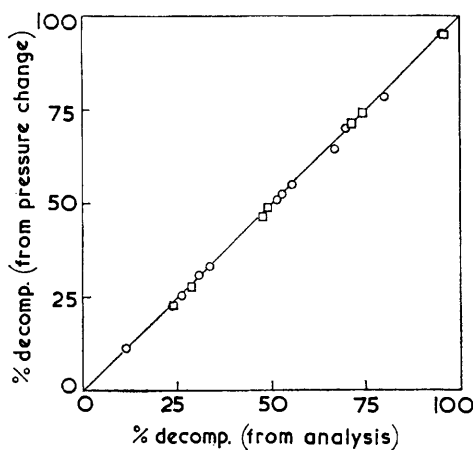
RESULTS

The variation in pressure during the reaction was completely reproducible; no ageing effect was observed and no surface deposits were apparent in the reaction vessel even after many runs. The ratio (p_{∞}/p_0) of final to initial pressure was nearly 2 (mean value 1.951, standard deviation of the mean 0.004), and the difference between the experimental value and the value 2.0 expected for the reaction



is satisfactorily accounted for by the dead-space in the apparatus.

The products of reaction were always completely condensable at -196° , and infrared analysis showed that the reaction mixture at any time contained only unchanged reactant, vinyl fluoride, and silicon tetrafluoride. Chemical analysis showed that the two products were always present in equal amounts. The extent of reaction measured by chemical



Comparison of the extent of decomposition found by analysis with that calculated from pressure changes.

○, ca. 160°; □, ca. 210°.

analysis was in excellent agreement with that calculated from the pressure change on the basis of reaction (1), and the comparison is illustrated in the Figure. These results confirm the simple nature of the reaction and justify the use of pressure measurements to follow the course of the reaction.

The reaction was kinetically of the first order; plots of $\log(\text{pressure of reactant})$ against time were linear up to at least 75% decomposition, and the deviations from linearity towards the end of the reaction can be explained quantitatively in terms of the dead-space in the apparatus, using the correction suggested by Allen.⁹ In agreement with the first-order nature of the reaction, the first-order rate constants, obtained from the logarithmic plots were statistically independent of pressure from 10 to 180 mm. initial pressure.

The reaction, studied over the temperature range $151\text{--}221^\circ$, gave the rate constants summarised in Table 1. The plot of $\log(\text{rate constant})$ against $1/T$ ($^\circ\text{K}^{-1}$) is accurately linear, and corresponds to the Arrhenius equation:

$$\log_{10} k(\text{sec.}^{-1}) = (12.27 \pm 0.27) \exp [-(32,720 \pm 530)/4.576T] \quad (2)$$

where the error limits are the statistical 95% confidence limits.

⁸ Noyes, *J. Amer. Chem. Soc.*, 1931, **53**, 514.

⁹ Allen, *J. Amer. Chem. Soc.*, 1934, **56**, 2053.

TABLE 1.

Mean first-order rate constants, \bar{k} .									
Temp. (°C)	No. of runs	Initial press. (mm.)	$10^5\bar{k}$ (sec. ⁻¹)	$10^5\sigma(\bar{k})$ * (sec. ⁻¹)	Temp. (°C)	No. of runs	Initial press. (mm.)	$10^5\bar{k}$ (sec. ⁻¹)	$10^5\sigma(\bar{k})$ * (sec. ⁻¹)
151.0	5	21—130	2.49	0.03	201.0	5	21—132	149	5
161.0	9	20—138	6.03	0.07	211.0	8	11—128	310	8
171.0	6	21—151	14.6	0.1	212.7	6	17—177	346	9
181.0	12	11—160	33.3	0.8	221.0	13	21—157	629	14

* $\sigma(\bar{k})$ is the estimated standard deviation of \bar{k} (the first-order rate constant) in a large number of determinations.

When the surface : volume ratio of the reaction vessel was increased 8.5 times, by using a vessel packed with Pyrex tubes, a slight increase in the rate constant was observed. The reaction in the packed vessel was still accurately first-order, and the first-order rate constants are compared in Table 2 with those obtained in the unpacked vessel. The increase in rate constant is significant and presumably, therefore, there is a small heterogeneous component of the reaction in the unpacked Pyrex vessels. However, in the unpacked vessel this could not account for more than 1—2% of the reaction, and the overall process is essentially homogeneous. This is confirmed by the absence of ageing effects and of surface deposits.

TABLE 2.

Comparison of mean rate constants, \bar{k} , in the packed and unpacked reaction vessels.

Temp. (°C)	Reaction vessel	Number of runs	Initial pressures (mm.)	$10^5\bar{k}$ (sec. ⁻¹)	$10^5\sigma(\bar{k})$ (sec. ⁻¹)
161.0	Packed	4	22—122	6.81	0.25
161.0	Unpacked	9	20—138	6.03	0.07
211.0	Packed	4	26—95	366	18
211.0	Unpacked	8	11—128	310	8

The reaction was also studied in the presence of nitric oxide or cyclohexene, at temperatures from 151 to 211°, initial pressures of reactant from 21 to 119 mm., and with pressures of inhibitor varying from 24 to 104% of the initial pressure of reactant. The reaction was still accurately first-order, and the rate constants (Table 3) were not significantly different from those for the uninhibited reaction. Evidently these inhibitors have no effect on the reaction under the conditions studied.

TABLE 3.

Comparison of mean rate constants, \bar{k} , in the presence and absence of inhibitors.

Temp. (°C)	Number of runs	Initial pressures of reactant (mm.)	Nature and amount * of inhibitor	$10^5\bar{k}$ (sec. ⁻¹)	$10^5\sigma(\bar{k})$ (sec. ⁻¹)
151.0	5	30—116	25—101% nitric oxide	2.53	0.03
151.0	5	21—130	None	2.49	0.04
161.0	3	22—97	33—96% cyclohexene	6.01	(0.13)
161.0	9	20—138	None	6.03	0.07
211.0	5	21—112	24—104% nitric oxide	307	7.8
211.0	2	22—119	33—97% cyclohexene	311	(3)
211.0	8	11—128	None	310	7.7

* Expressed as percentage of the initial pressure of reactant.

DISCUSSION

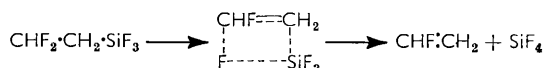
It has been shown that the gas-phase thermal decomposition of 2,2-difluoroethyltrifluorosilane into vinyl fluoride and silicon tetrafluoride is first-order at temperatures from 151 to 221° and pressures from 10 to 180 mm. The reaction is essentially homogeneous and is completely unaffected by the addition of nitric oxide or cyclohexene. The first-order rate constant is given by equation (2).

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In general, there are three types of mechanism by which homogeneous thermal decompositions may proceed: radical-chain, radical non-chain, and molecular processes. In the present case, however, a radical-chain mechanism is clearly not operative, since the rate of reaction is not affected by the addition of nitric oxide or cyclohexene, which are well known to be powerful inhibitors of radical-chain processes.

A radical non-chain process has an overall activation energy equal to the dissociation energy of the bond broken in the first and rate-controlling step of the reaction. The dissociation energies of the bonds in 2,2-difluoroethyltrifluorosilane will be similar in magnitude to the corresponding thermochemical bond-energy terms,¹⁰ *i.e.*, C-H 99, C-F 116, C-C 83, Si-C 76, and Si-F 135 kcal. mole⁻¹; although they may differ slightly from these values, it is unlikely that the dissociation energy of the weakest bond will be much less than 70 kcal. mole⁻¹. The activation energy of any possible radical non-chain process would thus be of the order of 70 kcal. mole⁻¹, and, since the observed activation energy is only 32.7 kcal. mole⁻¹, it is concluded that the decomposition is not a radical non-chain process.

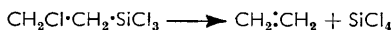
The decomposition of 2,2-difluoroethyltrifluorosilane is therefore considered to be a unimolecular process involving a four-centre transition state:



and such a mechanism is consistent with all the experimental observations. It accounts for the first-order kinetics and for the independence of rate constant on pressure; the Lindemann fall-off of the rate constant is likely to be small at a pressure of 10 mm. for a molecule of the complexity of 2,2-difluoroethyltrifluorosilane. The observed activation energy is not unreasonable for a process of this type, although the pre-exponential factor [$\log_{10} A$ (sec.⁻¹) = 12.27] is rather higher than that [$\log_{10} A = 9.0-11.5$] usually found¹¹ for a unimolecular reaction in which the transition state is a ring of four heavy atoms. Thus, the entropy of activation ($\Delta S^\ddagger = -5.4$ cal. mole⁻¹ deg.⁻¹) is less negative than the usual value for reactions of this type ($\Delta S^\ddagger = -9$ to -20 cal. mole⁻¹ deg.⁻¹).

This can be explained in terms of some restriction to free rotation within the molecule. A model of the molecule suggests that the bulky nature of the SiF₃ group and the electrostatic interactions within the molecule will produce abnormally high energy barriers to rotation about the C-C and C-Si bonds. As a result, the loss of rotational entropy on formation of the transition state will be less than usual, and the pre-exponential factor will be correspondingly higher than usual.

It is clear, therefore, that when the halogenoalkyl group in a halogenoalkylsilane contains a fluorine atom on the 2-carbon atom, the thermal decomposition can proceed very easily by a unimolecular process. During the course of the present work results were reported¹² for a kinetic study of the thermal decomposition of trichloro-2-chloroethylsilane, where the predominant reaction:



is believed to be a homogeneous unimolecular process, also involving a four-centre transition state. It thus appears that this type of mechanism may be a general type for 2-halogenoalkylsilanes.

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¹⁰ Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 2nd edn., 1958, pp. 270-280.

¹¹ Trotman-Dickenson, "Gas Kinetics," Butterworths, London, 1955, p. 133.

¹² Davidson, *Chem. and Ind.*, 1960, 1107.