The Kinetics of the Reactions of Silicon Compounds. Part VIII.[1] The Gas-phase Thermal Decomposition of Trifluoro-1,1,2,2-Tetrafluoroethylsilane

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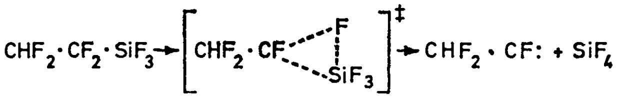
The gas-phase thermal decomposition of trifluoro-1.1.2.2-tetrafluoroethylsilane at 140—200 °C and 20—150 Torr initial pressure is a first-order reaction with a rate constant which is independent of pressure and of the nature and extent of the surface. and is given by equation (i). The rate-determining step (ii) is concluded to be the unimolecular

$$\log_{10} k/\mathrm{s}^{-1} = (13{\cdot}11 \pm 0{\cdot}10) - (137{\cdot}8 \pm 0{\cdot}9)\ \mathrm{kJ\ mol^{-1}}/2{\cdot}303\,RT \qquad \text{(i)}$$

transfer of α-fluorine to silicon by a three-centre transition state to give tetrafluorosilane and difluoromethylfluorocarbene. In the absence of other compounds the carbene isomerises quantitatively to trifluoroethylene. but in the presence of additives. or in the later stages of the reaction. it may undergo characteristic reactions. such as addition to olefins to give cyclopropane derivatives. or insertion into the SiH bond in trimethylsilane. The decomposition of reactant proceeds at the same rate independently of the presence of the additives. and this observation. together with the nature of the products formed. indicates clearly the two-step nature of the reaction. The reaction with trimethylsilane gave up to 95% of insertion product. demonstrating the virtual absence of any β-elimination.

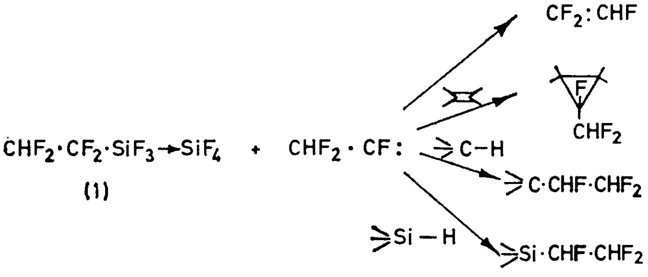


(ii)

EARLIER papers in this series have dealt largely with the decompositions of 2,2-difluoroethylsilicon compounds by β-fluorine elimination.[1-4] The reactant in the present study, trifluoro-1,1,2,2-tetrafluoroethylsilane (1), contains fluorine atoms in the β-position and might therefore decompose by a similar four-centre molecular elimination reaction. On the other hand α-elimination to give a carbene is also possible, as was proposed earlier for other α-fluoroalkylsilicon compounds, *e.g.* equations (1) and (2).[5] Preliminary kinetic studies [6] confirmed the formation of difluoromethylfluorocarbene from (1). In the absence of additives the carbene reacted mainly by isomerisation to trifluoroethylene, but in the presence of added hydrocarbon olefins it also added to the double bonds to give cyclopropane derivatives. More recently, the carbene has been reported to insert into C–H [7] and Si–H [8] bonds. The reactions are summarised in Scheme 1.

$$\mathrm{CFCl_2{\cdot}CF_2{\cdot}SiCl_3} \longrightarrow \mathrm{SiFCl_3} + \mathrm{CFCl_2{\cdot}CF\colon} \longrightarrow \mathrm{CFCl{:}CFCl} \qquad (1)$$

$$\mathrm{CH_2F{\cdot}CF_2{\cdot}SiF_3} \longrightarrow \mathrm{SiF_4} + \mathrm{CH_2F{\cdot}CF\colon} \longrightarrow \mathrm{CHF{:}CHF} \qquad (2)$$



SCHEME 1

We now report the results of a detailed kinetic investigation which has confirmed these overall features and provided detailed information about the primary decomposition reaction. Studies of the secondary reactions involving the carbene will be reported later.

EXPERIMENTAL

The apparatus was similar to that described previously.[3] Since the Arrhenius parameters obtained in this work differed somewhat from those in the preliminary report,[6] particular care was taken in the calibration of thermocouples and in checking the calibrations at 140—340 °C against two independently calibrated thermocouples. As a further check, a brief reinvestigation of the decomposition of 2,2-difluoroethylmethyldifluorosilane at 189—224 °C gave $\log_{10}(A/\mathrm{s}^{-1}) = 11{\cdot}31$ and $E = 136{\cdot}4$ kJ mol^{-1} compared with the previously reported values [3] of 11·32 and 136·2 kJ mol^{-1} respectively.

Analysis of reaction mixtures was by g.l.c. using a 6 m column of 6 wt. % Kel-F 10 on Teflon at 25 °C, and katharometric detection. Analyses of synthetic mixtures showed the techniques to be accurate to within 1 or 2% for most of the compounds present. The addition and insertion products (2)—(4) suffered substantial losses during transfer and analysis, however, and these were preferably estimated by difference.

Materials.—Trichloro-1,1,2,2-tetrafluoroethylsilane [9] (250 g, 1·06 mol), allowed to react with antimony trifluoride (280

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[1] Part VII, D. Graham, R. N. Haszeldine, and P. J. Robinson, *J. Chem. Soc.* (*B*), 1971, 611.

[2] R. N. Haszeldine, P. J. Robinson, and R. F. Simmons, *J. Chem. Soc.*, 1964, 1890.

[3] D. Graham, R. N. Haszeldine, and P. J. Robinson, *J. Chem. Soc.* (*B*), 1969, 652.

[4] R. N. Haszeldine, P. J. Robinson, and J. A. Walsh, *J. Chem. Soc.* (*B*), 1970, 578; G. Fishwick, R. N. Haszeldine, P. J. Robinson, and R. F. Simmons, *ibid.*, p. 1236.

[5] R. N. Haszeldine and J. C. Young, *Proc. Chem. Soc.*, 1959, 394; W. Bevan, R. N. Haszeldine, and J. C. Young, *Chem. and Ind.*, 1961, 789; R. N. Haszeldine, 'Polyfluoroalkyl Silicon Compounds,' in 'New Pathways in Inorganic Chemistry,' eds. E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Cambridge University Press, Cambridge, 1968, p. 115.

[6] G. Fishwick, R. N. Haszeldine, C. Parkinson, P. J. Robinson, and R. F. Simmons, *Chem. Comm.*, 1965, 382.

[7] R. N. Haszeldine and J. G. Speight, *Chem. Comm.*, 1967, 995.

[8] R. N. Haszeldine, A. E. Tipping, and R. O'B. Watts, *Chem. Comm.*, 1969, 1364.

[9] R. N. Haszeldine and R. J. Marklow, *J. Chem. Soc.*, 1956, 962.

g, 1·5 mol) in a manner similar to that described [2] for the preparation of 2,2-difluoroethyltrifluorosilane, gave *trifluoro*-1,1,2,2-*tetrafluoroethylsilane* (156 g, 0·84 mol, 79%) (Found: C, 13·0; H, 0·5%; *M*, 187. C_2HF_7Si requires C, 12·9; H, 0·5%; *M*, 186), with a vapour pressure in the range −41 to −20 °C given by the equation $\log_{10}(p/\text{Torr}) = 7{\cdot}693 - 1292/(T/\text{K})$, corresponding to a normal boiling point of 268·5 K, a latent heat of vaporisation of 24·77 kJ mol^{-1}, and a Trouton constant of 92·5 J mol^{-1} K^{-1} (22·1 cal mol^{-1} K^{-1}).[10] The i.r. spectrum (Perkin-Elmer model 21) showed main bands at 651m, 797m, 870vs, 907m, 1016vs, 1049s, 1083s, 1126vs, 1209s, 1287m, 1344s, 1379s, and 2994m cm^{-1}. The n.m.r. spectra (Perkin-Elmer R10, neat liquid; assignments, shifts, band structures, and derived coupling constant moduli in Hz given) were consistent with structure (1); $H{-}CF_2{-}CF_2{-}SiF_3$ was partially analysed as an X AA′ PP′ K_3 system and gave the following data. ^{1}H Spectrum: X, 1·35 p.p.m. to high field of external benzene reference [τ(Me_4Si) 5·77], ttq, *J*(XA) 54·9, *J*(XP) 4·5, *J*(XK) 2·5. ^{19}F Spectrum [' deceptively simple ', *J*(AP) + *J*(AP′) *ca.* 6 $\leqslant$ *J*(AA′), *J*(PP′)]: P,P′, 54·5 p.p.m. to high field of external trifluoroacetic acid, ' qdt ', *J*(PK) 5·4, *J*(PX) 4·5; A,A′ 57·4 p.p.m., ' dtq ', *J*(AX) 54·2, *J*(AK) 2·7; K, 71·6 p.p.m., complex band interpreted as ttd, *J*(KP) 5·4, *J*(KA) 2·6, *J*(KX) 2·3.

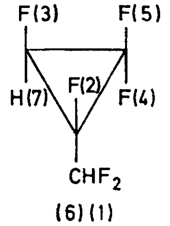
TABLE 1

N.m.r. spectra of *cis*-(2) and *trans*-(2)

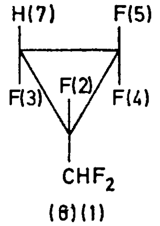
Nucleus	Chemical shift [a]	Band structure	Coupling constants to nuclei: 2	3	4	5	6	7
cis-(2)								
F(1)	53·9	*ca.* dt [b]	10·4	2·4	9·8	3·0	54·1	0·6
F(2)	153·2	Complex		17·7	2·1	4·1	6·2	*ca.* 0
F(3)	170·4	ddd [b]			7·4	2·1	1·5	56·2
F(4)	69·8	AB [b]				209	0·8	11·8
F(5)	81·8						*ca.* 0	0·9
H(6)	0·84	*ca.* tddt						1·0
H(7)	1·97	dd [b]						
trans-(2):								
F(1)	55·9	d [b]				5·7	51·3	1·6
F(2)	148·7	Complex				8·7 and 5·7	14·6	18·2
F(3)	162·6	d [b]					1·8 and 1·5	55·6
F(4)	77·7	AB [b]				211		1·6
F(5)	71·7						*ca.* 0	11·2
H(6)	0·84	tdt						*ca.* 0
H(7)	1·86	dddq						

[a] P.p.m. to high field of external benzene or trifluoroacetic acid. [b] With complex further splitting.

Pyrolysis of trifluoro-1,1,2,2-tetrafluoroethylsilane at 150 °C for 24 h in the presence of trifluoroethylene (see later), followed by fractional condensation and g.l.c. separation (10 m Kel-F 10 on Celite at 25 °C) gave cis- and trans-1-*difluoromethyl*-1,2,2,3-*tetrafluorocyclopropane* [*cis*-(2) and *trans*-(2)] [Found for *cis*-(2): *M*, 163; for *trans*-(2): *M*, 162. $C_4H_2F_6$ requires *M*, 164]. The i.r. spectra were similar: *cis*-(2) $\nu_{\max.}$ 685s, 710m, 760s, 813m, 834s, 880m, 940s, 1000w, 1040m, 1110vvs, 1160m, 1175vs, 1200vs, 1225vs, 1260m, 1320s, 1340w, 1400s, 1490s, 1720w, and 2930m; *trans*-(2) 716s, 810s, 840s, 962s, 1000w, 1030w, 1100vvs, 1150vs, 1250vs, 1290vs, 1340m, 1390s, 1480m, 1710w, and 2930w cm^{-1}. The main evidence for structure came from the n.m.r. spectra, which were approximately first order (particularly in the case of the *cis*-isomer), and were analysed on this basis to give the partial interpretation shown in Table 1.[11] Thus the compound designated *trans*-(2) correctly [12,13] showed two large *cis*-H, F couplings (J_{27} and J_{57}) whereas the *cis*-compound showed only one (J_{47}). The large magnitudes of the geminal H(7), F(3) and F(4), F(5) couplings are characteristic of the cyclopropane ring structure. The chemical shifts of F(4) and F(5) were consistent with the values predicted from the known [12] deshielding effects of substituents [calc. for *cis*-(2): δ_4 = 67·8, δ_5 = 81·9; calc. for *trans*-(2) δ_4 = 79·3, δ_5 = 70·4 p.p.m., *cf.* observed values 69·8, 81·8, 77·7, and 71·7 p.p.m. respectively].



cis-(2)



trans-(2)

Decomposition of 1,1,2,2-tetrafluoroethyltrifluorosilane in the presence of propene at 144—177 °C similarly gave a mixture of cis- and trans-1-*difluoromethyl*-1-*fluoro*-2-*methylcyclopropane* (3) (Found: C, 48·6; H, 5·8%; *M*, 124. $C_5H_7F_3$ requires C, 48·4; H, 5·7%; *M*, 124), $\nu_{\max.}$ 725m, 750m, 795m, 825m, 881m, 909m, 940m, 995m, 1031s, 1093vs, 1163m, 1212m, 1242m, 1289m, 1353m, 1385m, 1420s, 1460m, 2915m, 2994s, and 3049m cm^{-1}. The n.m.r. spectra [14] verified the structure and showed the isomers to be present in the ratio *trans* : *cis ca.* 2 : 3.

Decomposition of trifluoro-1,1,2,2-tetrafluoroethylsilane in the presence of trimethylsilane similarly gave trimethyl-1,2,2-trifluoroethylsilane (4) (Found: *M*, 154. Calc. for $C_5H_{11}F_3Si$: *M*, 156), $\nu_{\max.}$ 679w, 704m, 758m, 766m, 779m, 848vs, 909m, 965m, 1008s, 1045m, 1070s, 1143s, 1212w,

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[10] Results obtained by G. Fishwick.

[11] We thank M. G. Barlow for comments on the n.m.r. spectra.

[12] M. G. Barlow and F. P. Temme, to be published.

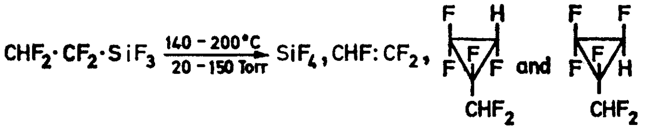
[13] P. B. Sargeant, *J. Org. Chem.*, 1970, **35**, 678.

[14] J. Lee, C. Parkinson, P. J. Robinson, and J. G. Speight, *J. Chem. Soc.* (*B*), 1967, 1125.

1256s, 1316w, 1361m, 1385m, 1393m, 1418w, 1457w, 2924m, and 3003m cm^{-1}. The main structural evidence was again from the n.m.r. spectra for which CHFF–CHF–Si(CH$_3$)$_3$ was analysed as a PAB XG K$_9$ system. ^{1}H Spectrum: P, 0·85 p.p.m., tdd, J(PA) = J(PB) = 55·4, J(PG) = 10·5, J(PX) = 4·2; X, 2·38 p.p.m., dtd, J(XG) 46·5, J(XA) = J(XB) = 18·2, J(XP) 4·2; K, 6·61 p.p.m., complex. ^{19}F Spectrum: G, 166·4 p.p.m., dtd, J(GX) 45·7, J(GA) = J(GB) = 17·2, J(GP) = 10·4; AB, 47·8 p.p.m., AB pattern (outer bands not observed) of dt, J(AP) = J(BP) = 55·9, J(AX) = J(BX) = J(AG) = J(BG) = 17·2.

RESULTS

The gas-phase decomposition of trifluoro-1,1,2,2-tetrafluoroethylsilane was investigated in the temperature range 140—200 °C and pressure range 20—150 Torr.* G.l.c. analysis showed five components identified in order of elution as tetrafluorosilane, trifluoroethylene, trifluoro-1,1,2,2-tetrafluoroethylsilane [reactant (1)] and the *trans*- and *cis*-isomers of 1-difluoromethyl-1,2,2,3-tetrafluorocyclopropane (2) (Scheme 2).



trans-(2) *cis*-(2)

SCHEME 2

The variation in pressure during the reaction was completely reproducible, no ageing effect being observed. The ratio p_∞/p_0 of final to initial pressure was a linear function of the final ratio ([CHF:CF$_2$]/[SiF$_4$])$_\infty$ (see Figure 1), according to equation (3); this would be expected from the stoicheiometric equation (4), in which $C_4H_2F_6$ represents the cyclopropanes (2) illustrated above.

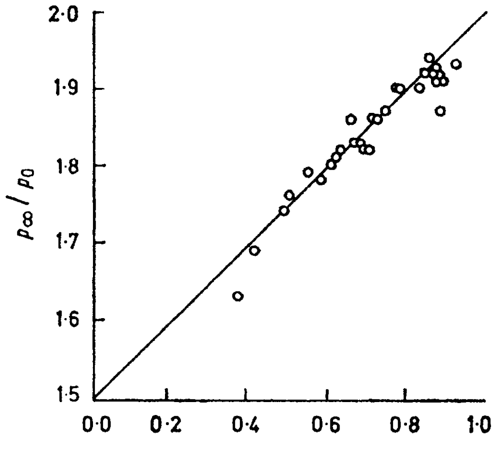


FIGURE 1 Correlation of final pressure with final product analysis; the solid line corresponds to equation (3)

$$p_\infty/p_0 = 1\cdot5 + 0\cdot5\,([CHF{:}CF_2]/[SiF_4])_\infty \quad (3)$$

$$CHF_2{\cdot}CF_2{\cdot}SiF_3 \longrightarrow SiF_4 + xCHF{:}CF_2 + \tfrac{1}{2}(1 - x)C_4H_2F_6 \quad (4)$$

The stoicheiometry suggested by the overall pressure change was confirmed by g.l.c. during the course of reactions. Figure 2 shows that (*a*) the amount of tetrafluorosilane formed, and (*b*) the amount of trifluoroethylene plus twice the amount of (2) formed, at any time during the reaction, are equal to each other and to the amount of (1) decomposed. Thus the reaction is correctly represented by equation (4).

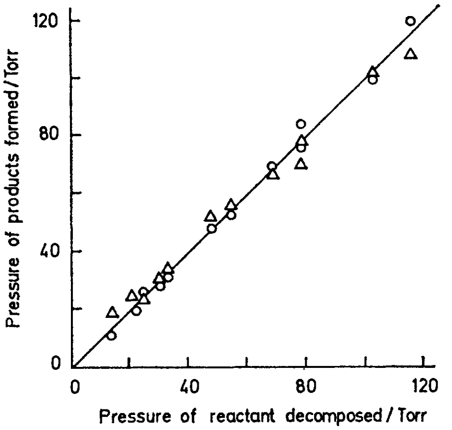


FIGURE 2 Plot to demonstrate stoicheiometry of equation (4); ○, SiF$_4$ formed; △, CHF:CF$_2$ formed plus 2 × cyclopropane (2) formed

Careful analysis in the early stages of the reaction at 139 and 189 °C showed that the cyclopropanes were secondary products, since the ratio ([CHF:CF$_2$]/[SiF$_4$])$_t$ was unity for at least the first 15—20% reaction, *i.e.* $x = 1$ in the early stages.

The consumption of reactant was found to be kinetically first order. Two methods were used for obtaining kinetic data, the first based on measurement of the pressure change and the second on g.l.c. analysis for reactant. Rate constants from the pressure change were obtained from the initial slopes of plots of log $(2p_0 - p)$ against time. Such plots were linear in the early stages where the decomposition proceeded cleanly to give tetrafluorosilane and trifluoroethylene, but were significantly curved after a half-life when cyclopropane formation was evident. The rate constants obtained were independent of initial pressure over a wide range, and are summarised in Table 2.

The analytical results were used to obtain kinetic data by means of equation (5) (in which R = reactant), since it has already been shown that $[R]_t = [R]_0 - [SiF_4]_t$, and the analytical technique provided concentration ratios more accurately than absolute values. Plots of log $([R]_0/[R]_t)$

$$[R]_0/[R]_t = 1 + ([SiF_4]/[R])_t \quad (5)$$

against time were linear, and first-order rate constants calculated as $(1/t)\ln([R]_0/[R]_t)$ were independent of initial pressure and constant up to at least three half-lives at 190 °C and two half-lives at 160 °C. The results are again summarised in Table 2. The analytical rate constants are consistently a little higher than those from pressure measurements, but the agreement is generally good.

The rate constants obtained by the two methods varied with temperature according to the Arrhenius equations (6) and (7), in which the error limits are the 95% confidence

$$\log_{10}(k/\mathrm{s}^{-1}) = (13\cdot26 \pm 0\cdot10) - (139\cdot2 \pm 0\cdot9)\ \mathrm{kJ\ mol^{-1}}/2\cdot303RT \quad (6)$$

$$\log_{10}(k/\mathrm{s}^{-1}) = (13\cdot02 \pm 0\cdot14) - (137\cdot0 \pm 1\cdot2)\ \mathrm{kJ\ mol^{-1}}/2\cdot303RT \quad (7)$$

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* 1 Torr = (101·325/760) kN m^{-2}.

TABLE 2

Average first-order rate constants $\bar{k}$ from pressure measurements and from g.l.c. analysis (some, but not all, runs were treated in both ways)

	log $(2p_0 - p)$ plots				G.l.c. analysis			
T/K	No. of runs	p_0/Torr	$10^5\bar{k}$/s^{-1}	$10^5\hat{\sigma}(k)$/s^{-1}	No. of runs	p_0/Torr	$10^5\bar{k}$/s^{-1}	$10^5\hat{\sigma}(k)$/s^{-1}
412·0	7	39—151	4·0	0·3	9	39—100	4·4	0·3
421·7	7	39—153	10·4	0·5	7	40	11·2	0·2
432·7	15	37—149	29·1	0·7	25	37—149	31·7	1·3
443·4	4	37—148	73·9	2·2				
452·0	5	20—147	150	5				
462·6	19	17—147	351	14	13	40	358	20
471·2	6	34—91	661	33	5	38	665	56

$\hat{\sigma}(k)$ Is the estimated standard deviation of k in a large number of runs.

limits, for the pressure change and g.l.c. results respectively. The A factors and activation energies obtained by the two methods differ by more than can be attributed to random fluctuations, but the differences are small by physical standards. A complete least-mean-squares treatment of all the results together, while not strictly justifiable statistically, gave equation (8) which can reasonably be regarded as the correct Arrhenius equation for the reaction.

$$\log_{10}(k/\text{s}^{-1}) = (13{\cdot}11 \pm 0{\cdot}10) - (137{\cdot}8 \pm 0{\cdot}9)\ \text{kJ mol}^{-1}/2{\cdot}303RT \quad (8)$$

Effect of Surfaces.—The nature and extent of the reaction vessel surface was varied without any effect on the product distribution or the rate of decomposition of trifluoro-1,1,2,2-tetrafluoroethylsilane. The reaction vessels used were: I, unpacked Pyrex, with $S/V = 0{\cdot}9$ cm^{-1}; II, packed Pyrex, with $S/V = 16{\cdot}6$ cm^{-1}; III, unpacked Pyrex, coated with carbon by three pyrolyses of chloroethane at 500 °C with initial pressures of 50 Torr and reaction times of 30 min; and IV, unpacked Pyrex, rinsed with aqueous hydrogen fluoride (40 wt. %) followed by rinses with distilled water; this last vessel was the one used for the bulk of the work as described above. Some rate constants obtained from the decompositions carried out in vessels I—IV are compared in Table 3, and some analytical results from I—III in Table 4. The results in the different vessels are indistinguishable, virtually eliminating the possibility of the involvement of the surface in either the primary or the secondary reactions occurring.

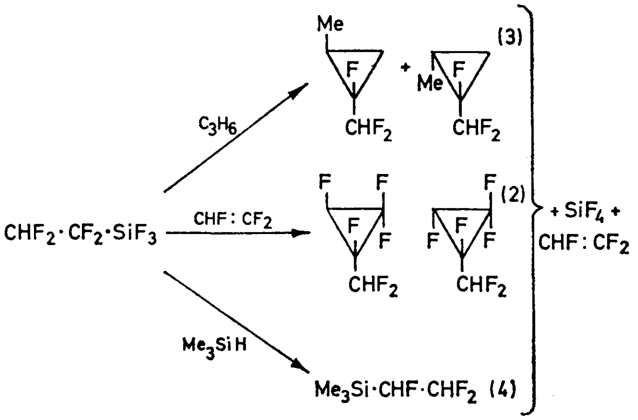
TABLE 3

Comparison of rate constants in different vessels

		$10^5\bar{k}$/s^{-1} (No. of runs in parentheses)			
T/K	p_0/ Torr	Vessel I	Vessel II	Vessel III	Vessel IV
462·6	40	344	334(2)		350(9)
	40 [a]	348(7) [a]	340(4) [a]	350(5) [a]	358(13) [a]
	100	338	345		342(3)
	150	355	343		348(3)
412·0	40	3·97	4·28		4·20(2)
	40 [a]	4·05(6) [a]	4·33(2) [a]		4·32(7) [a]
	150	3·88	3·88		3·87(3)

[a] Rate constants from g.l.c.; others are from pressure change.

Effect of Additives.—The reaction is thus homogeneous and first order, and so far the only indication of any complexity arises from the secondary formation of the cyclopropane derivatives. As noted earlier, however,[6-8] the presence of certain additives caused major changes in the nature of the products, and in the rate of pressure change. In the present investigation detailed studies were made of the reaction in the presence of propene, trimethylsilane, and initially-added trifluoroethylene. In each case the appropriate products shown in Scheme 3 were produced from the start of the reaction in addition to the normal primary products, trifluoroethylene and tetrafluorosilane.



SCHEME 3

Investigations into the product ratios of these reactions will be reported subsequently; in brief the stoicheiometry was shown to be represented in each case by equation (9), in which A represents propene, trifluoroethylene, or trimethylsilane, and [A·C_2HF_3] represents the addition or

$$\text{CHF}_2{\cdot}\text{CF}_2{\cdot}\text{SiF}_3 + (1 - x)\,\text{A} \longrightarrow \text{SiF}_4 + x\,\text{CHF}{:}\text{CF}_2 + (1 - x)\,[\text{A}{\cdot}\text{C}_2\text{HF}_3] \quad (9)$$

insertion products. For present purposes, however, the significant observation is that the rate of consumption of (1) was the same in the presence of these additives as in their absence (Table 5), indicating that the new products are formed in secondary reactions following an initial rate-determining reaction involving $CHF_2{\cdot}CF_2{\cdot}SiF_3$ alone. The inert gases CF_4 and SiF_4 had no effect on the rate or product distribution in the decomposition of (1) alone (Table 5).

TABLE 4

Variation of ([$CHF{:}CF_2$]/[SiF_4])$_t$ with time for runs in vessels I—III at 462·6 K and *ca.* 40 Torr initial pressure

	([$CHF{:}CF_2$]/[SiF_4])$_t$		
t/min	Vessel I	Vessel II	Vessel III
2	0·95	0·93	0·95
4	0·90	0·86	0·87
6	0·84	0·83	0·83
8	0·82	0·81	0·83
∞	0·80	0·79	

TABLE 5

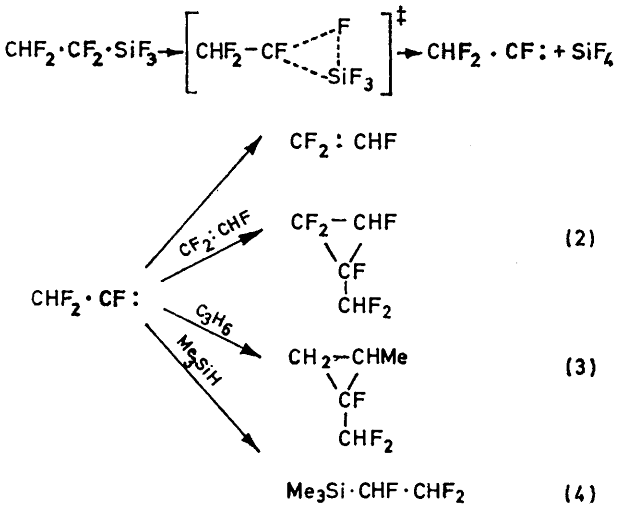
First-order rate constants for disappearance of $CHF_2{\cdot}CF_2{\cdot}SiF_3$ in the presence of additives (by g.l.c. analysis)

T/K	No. of runs	Initial press. reactant/Torr	Additive	$10^5\bar{k}$/s^{-1}	10σ/s^{-1}	$10^5\bar{k}$/s^{-1} No additive [a]
432·0	5	20—150	33—67% C_2HF_3	30·8	0·7	(28·9)
438·7	1	50	33% C_3H_6	51·0		(51·8)
442·1	1	37	33% Me_3SiH	75·4		(69·2)
444·1	1	43	50% Me_3CH	79·2		(81·7)
462·6	9	20—250	33—50% C_2HF_3	398	34	358
462·6	4	20—40	25—50% C_3H_6	395	9	358
462·6	3	33—52	20—33% Me_3SiH	400	7	358
462·6	2	25	SiF_4	378 [b]		358
462·6	3	25	CF_4	375 [b]		358

[a] Values in parentheses are calculated from equation (7). [b] Rate constants from pressure change.

DISCUSSION

Thus the decomposition of trifluoro-1,1,2,2-tetrafluoroethylsilane at 140—200 °C and 20—150 Torr initial pressure is a first-order process whose rate is independent of the extent or nature of the surface or the presence of various additives. In the absence of additives the sole initial products are tetrafluorosilane and trifluoroethylene. In the presence of olefins (*e.g.*, propene) cyclopropane derivatives are formed in addition to trifluoroethylene, and in the presence of certain saturated additives (*e.g.*, trimethylsilane) other products are formed (Scheme 3). Nevertheless the rate of disappearance of trifluoro-1,1,2,2-tetrafluoroethylsilane is the same irrespective of whether additives are present or absent. These observations can only be explained in terms of a two-step mechanism in which the rate-controlling step is the decomposition of the reactant to give a reactive intermediate, with formula C_2HF_3, which undergoes different reactions depending on the conditions. It is also clear from the reaction of this intermediate with olefins to give 1-difluoromethyl-1-fluorocyclopropane derivatives that the intermediate is difluoromethylfluorocarbene (1,2,2-trifluoroethylidene, $CHF_2{\cdot}CF\colon$). Since the decomposition of reactant to give the carbene is first order and homogeneous, it is concluded that it is unimolecular and proceeds by an intramolecular 3-centre transition state, as shown in the overall reaction scheme, Scheme 4.



SCHEME 4

The observed pre-exponential factor, $\log_{10}(A/\mathrm{s}^{-1}) = 13{\cdot}11$, is reasonable for such a process, a 'normal' value being predicted, mainly because no internal rotations are lost on formation of the transition state.[15] The relatively low activation energy (137·8 kJ mol^{-1}), like those for β-fluorine elimination[1-4] (137—154 kJ mol^{-1}), presumably reflects the great strength of the silicon–fluorine bond formed. The rates of α- and β-elimination are in fact very similar for the corresponding compounds $CHF_2{\cdot}CF_2{\cdot}SiF_3$ (1) and $CHF_2{\cdot}CH_2{\cdot}SiF_3$ (5); $k_{1,\alpha}/k_{5,\beta} = 5{\cdot}7$ at 160—210 °C. However, it was clear from the present results in the presence of additives that little if any β-elimination was involved in the decomposition of (1), since the carbene trapping products (3) or (4) were obtained in yields which approached 100% as the pressure of additive was increased. With propene, yields greater than 80% were recorded, with no apparent levelling off as the propene pressure increased, and with trimethylsilane yields up to *ca.* 95% were obtained. Thus although a small amount of β-elimination cannot conclusively be ruled out, the results demonstrate that the decomposition of (1) involves at least 95% α-elimination under the conditions studied.

In the absence of additives the main reaction of the carbene is its isomerisation to trifluoroethylene, and this probably proceeds by hydrogen atom migration (*cf.* $CH_2F{\cdot}CF\colon \longrightarrow CHF{:}CHF$, *etc.*[5,16]), although the present results would be equally consistent with fluorine migration. In the presence of hydrocarbon olefins the main reaction is addition to the olefin, and this contrasts with the behaviour of ethylidene itself, which has been found preferentially to isomerise rather than add to an olefin.[17]

Decomposition of trifluoro-1,1,2,2-tetrafluoroethylsilane in the presence of varying amounts of additive gives varying product ratios which permit a study of the kinetic behaviour and properties of the carbene itself; these results will be reported in a subsequent publication.[18]

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