The Kinetics of the Reactions of Silicon Compounds. Part IX.[1] The Gas-phase Thermal Decomposition of Trimethyl-1,1,2,2-tetrafluoroethylsilane

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The gas-phase thermal decomposition of trimethyl-1,1,2,2-tetrafluoroethylsilane into trifluoroethylene and fluorotrimethylsilane, at temperatures from 300 to 370 °C and with initial pressures from 9 to 197 Torr, is kinetically first order; the rate constant is independent of pressure and surface: volume ratio, and is given by equation (i).

$$\log_{10}(k/\mathrm{s}^{-1}) = (13{\cdot}93 \pm 0{\cdot}22) - (197{\cdot}7 \pm 2{\cdot}5)\ \mathrm{kJ\ mol^{-1}}/2{\cdot}303\,RT \qquad \text{(i)}$$

In the presence of *cis*-but-2-ene the reaction remains first order and the rate of decomposition is unchanged, but two cyclopropanes are now found in the products, having the structures expected for the products of stereospecific addition of the carbene $CHF_2{\cdot}CF\!:$ to *cis*-but-2-ene. It is concluded that the reaction, like the decomposition of trifluoro-1,1,2,2-tetrafluoroethylsilane, involves unimolecular α-fluorine elimination to give fluorotrimethylsilane and difluoromethylfluorocarbene which isomerises to trifluoroethylene or undergoes other characteristic carbene reactions.

In Part VIII[1] kinetic studies were described on the decomposition of trifluoro-1,1,2,2-tetrafluoroethylsilane by α-fluorine elimination to give tetrafluorosilane and difluoromethylfluorocarbene [equation (1)]. The carbene isomerised to trifluoroethylene or could be trapped, *e.g.* by addition to the double bond of an olefin to give a cyclopropane derivative. Similar studies are now reported for the decomposition of trimethyl-1,1,2,2-tetrafluoroethylsilane.

$$CHF_2{\cdot}CF_2{\cdot}SiF_3 \longrightarrow SiF_4 + CHF_2{\cdot}CF\!: \qquad (1)$$

EXPERIMENTAL

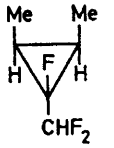
The apparatus was similar to that described previously.[2] Analysis of reaction mixtures was carried out by g.l.c. with katharometric detection. A 4 m column of 30% squalane on Celite at 56 °C was used to separate the products of the decomposition of pure trimethyl-1,1,2,2-tetrafluoroethylsilane. Two columns were used to separate all six components of the reaction mixture when decomposition occurred in the presence of *cis*-but-2-ene. A 1·5 m column of 2% Kel-F 10 oil on alumina at 120 °C separated *cis*-but-2-ene from the other components, and a 3 m column of 30% didecyl phthalate on Celite at 120 °C separated trifluoroethylene, the two *cis*-isomers of 1-difluoromethyl-1-fluoro-2,3-dimethylcyclopropane (see later), and the remaining reactant. A third 2 m column of 30% β,β'-oxydipropionitrile on Celite at 75 °C was used to check the nonappearance of the *trans*-cyclopropane isomer. Straight-line calibration graphs of peak area against sample pressure were constructed for each component of the various reaction mixtures, with the exception of fluorotrimethylsilane and tetrafluorosilane. The former material did not give a straight-line calibration, and the latter was usually absorbed irreversibly by the column packings. Partial pressures of these materials were found by difference.

Materials.—The reactant (1) was prepared by the addition of trimethylsilane to tetrafluoroethylene under the influence of u.v. light [equation (2)]. A number of 350 cm³ silica tubes were each charged with trimethylsilane (3·6 l at S.T.P.; 160 mmol) and tetrafluoroethylene (1·8 l at S.T.P.; 80 mmol), hooded so that only the liquid was visible, and irradiated for periods of 6—66 h at distances of 10—20 cm from a Hanovia Type 6743 500 W mercury resonance lamp. The highest yields (*ca.* 90%) of crude 1 : 1 adduct were found when the tube was 20 cm away from the lamp for only 10 h. The contents of the tubes were fractionally condensed in a vacuum system, and distillation of the combined −72 °C fractions of 15 such irradiations through a 40 cm Podbielniak Helipak column, with a Flexopulse control unit, gave *trimethyl*-1,1,2,2-*tetrafluoroethylsilane*. The characterisation of this compound was reported in connection with a subsequent kinetic investigation of reaction (2) in Part VI.[3]

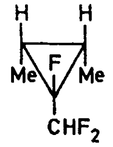
$$SiHMe_3 + C_2F_4 \xrightarrow{\text{u.v.}} \underset{(1)}{CHF_2{\cdot}CF_2{\cdot}SiMe_3} \qquad (2)$$

cis- and *trans*-But-2-ene (Phillips Petroleum Co.) and tetrafluorosilane[4] were purified by fractional condensation and shown by molecular weight measurement, i.r., and g.l.c. to contain negligible amounts of impurity.

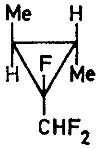
Pyrolysis of trimethyl-1,1,2,2-tetrafluoroethylsilane (8 mmol) and *cis*-but-2-ene (32 mmol) in a 400 cm³ Pyrex tube at 290 °C for 16 h, followed by fractional condensation and preparative g.l.c. (2 m didecyl phthalate on Celite at 120 °C) gave 1α-*difluoromethyl*-1β-*fluoro*-2β,3β-*dimethylcyclopropane* (2a) [24% based on (1) taken] (Found: C, 52·0; H, 6·5%; *M*, 138. $C_6H_9F_3$ requires C, 52·2; H, 6·5%; *M*, 138) and 1α-*difluoromethyl*-1β-*fluoro*-2α,3α-*dimethylcyclopropane* (2b) (9%) (Found: C, 52·1; H, 6·4%; *M*, 138). Pyrolysis of (1) in the presence of *trans*-but-2-ene similarly gave 1α-*difluoromethyl*-1β-*fluoro*-2α,3β-*dimethylcyclopropane* (2c) (Found: C, 52·2; H, 6·6%; *M*, 139).



(2a)



(2b)



(±)(2c)

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[1] Part VIII, R. N. Haszeldine, P. J. Robinson, and W. J. Williams, preceding paper.

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

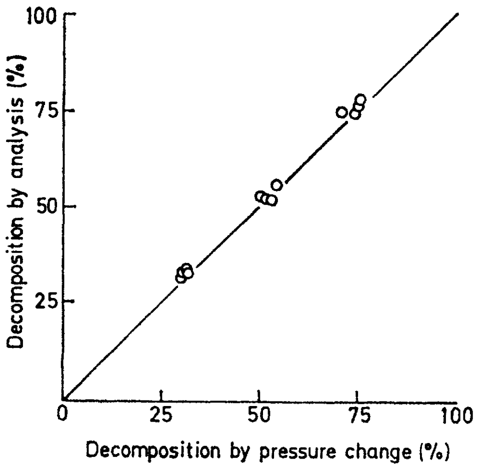
[3] R. N. Haszeldine, S. Lythgoe, and P. J. Robinson, *J. Chem. Soc.* (*B*), 1970, 1634.

[4] C. J. Hoffmann and H. S. Gutowsky, *Inorg. Synth.*, 1953, **4**, 145.

The assignment of structures (2a)—(2c) on the basis of n.m.r. spectra has been described previously.[5] The mass spectra were virtually identical, *m/e* (intensity in %, assignment) 138 (2, parent), 123 (11, $P - CH_3$), 103 (13, $P - CH_3 - HF$), 95 (6, $CHF_2{\cdot}CF{\cdot}CH^+$), 88 (7, $P - 2CH_3 - HF$), 87 (100, $P - CHF_2$), 83 (6, $P - CH_3 - 2HF$), 77 (27, $C_3H_3F_2^+$), 73 (7, $C_4H_6F^+$), 71 (5, $P - CH_3 - CHF_2$), 67 (13, $P - CHF_2 - HF$), 65 (8, $C_5H_5^+$), 61 (21, $C_4H_5F^+$), 59 (100, $CH_3{\cdot}CH{\cdot}CF^+$), 57 (7, $C_3H_2F^+$), 53 (6, $C_4H_5^+$), 52 (6, $C_4H_4^+$), 51 (8, CHF_2^+), 47 (10, $C_2H_3F^+$), 42 (8, $C_3H_6^+$), and 41 (34, $C_3H_5^+$). The i.r. spectra (Perkin-Elmer model 21 spectrophotometer) were also similar but not identical: compound (2a), $\nu_{max.}$ 707s, 785m, 836m, 893s, 940s, 1020vs, 1090vvs, 1130vvs, 1157m(sh), 1226m, 1274vs, 1310m, 1351m, 1387vs, 1410vs, 1470s, 2920m, 2980vs, and 3060m(sh); compound (2b), 786m, 825m, 880m, 1017m, 1086vvs, 1120vvs, 1229m, 1304m, 1410s, 1460m, 2910m, 2980s, and 3050m(sh); compound (2c), 729m, 746m, 831s, 895m, 929s, 997s, 1087vvs, 1109vs, 1212s, 1264m, 1282m(sh), 1413vs, 1465s, 2925m, 2975vs, and 3020vs cm^{-1}.

RESULTS

Preliminary experiments showed decomposition to occur at temperatures above 300 °C to give trifluoroethylene and fluorotrimethylsilane as the only volatile products. Thus the reaction mixtures were completely condensable at −196 °C and i.r. spectroscopy and g.l.c. analysis showed no material other than the reactant and these two products. The variation of pressure during the reaction was reproducible from the first kinetic run, and no surface deposit appeared in the reaction vessel, even after many experiments. The reaction occurring was therefore (3), and as



Decomposition (%) by analysis compared with that from pressure change on the basis of reaction (3) (319 and 352 °C, p_0 = 32 and 96 Torr)

$$CHF_2{\cdot}CF_2{\cdot}SiMe_3 \longrightarrow CHF{:}CF_2 + Me_3SiF \quad (3)$$

expected the ratio of final to initial pressure was always nearly 2 (mean of 17 values 1·94, standard deviation of the mean 0·02). The difference between the experimental value and the ideal value of 2·00 is satisfactorily accounted for by the dead-space in the apparatus.[6] G.l.c. analysis showed that the two products were always present in amounts which were equal to each other and to the pressure of reactant decomposed, and the extent of reaction measured by analysis was in good agreement with that calculated from the pressure change on the basis of reaction (3) (see Figure). Thus the reaction is accurately represented by equation (3), and pressure measurements could be used to follow the course of the reaction. The contrast between this simple reaction and the more complex overall reaction of trifluoro-1,1,2,2-tetrafluoroethylsilane [1] will be discussed later.

Kinetic experiments were carried out at temperatures from 300 to 370 °C and with initial pressures from 9 to 197 Torr.† The reaction was found to be first order throughout. Thus, plots of log (pressure of reactant) against time were linear for at least 50% of the decomposition, and deviations from linearity towards the end of the reaction could be correlated quantitatively to the volume of dead-space in the apparatus.[6] Different runs at the same temperature all gave the same first-order rate constant, irrespective of the initial pressure of reactant.

The rate constants for the reaction are summarised in Table 1. The Arrhenius plot of log (rate constant) against the reciprocal of the absolute temperature was accurately linear, and corresponds to the equation (4) in which the error limits are the statistical 95% confidence limits.

TABLE 1

Mean first-order rate constants $\bar{k}$ for the thermal decomposition of trimethyl-1,1,2,2-tetrafluoroethylsilane

T/K	Number of runs	Initial pressure/ Torr	$10^5\bar{k}/s^{-1}$	$\hat{\sigma}(k)/\bar{k}$ *
573·2	5	10—137	7·99	0·06
581·7	2	51—69	16·1	0·03
591·5	15	22—197	29·8	0·08
597·7	6	13—136	43·9	0·06
605·2	5	10—138	70·5	0·06
625·2	12	12—136	250	0·05
636·8	8	11—154	522	0·09
643·2	5	9—139	764	0·03

* Estimated fractional population standard deviations.

$$\log_{10}(k/s^{-1}) = (13{\cdot}93 \pm 0{\cdot}22) - (197{\cdot}7 \pm 2{\cdot}5)\ kJ\ mol^{-1}/2{\cdot}303\,RT \quad (4)$$

Increasing the surface : volume ratio of the reaction vessel from 1·3 to 17 cm^{-1} by packing it with Pyrex tubing caused no change in the rate of decomposition. Fourteen experiments with initial pressures from 13 to 140 Torr, at temperatures of 318, 340, and 364 °C all gave rate constants (Table 2) which lay within one standard deviation of the mean rate constant for the unpacked vessel experiments. The reaction is therefore completely homogeneous under the conditions studied, a conclusion which is supported by the absence of ageing effects and surface deposits in the vessel.

TABLE 2

Effect of surface : volume ratio

T/K	Number of runs	Initial pressure/ Torr	$10^5\bar{k}/s^{-1}$	
			Packed	Unpacked
591·5	4	36—140	29·9	30·8
614·0	2	64, 96	127	129
637·3	8	13—133	486	522

Decomposition in the Presence of cis-*But-2-ene.*—It was immediately obvious in preliminary experiments that the

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† 1 Torr = (101·325/760) kN m^{-2}.

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

[6] P. J. Robinson, *Trans. Faraday Soc.*, 1965, **61**, 1655.

decomposition was sensitive to the presence of *cis*-but-2-ene. As was noted in similar experiments with trifluoro-1,1,2,2-tetrafluoroethylsilane and propene, the presence of the olefin caused a marked reduction in the rate of pressure change and in the extent of the overall pressure change. G.l.c. analysis showed the presence in the products of the two cyclopropanes (2a) and (2b) expected from stereospecific addition of the carbene $\mathrm{CHF_2{\cdot}CF{:}}$ to the double bond of the butene. The stoicheiometry was established as being given by equation (5),[7] and Table 3 shows that the rate of

$$\mathrm{CHF_2{\cdot}CF_2{\cdot}SiMe_3} + (1-x)\mathrm{C_4H_8} \longrightarrow \mathrm{Me_3SiF} + x\mathrm{CHF{:}CF_2} + (1-x)\overline{\mathrm{CHMe{\cdot}CHMe{\cdot}C}}\mathrm{F(CHF_2)} \qquad (5)$$

disappearance of (1) was unaffected by the presence of the olefin. The inert gas tetrafluorosilane had no effect on the rate or products of the decomposition of (1) alone.

TABLE 3

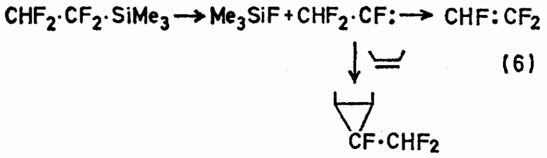
Effect of additives

T/K	No. of runs	Additive	$10^5\bar{k}/\mathrm{s^{-1}}$	$10^5\hat{\sigma}(k)/\mathrm{s^{-1}}$	$10^5\bar{k}/\mathrm{s^{-1}}$ No additive
591·5	8	Butene [a]	31·1	0·9	30·8
623·1	7	Butene [a]	236	12	226 [b]
623·1	2	$\mathrm{SiF_4}$ [c]	254		226 [b]

[a] 22 or 72 Torr (1) with 1 : 1 or 3 : 1 mole ratio *cis*-but-2-ene for 0·5, 1·0, or 2·0 half-lives. [b] Estimated from equation (4). [c] 23 or 73 Torr (1) with 2 : 1 mole ratio tetrafluorosilane.

DISCUSSION

It is clear from the above results that the decomposition of trimethyl-1,1,2,2-tetrafluoroethylsilane (1), like that of trifluoro-1,1,2,2-tetrafluoroethylsilane (3),[1] proceeds predominantly by α-fluorine elimination [equation (6)]. The formation of different products in the presence of *cis*-but-2-ene, but at the same rate as in its absence, can only be explained by a two-step mechanism involving an active intermediate, which from the nature of the products must be difluoromethylfluorocarbene (1,2,2-trifluoroethylidene, $\mathrm{CHF_2{\cdot}CF{:}}$).



The carbene-trapping reactions are less favourable relative to isomerisation at the higher temperatures needed for the decomposition of (1) [*cf.* (3)], but up to 60% yields of the cyclopropanes were measured in kinetic experiments, and in qualitative experiments * with 2 atm *cis*-but-2-ene present at 581 K the yield was 82%, approximately in line with the kinetic results at lower butene pressures, and showing no tendency to approach a limit below 100%. Thus if β-elimination occurs at all in (1) it must certainly be a minor process. The A factor for α-elimination is close to that found for (3) [$\log_{10}(A/\mathrm{s^{-1}}) = 13{\cdot}9$ for (1), *cf.* 13·1 for (3)]. The activation energy is considerably higher for (1) [198 kJ mol^{-1}, *cf.* 138 kJ mol^{-1} for (3)], and the difference † can be interpreted on the basis that the silicon atom in (1) is less electropositive than that in (3), with electron donation from the methyl groups compared with electron withdrawal by the fluorine atoms. The forming Si–F bond will therefore release less energy in the transition state for (1) than in that for (3), and the activation energy will be higher. On the basis of our previous arguments[8] it would appear that the forming Si–F bond is the predominant feature of the reaction coordinate for α-fluorine elimination, the breaking Si–C bond being less important than in β-fluorine elimination.

In the absence of additives, the carbene in the present system isomerises quantitatively to trifluoroethylene, and this contrasts with its behaviour in the decomposition of (3) at lower temperatures, where some of the carbene adds to the initially formed trifluoroethylene to give a cyclopropane derivative analogous to (2). It will be shown in another paper[7] that this contrast arises from the higher activation energy for isomerisation of the carbene compared with its addition to trifluoroethylene. The products of addition of the carbene to *cis*-but-2-ene were the cyclopropane isomers (2a) and (2b) with *cis*-methyl groups, indicating that the carbene adds stereo-specifically to the double bond and is presumably in a singlet state. Similarly, qualitative experiments with *trans*-but-2-ene gave only the isomer with *trans*-methyl groups. The absence of triplet carbene was also demonstrated by the fact that decomposition of (1) in the presence of 20% oxygen gave the same rate of pressure change and the same products as in its absence; molecular oxygen is an efficient scavenger of triplet methylene[9] and would be expected to behave similarly towards triplet difluoromethylfluorocarbene. Quantitative studies of the product distributions obtained with varying pressures of butene and inert gas lead to information about the kinetics of the addition and isomerisation reactions of the carbene, and these will be reported in a subsequent publication.[7]

[2/2224 *Received*, 25*th September*, 1972]

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* We thank Dr. J. Freear for carrying out these experiments.

† Even if a compensation error had occurred such that the A factors should be identical, the activation energies would still differ by 53 kJ mol^{-1}.

[7] R. N. Haszeldine, C. Parkinson, P. J. Robinson, and W. J. Williams, to be published.

[8] R. N. Haszeldine, P. J. Robinson, and J. A. Walsh, *J. Chem. Soc.* (*B*), 1970, 578.

[9] See, *e.g.*, T. W. Eder and R. W. Carr, *J. Phys. Chem.*, 1969, **73**, 2074; R. A. Cox and K. F. Preston, *Canad. J. Chem.*, 1969, **47**, 3345.