

## Carbene Chemistry. Part VIII.<sup>1</sup> The Thermal Decomposition of Trichloromethyltrifluorosilane: a Kinetic Investigation

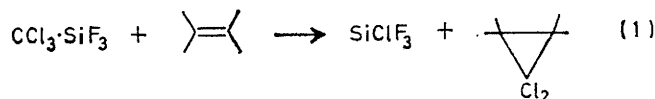
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The gas-phase thermal decomposition of trichloromethyltrifluorosilane ( $\text{CCl}_3\cdot\text{SiF}_3$ ) at 100–160 °C and 10–100 Torr initial pressure in the presence of alkenes (2,3-dimethylbut-2-ene, *cis*-, or *trans*-but-2-ene) is first order in silane; the rate constant is independent of the olefin used and the surface to volume ratio and is given by (i).

$$\log_{10}(k/\text{s}^{-1}) = 12.794 \pm 0.110 - (126.0 \pm 2.6) \text{ kJ mol}^{-1}/2.303RT \quad (\text{i})$$

These results provide strong evidence for the participation of free dichlorocarbene in these reactions.

THE gas-phase reaction between trichloromethyltrifluorosilane and olefins at *ca.* 140 °C provides an excellent preparative route to *gem*-dichlorocyclopropanes, proceeding at high conversion essentially according to equation (1).<sup>2</sup> Stereospecific reactions are observed with the but-2-enes, and the participation of dichlorocarbene has



been inferred.<sup>2</sup> Detailed kinetic investigation of these reactions is now reported.

### EXPERIMENTAL

*Apparatus.*—The vacuum apparatus was of a conventional design.<sup>3</sup> Greaseless taps (Springham with neoprene diaphragms or Quickfit Rotaflo) were used in all sections where

<sup>1</sup> Part VII, W. I. Bevan, R. N. Haszeldine, J. Middleton, and A. E. Tipping, *J.C.S. Dalton*, 1975, 620.

the silane was stored, purified, or handled before reaction. Pressures were measured by a spiral gauge. The reaction vessels used were made from a length of Pyrex tubing, closed at each end by a Fischer and Porter Labcrest right-angle tap. Two such vessels were used. Vessel A was a single U of 10.9 cm length, 3.70 cm<sup>3</sup> volume, and an overall surface : volume (*S/V*) ratio of 7.8 cm<sup>-1</sup>. Vessel B was a coil made from 0.15 cm i.d. tubing, of length 109 cm, volume 2.99 cm<sup>3</sup>, and an overall *S/V* 18.6 cm<sup>-1</sup>. Owing to the widening of the tubes near the taps, each vessel is more accurately described as containing a long section of high *S/V* and a short section of appreciably lower *S/V*. Thus, vessel B consisted of 1.93 cm<sup>3</sup> at *S/V* = 27 cm<sup>-1</sup> and 1.06 cm<sup>3</sup> at 3.9 cm<sup>-1</sup>. Vessel temperatures were measured using calibrated chromel-alumel thermocouples.

The reaction vessel also served as the sample injection loop, being connected by a six-port injection valve to a Pye 104/44 gas chromatograph, which used a four-filament

<sup>2</sup> J. M. Birchall, G. N. Gilmore, and R. N. Haszeldine, *J.C.S. Perkin I*, 1974, 2530.

<sup>3</sup> F. Anderson, Ph.D. Thesis, Manchester, 1971.

katharometer detector and had a temperature programming facility. The connections between the reaction vessel, injection valve, and chromatograph were 1/16 in bore, 18/8 stainless-steel tube, heated to 80 °C.

**Procedure.**—Before each experiment, the system was evacuated to  $<10^{-3}$  Torr, and the silane was then evaporated from a liquid sample into a 250 cm<sup>3</sup> vessel. If a mixture was to be used the other components were then added and allowed to mix for 15 min. Reaction was initiated by allowing the mixture to expand into the evacuated reaction vessel. The vessel was finally isolated 3–5 s after the first admission of the reactants by closure of the Labcrest valves. The lines adjacent to the reaction were then evacuated and refilled with helium (the g.l.c. carrier gas) at the inlet pressure of the column. Each reaction was terminated by opening the Labcrest valves, followed immediately by operation of the g.l.c. injection valve. This procedure, which took *ca.* 2 s, redirected the carrier gas stream through the reaction vessel, so sweeping its entire contents into the chromatograph.

The chromatograph detector was operated at 200 °C with a flow rate of 50 cm<sup>3</sup> He min<sup>-1</sup> and a bridge current of 190 mA. Quantitative analysis was achieved with 6 mm o.d. glass columns, packed with 80–120 mesh Celite, which had been heated under reflux with dichlorodimethylsilane in light petroleum and then with methanol. A 2.1 m column with 10% Apiezon L and a 2.7 m column with 15% Silicone MS 200/50 were used. Calibration was by syringe injection from standard solution except for silicon compounds, for which a gas-phase sample was injected from the reaction vessel. Peak areas were determined by cutting and weighing. The calibration plots were linear except that for trichloromethyltrifluorosilane. Frequent checks were made of these plots, and the response factors obtained from them were reliable to within 1%. Experiments with trichloromethyltrifluorosilane showed that material was lost on the column, and although this loss could be reduced by pre-injection of the silane, no reproducible procedure was found. Only approximate analysis for this silane was therefore achieved.

**Materials.**—Trichloromethyltrifluorosilane<sup>2</sup> was purified by fractional distillation in a closed system at *ca.* 1 atm.; the only detectable impurity (g.l.c.) was chloroform. Commercial samples of *cis*- and *trans*-but-2-ene and of 2,3-dimethylbut-2-ene were used without purification. 1,1-Dichloro-*cis*-2,3-dimethylcyclopropane,<sup>4</sup> its *trans*-isomer,<sup>2</sup> and 1,1-dichlorotetramethylcyclopropane<sup>2</sup> were obtained by reported routes. Not more than 1% impurity was detected in any of these compounds (g.l.c.).

## RESULTS

The preparative experiments with the olefins involved here were carried out with a large excess of each olefin at total pressures of *ca.* 1 atm. and gave yields of dichlorocyclopropanes of  $\geq 88\%$ .<sup>2</sup> The stoichiometry of the reactions of the silane with *cis*- or *trans*-but-2-ene (CB, TB) or with 2,3-dimethylbut-2-ene (DMB) was examined here with a range of reactant ratios at pressures in a range more convenient for kinetic analysis (Table 1). The only products found in experiments with an excess of the olefin were chlorotrifluorosilane and the expected dichlorocyclopropane, the latter formed stereospecifically from the *cis*- or *trans*-butene. When an excess of trichloromethyltri-

<sup>4</sup> W. E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, 1954, **76**, 6162.

fluorosilane was used, other products did appear, but only when the bulk of the alkene had reacted. Essentially quantitative yields of the cyclopropane were obtained in all reactions (Table 1), in accord with the stoichiometry of equation (1). Confirmation of this has been obtained from experiments at 160 and 180 °C in a 126 cm<sup>3</sup> vessel, where no pressure change was detectable ( $<0.25$  Torr) during the reaction period used (up to one half-life).<sup>5</sup>

TABLE 1

Yields of cyclopropanes after complete reaction<sup>a</sup>

T/K	Alkene	$p_0$ /Torr		Yield <sup>b</sup>
		CCl <sub>3</sub> ·SiF <sub>3</sub>	Alkene	
130	DMB	20	10	98.2
140	CB	40	80	99.2
140	TB	40	80	99.4
150	DMB	20	5	96.3
150	DMB	20	40	101.0

<sup>a</sup> In vessel A. <sup>b</sup> Cyclopropane as mole % of the initial amount of the minor component of the reaction mixture.

TABLE 2

First-order rate constants

T/ °C	Vessel <sup>a</sup>	Alkene	$p_{\text{CCl}_3\text{SiF}_3}$ /Torr	$p_{\text{Alkene}}$ $p_{\text{CCl}_3\text{SiF}_3}$	Maxi- mum extent of reaction (%)	10 <sup>5</sup> k/s <sup>-1</sup> <sup>b</sup>
110	A	CB	100	1.0	16	4.07 ± 0.62
120	A	CB	20–100	0.5–5.0	34	11.4 ± 0.4
130	A	DMB	20	0.25–1.0	30	28.7 ± 1.3
130	A	DMB	40	0.25–0.50	30	28.4 ± 1.6
130	B	CB	60	1.0	77	31.0 ± 2.3
140	A	CB	10	2.0	86	74.7 ± 9.7
140	A	CB	20	1.0–2.0	85	74.1 ± 11.5
140	A	CB	20	2.0	70	57.7 ± 11.9 <sup>c</sup>
140	A	CB	40	1.0–2.0	82	72.2 ± 5.5
140	A	CB	100	1.0	83	75.7 ± 2.2
140	A	TB	100	2.0	83	72.6 ± 3.5
150	A	DMB	20	2.0	99	205 ± 4.5
160	C	TB	10	2.0	80	320 ± 19 <sup>c</sup>
160	A	CB	20	2.0	90	347 ± 11 <sup>c</sup>
160	A	DMB	20	1.0	96	445 ± 50
160	B	CB	60	1.2	90	382 ± 29

<sup>a</sup> A,  $S/V = 7.8$  cm<sup>-1</sup>; B,  $S/V = 18.6$  cm<sup>-1</sup>; C, 126 cm<sup>3</sup> spherical vessel,  $S/V = 0.97$  cm<sup>-1</sup>, products frozen out and then dissolved in CCl<sub>4</sub> for syringe injection to g.l.c. <sup>b</sup> 95% Confidence limits quoted. <sup>c</sup> Experimental work by A. Jervis.

Kinetic data were obtained at 100–160 °C, with total pressure 30–200 Torr and with various ratios of trichloromethyltrifluorosilane to alkene. Reaction orders were determined from sets of experiments with identical initial conditions, with quenching and analysis at varying times. In each analysis the amount of cyclopropane present was determined, and this value was used to calculate the amount of unchanged silane and alkene, assuming reaction (1) to be a complete description of the process. These experiments showed the reaction to be of zero order with respect to the alkene, since the reaction rate was independent of the nature of the alkene used and of the pressure, provided that some alkene remained unchanged at the time of analysis. The reaction was first order with respect to trichloromethyltrifluorosilane,

<sup>5</sup> J. M. Birchall, R. N. Haszeldine, A. Jervis, and B. J. Tyler, unpublished results.

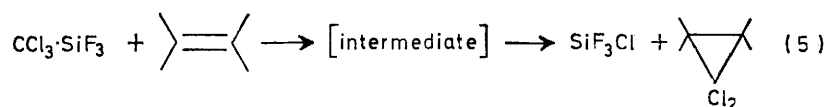
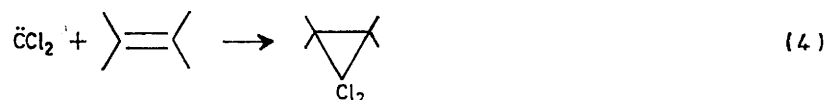
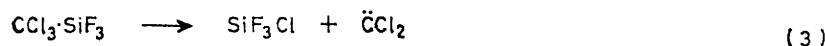
the integrated function plot being linear for at least three half-lives. Representative examples of the data confirming these orders are shown in the Figure and results for 18 series, each comprising on average eight individual experiments, are given in Table 2. The rate constants obtained are independent of the total pressure used, and show no obvious dependence on  $S/V$ . The greatest spread of values was observed at 160 °C, where the rate constants obtained give an overlapping sequence but show a significant difference between the largest and smallest values. The lowest value obtained at this temperature was from experiments done in a 126 cm<sup>3</sup> spherical vessel with a different sampling technique from that used in all other runs, and the lower value could indicate a systematic difference between the methods or the presence of a minor surface component in the usual vessels. Since the method used with the 126 cm<sup>3</sup> vessel could not be used at lower temperatures, no further evidence is available to distinguish these possibilities.

The rate constants given in Table 2 have been fitted to the Arrhenius equation by weighted least squares,<sup>6</sup> giving expression (2) (standard deviations given).

$$\log_{10}(k/s^{-1}) = 12.794 \pm 0.110 - (126.0 \pm 2.6) \text{ kJ mol}^{-1}/2.303RT \quad (2)$$

#### DISCUSSION

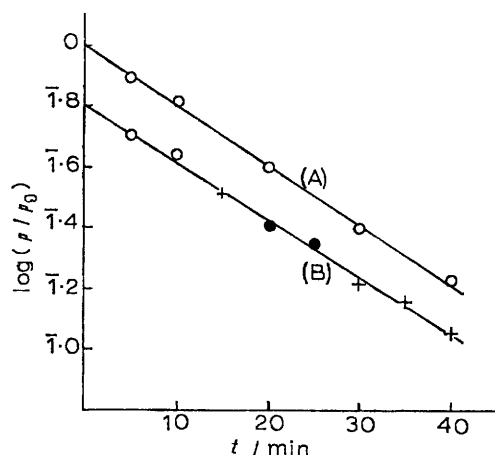
The results are satisfactorily explained by reactions (3) and (4) where (3) is rate determining, *i.e.* there is no effective competitor to reaction (4) for the dichlorocarbene produced in step (3). The reverse of reaction (3) which



has been observed under other conditions<sup>3</sup> cannot compete with reaction (4) under the experimental conditions used here. The carbenoid reaction (5) must be excluded since such a reaction would be first order with respect to both reactants and the rate constant would be expected to depend upon the particular alkene used. Thus, the observed kinetics provide convincing evidence for the occurrence of dichlorocarbene as a free species, and yield an experimental rate constant which can be equated to that of reaction (3).

This assignment gives the entropy of activation of reaction (2) as  $-10.8 \pm 2.1 \text{ J K}^{-1} \text{ mol}^{-1}$ , which is compatible with the postulated transition state in which one chlorine atom is bridged between the carbon and the silicon atoms. The entropy increase owing to the sym-

metry change from 9 in the reactant to unity in the transition state is outweighed by the entropy loss in the reaction co-ordinate (Si-C-Cl bend) and the replacement



Typical first order function plots for the decomposition of trichloromethyltrifluorosilane (140 °C, vessel A): (A) 100 Torr silane + 100 Torr CB; (B) (depressed by 0.2 log units) 40 Torr silane, ○ with 20 Torr CB; ● with 40 Torr CB; + with 80 Torr CB.

of a hindered rotation by a low frequency torsion, giving a small net decrease in entropy.

Data for other work on this system and other  $\alpha$ -elimination reactions are given in Table 3. Lee and Roberts' results<sup>7</sup> for trichloromethyltrifluorosilane are not strictly comparable with ours since some liquid-phase

reaction occurred in their experiments. Over the common range of 100–130 °C, the rate constants reported by them are always greater (ranging from 50% at 100 to 15% at 130 °C) than those obtained in the present work; presumably a smaller proportion of the reactions occurred in the liquid phase at the higher temperature. That the two sets of Arrhenius parameters are not significantly different follows from the large error limits in Lee and Roberts' results, a consequence of the appreciable scatter and small number of data points available to them.

It is surprising that the pre-exponential factor for the completely chlorinated compound,  $\text{CCl}_3\text{SiCl}_3$  (Table 3),<sup>8</sup> is so much lower than that reported here for the trichloro-compound  $\text{CCl}_3\text{SiF}_3$ . The decomposition of the perchloro-compound also produces dichlorocarbene,<sup>9</sup> and a

<sup>8</sup> D. Siebt and H. Heydtmann, *Z. Phys. Chemie*, 1973, **83**, 256.

<sup>6</sup> P. G. Guest, 'Numerical Methods of Curve Fitting,' Cambridge University Press, Cambridge, 1961.

<sup>7</sup> E. Lee and D. W. Roberts, *J.C.S. Perkin II*, 1973, 437.

<sup>9</sup> W. I. Bevan, R. N. Haszeldine, and J. C. Young, *Chem. and Ind.*, 1961, 789; W. I. Bevan and R. N. Haszeldine, *J.C.S. Dalton*, 1974, 2509.

similar transition state for the two compounds would be expected; it is difficult to envisage how such a large negative entropy of activation could be obtained.

TABLE 3

Arrhenius parameters for  $\alpha$ -elimination reactions

Compound	$\log_{10} (A/s^{-1})$	$E/kJ\ mol^{-1}$
$CCl_3\cdot SiF_3^a$	$12.79 \pm 0.11$	$126.0 \pm 2.6$
$CCl_3\cdot SiF_3^b$	$10.8 \pm 3.2^f$	$110 \pm 23$
$CCl_3\cdot SiCl_3^c$	$10.0 \pm 0.8$	$124.3 \pm 6.7$
$CHF_2\cdot CF_2\cdot SiF_3^d$	$13.11 \pm 0.11$	$137.8 \pm 0.9$
$CHF_2\cdot CF_2\cdot SiMe_3^e$	$13.93 \pm 0.22$	$197.7 \pm 2.5$

<sup>a</sup> This work. <sup>b</sup> Ref. 7. <sup>c</sup> Ref. 8. <sup>d</sup> Ref. 10. <sup>e</sup> R. N. Haszeldine, C. Parkinson, and P. J. Robinson, *J.C.S. Perkin II*, 1973, 1019. <sup>f</sup> Based on  $\Delta S^\ddagger = -49.8 \pm 61.1\ J\ K^{-1}\ mol^{-1}$ .

Our observed activation energy is comparable to that found for the decomposition of the silane  $CHF_2\cdot CF_2\cdot SiF_3$ <sup>10</sup>

<sup>10</sup> R. N. Haszeldine, P. J. Robinson, and W. J. Williams, *J.C.S. Perkin II*, 1973, 1013.

and, as in that case, the relatively low value can be attributed to the electropositive nature of the silicon atom caused by the electron-withdrawing fluorine atoms.

No indication of decomposition or isomerisation of the initially formed cyclopropanes has been observed during the work described here. This contrasts with the results obtained during the addition of dichlorocarbene (from  $CCl_3\cdot SiCl_3$ ) to ethylene<sup>8</sup> when some isomerisation was observed, and in addition of the carbene (from  $CCl_3\cdot SiF_3$ ) to tetrafluoroethylene where difluorocarbene is ejected from the cyclopropane.<sup>11</sup> The stability of the cyclopropanes formed in our experiments is probably a consequence of their larger number of modes of vibration.

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<sup>11</sup> J. M. Birchall, R. N. Haszeldine, and D. W. Roberts, *J.C.S. Perkin I*, 1973, 1071.