

## Trifluoromethylfluorocarbene Formation and Reactions under $C_2F_5SiF_3$ Pulsed Adiabatic Compression Pyrolysis

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The formation of  $:CFCF_3$ ,  $SiF_4$  and  $(cis+trans)-2-C_4F_8$  is demonstrated under the strictly homogeneous pyrolysis of  $C_2F_5SiF_3$ , using kinetic spectroscopy (at 250 and 465 nm) and chromatographic analysis, respectively. Pyrolysis of  $2-C_4F_8$  under the same conditions leads to the formation of an intermediate  $(C_4)^*$  which reveals absorption at 250 nm.

The purpose of the present work is to study the kinetics of the formation and disappearance of trifluoromethylfluorocarbene (TFMFC) under the homogeneous pyrolysis of  $C_2F_5SiF_3$ , carried out in the free-piston adiabatic compression set-up (ACS) described in ref. 1. Pyrolysis under pulsed adiabatic compression conditions is principally anisothermal. The free-piston, in a cylinder with a closed end, is accelerated by driving gas up to velocities of 10–15  $m\ s^{-1}$  and compresses almost adiabatically the gas under study inside the cylinder. The temperature  $T$  of the compressed gas rises in accordance with the well known Poisson adiabatic equation  $T = T_0 \varepsilon^{\gamma-1}$ , where  $T_0$  is the initial temperature of gas;  $\varepsilon = V_0/V$  is the geometric compression ratio, where  $V_0$  and  $V$  are initial and current values of the volume of gas;  $\gamma = C_p/C_v$  is the adiabatic factor; and  $C_p$  and  $C_v$  are the specific heats at constant pressure and constant volume, respectively. The piston stops at the moment of maximum compression and then goes back, promoting expansion and cooling of the heated gas. Under pressures not less than 1 atm the volume of the thermal boundary layer is negligibly small as compared to the total volume of the compressed gas, thus allowing spatially-homogeneous chemical reactions to take place. The temperature of the ACS walls during the compression hardly changes, excluding any 'chemical influence' of the walls. These features of the ACS mean that chemical reactions are conducted under strictly homogeneous conditions.

To describe all of the physicochemical processes occurring in the compressed gas a mathematical model has been developed which includes differential equations for the piston movement, energy and species concentrations, and the algebraic equations of state, temperature-dependent adiabatic factor as well as Arrhenius parameters for chemical reaction rate constants. The values being measured are the pressure (rms error  $\pm 0.2\%$ ) as a function of the time (rms error  $\pm 4\ \mu s$ ), the maximum compression ratio (rms error  $\pm 0.1\%$ ) and the absorption spectra of the compressed gas. The final reaction-product composition was analysed chromatographically (rms error  $\pm 5\%$ ). The temperature of the reacting mixture as a function of temperature and the kinetics of all the species were calculated from these measurements by means of the mathematical model. The initial mechanism of thermal reactions was derived from published data. Some examples of the application of rapid compression machines can be found in previous publications.<sup>2-9</sup>

$C_2F_5SiF_3$  was chosen as a source of TFMFC since published data<sup>10-12</sup> concerning thermal decomposition products and mechanism seemed to be sufficiently well known. Thus the initial reactions of the decomposition are reliably known to be as follows, reactions (1) and (2).

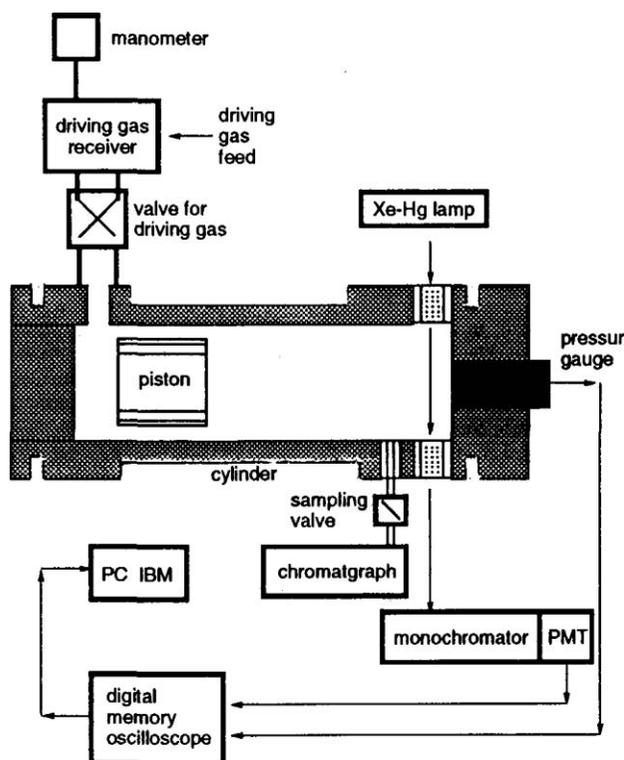
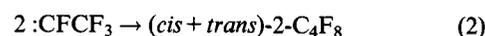
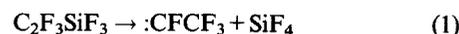


Fig. 1 Basic diagram for the adiabatic compression unit.

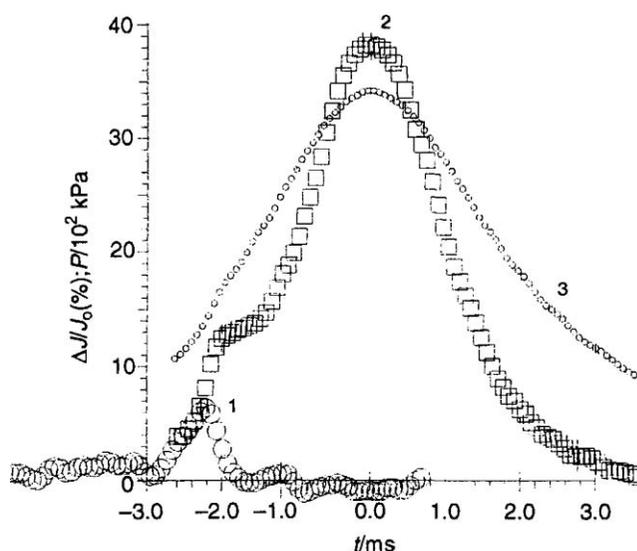


Fig. 2 Time dependences of the light absorbance at 465 nm (1) and 250 nm (2), and of the pressure (3) under adiabatic compression of the mixture A. Light absorbance is measured as  $\Delta J/J_0 = (J_0 - J)/J_0$  where  $J$  and  $J_0$  are light fluxes incident onto the photomultiplier in the presence and in the absence of the absorptive media, respectively.

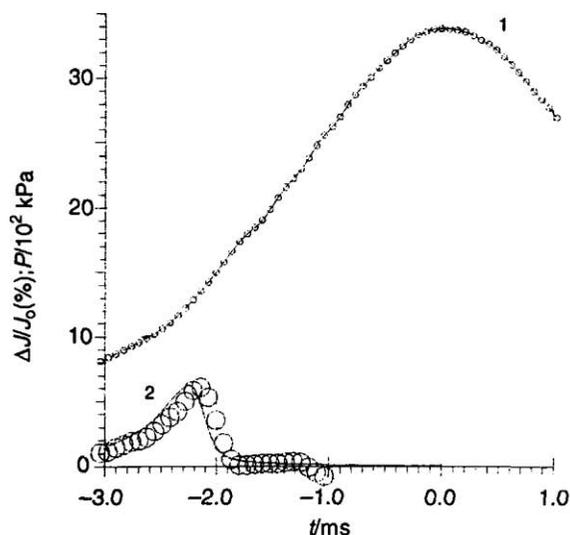


Fig. 3 Results of calculations (full lines) and measurements (points) for the pressure (1) and for the light absorbance at 465 nm (2) under adiabatic compression of the mixture A.

A mixture of 1.2 vol.% of  $C_2F_5SiF_3$  with krypton (mixture A) and a mixture of 1.5% of 2- $C_4F_8$  with Ar (mixture B) was pyrolysed. Purified Kr and Ar gases were used, while the purities of  $C_2F_5SiF_3$  and 2- $C_4F_8$  were ca. 99.99%<sup>†</sup> and 99.98%, respectively (*trans/cis* 2- $C_4H_8$  ratio = 4.8).

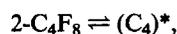
Carbene :CFCF<sub>3</sub> reveals two relatively wide absorption bands around 250 and 465 nm.<sup>13</sup> It is seen from Fig. 2 that maximum absorption at 465 nm is observed ca. 2.1 ms before the maximum compression marked as zero on the time axis. This implies that :CFCF<sub>3</sub> is formed and disappears before the reactive mixture reaches its maximum temperature. Chromatographic analysis of the final reaction-products showed only SiF<sub>4</sub> and (*cis* + *trans*)-2- $C_4F_8$  to be present, the ratio of *trans*-2- $C_4F_8$  to *cis*-2- $C_4F_8$  being 2.24. Supposing the mechanism of  $C_2F_5SiF_3$  conversion to include only reactions (1) and (2), the time dependence of the pressure and the kinetics of :CFCF<sub>3</sub> are described satisfactorily with the following Arrhenius parameters:

$$\lg(A_1/s^{-1}) = 11.3 \pm 0.1 \quad E_1 = 117 \pm 8 \text{ kJ mol}^{-1}$$

$$\lg(A_2/cm^3 \text{ mol}^{-1} s^{-1}) = 12.1 \pm 0.1 \quad E_2 = 8 \pm 4 \text{ kJ mol}^{-1}$$

Fig. 3 depicts the results of calculations and measurements concerning the time-dependent pressure and light absorption at 465 nm.

It is clear from Fig. 2 that the absorption curve at 250 nm with a characteristic feature near  $t = -1.8$  ms is the sum of absorptions of, at least, two intermediates. The second intermediate (the source of which may be only 2- $C_4F_8$ ) appears after the completion of the reactions (1) and (2) when mainly SiF<sub>4</sub> and (*cis* + *trans*)-2- $C_4F_8$  are present in the system. To clear it the authors carried out the pyrolysis of the mixture B. Experiments under relatively low temperatures showed only *cis/trans* isomerization of 2- $C_4F_8$  to occur (*trans-cis* 2- $C_4F_8$  = 3.6) and a rather strong light absorption at 250 nm by an intermediate marked here as ( $C_4$ )<sup>\*</sup> (*cf.*, Fig. 4). The light absorption curve is symmetric relative to the maximum-compression point. This implies under the adiabatic compression conditions that the intermediate concentration is an equilibrium one during the compression-expansion cycle.<sup>1</sup> The full line in Fig. 4 depicts the result of calculations of the equilibrium in the system



<sup>†</sup> A modified method<sup>10</sup> of  $C_2F_5SiF_3$  synthesis was used.

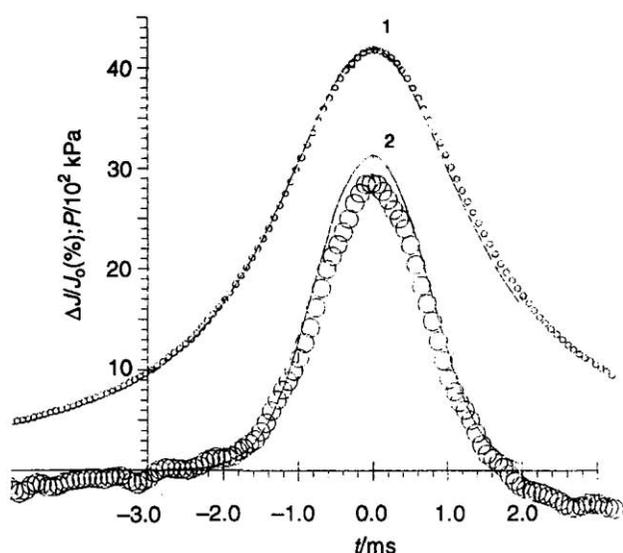


Fig. 4 Results of calculations (full lines) and measurements (points) for the pressure (1) and for the light absorbance at 250 nm (2).

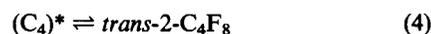
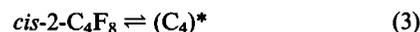
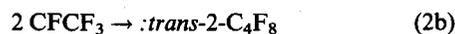
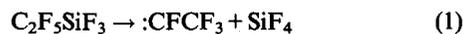
the product of the equilibrium constant ( $K$ ) and the extinction coefficient ( $\epsilon$ ) being determined from the present experiment

$$\epsilon K = 10^{7.48} \exp\left(-\frac{105 \text{ kJ mol}^{-1}}{RT}\right) \text{ cm}^3 \text{ mol}^{-1}$$

Using this value in calculations it is possible to describe experiments with maximum temperatures from 1000–1160 K.

The authors believe the mechanism of *cis-trans* isomerization to be connected with the formation of the intermediate observed.

Based on the results obtained the mechanism of the homogeneous pyrolysis of  $C_2F_5SiF_3$  seems to include reactions (1)–(4) below.



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