

# Shock wave and modelling studies of the pyrolysis of fluorinated hydrocarbons

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The thermal decomposition of various fluorinated compounds ( $C_2F_4$ ,  $C_3F_6$ ,  $c\text{-}C_3F_6$ ,  $c\text{-}C_4F_8$ ,  $C_2HF_5$ ,  $C_3HF_7$ ) was studied in incident and reflected shock waves monitoring the UV absorption of  $CF_2$ . Absorption coefficients and rate constants in the falloff region, as well as  $CF_2$  yields were determined. The experimental results were combined with quantum-chemical calculations and kinetic modelling identifying the contributions from various primary dissociation steps.

For the thermal dissociation  $C_2F_4 (+M) \leftrightarrow 2 CF_2 (+M)$ , rate constants as functions of bath gas concentration  $[M]$  and temperature were analysed and equilibrium constants determined. High pressure limiting rate constants for dissociation and recombination were found to be unusually small. This phenomenon can be attributed to an unusually pronounced anisotropy of the potential energy surface such as supported also by quantum-chemical calculations.

The thermal dissociation of  $C_3F_6$  was studied between 1330 and 2210 K.  $CF_2$  yields of about 2.6 per  $C_3F_6$  decomposed were obtained at reactant concentrations of 500 – 1000 ppm in the bath gas Ar. These yields dropped to about 1.8 when reactant concentrations were lowered to 60 ppm. The effect is attributed to bimolecular reactions between primary and secondary dissociation products. Falloff representations of the rate constants are given.  $c\text{-}C_3F_6$  at much lower temperatures rapidly leads to  $CF_2$  and  $C_2F_4$  and allows for the study of the subsequent dimerization  $2 CF_2 \rightarrow C_2F_4$ .

The thermal dissociation of  $c\text{-}C_4F_8$  was studied over the range 1150 – 2300 K. It was found that the primary reaction nearly exclusively produces 2  $C_2F_4$  which afterwards decomposes to 4  $CF_2$ . The reaction was shown to be close to its high pressure limit. Combining high and low temperature results leads to a rate constant for the primary dissociation of  $k_1 = 10^{15.97} \exp(-310.5 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$  in the range 630 – 1330 K, with  $k_1$  varying over nearly 14 orders of magnitude.

The thermal decomposition reactions of  $CF_3CF_2H$  and  $CF_3CFHCF_3$  were studied for temperatures in the range 1400 – 2000 K. It was shown that the reactions are initiated by C-C bond fission and not by HF elimination. By increasing the initial reactant concentrations from 60 to 1000 ppm in Ar, a retardation of  $CF_2$  formation was observed while the final  $CF_2$  yields remained close to two  $CF_2$  per  $C_2F_5H$  or three  $CF_2$  per  $C_3F_7H$  decomposed. This is explained by secondary bimolecular reactions which lead to comparably stable transient species like  $CF_3H$ , releasing  $CF_2$  at a slower rate.

## References

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