Hydrogen Fluoride Elimination from Shock-heated 1,1,2,2-Tetrafluoroethane

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Summary The thermal decomposition of 1,1,2,2-tetrafluoroethane in argon has been studied using a single pulse shock tube, over the temperature range 1200—1400 K, at pressures of *ca.* 400 kN m^{-2}, and for reaction times of *ca.* 1 ms, HF elimination yields C_2HF_3 with an activation energy of 293·3 ± 14·7 kJ mol^{-1}.

FOLLOWING earlier unsuccessful attempts,[1,2] the thermal decomposition of simple alkyl and alkenyl fluorides has recently received considerable attention.[2-10] Fluorohydrocarbons show a different trend in their reactivity from that of other halogeno-hydrocarbons,[1] *e.g.*, $CH_3CH_{3-i}X_i$ (i = 1,2,3) for X = Cl, Br, I, although there is some dispute over this.[3] With one exception,[2] these studies have been carried out over a wide temperature range in both subsonic[3] and supersonic flow systems.[4-10] The predominant mode of decomposition is molecular elimination of hydrogen fluoride. The present study of the thermal dehydrofluorination of CHF_2CHF_2 is a logical extension of the previous work, and the first one involving an $\alpha\beta$-fluoro-substituted ethane.

Decomposition was studied in a single-pulse shock tube equipped with a ball valve sample injection system.[11,12] The diluted reaction mixture (0·6% $C_2H_2F_4$; 99·4% Ar) was prepared in a stainless steel tank and allowed to mix. The

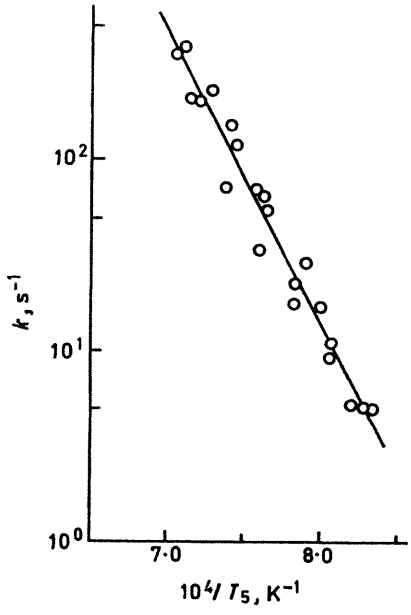

FIGURE. *Temperature dependence of the rate constant for* HF *elimination from* CHF_2CHF_2.

downstream pressure was kept constant at 20 kN m^{-2} for all runs, and varying shock strengths were achieved by adjusting the driver pressure in the range 300—600 kN m^{-2}. Reflected shock temperatures were computed[13] from measured incident and reflected shock velocities. The product : reactant ratio was determined for each run by g.l.c. and quantitative identification achieved by use of standard mixtures of CHF_2CHF_2 and C_2HF_3 in argon.

By working at conversions of $< 50\%$ it was possible to observe the unimolecular elimination of HF from CHF_2-CHF_2. The results, for the temperature range 1200—1400 K, are shown in the Figure. Comparison of our reaction conditions with those for the work on ethyl fluoride[2] suggests that the rate constants reported here are high-pressure limiting values. The variation of the first-order rate constant with temperature is given by the equation (1),

$$\log_{10}k\ (k \text{ in } s^{-1}) = 13{\cdot}4 \pm 0{\cdot}6 - (293{\cdot}3 \pm 14{\cdot}7)/2{\cdot}303\boldsymbol{R}T \qquad (1)$$

where $\boldsymbol{R}$ is in kJ mol^{-1} K^{-1}. This bears out the previous work of Tschuikow-Roux *et al.*[7,9,10] and Cadman *et al.*[4,5] and demonstrates conclusively the increase in activation energy with increasing fluorination. The Arrhenius parameters are summarized in the Table. Within the limits of the experiment, the results from the different laboratories are in reasonable agreement.

TABLE. *Arrhenius parameters for* HF *elimination from fluoroethanes*

Compound	Cadman *et al.*[a]		This laboratory[b]	
	E(kJ mol^{-1})	$\log(A/s^{-1})$	E(kJ mol^{-1})	$\log(A/s^{-1})$
C_2H_5F	250·6 ± 4·2	13·42 ± 0·3		
CH_3CHF_2	278·7	13·74	258·9 ± 7·5	13·9 ± 0·3
CH_3CF_3	297·5	13·47	287·4 ± 10·0	14·0 ± 0·4
CHF_2CHF_2			293·3 ± 14·6	13·4 ± 0·6
CHF_2CF_3			302·5 ± 10·9	13·7 ± 0·4

[a] Ref. 4, 5. [b] Ref. 7, 9, 10.

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