Thermal Decomposition of Vinylidene Fluoride behind Reflected Shock Waves

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Summary Thermolysis of dilute mixtures of 1,1-$C_2H_2F_2$ in argon in a single-pulse shock tube at 1290—1480K, 440kN m^{-2} total pressure, and reaction times of *ca.* 1 ms yields monofluoroacetylene with an activation energy of *ca.* 335 kJ mol^{-1}.

KINETIC data on the hydrogen halide elimination reactions of fluorohydrocarbons are of interest since they differ in some aspects, *e.g.* relative reactivity of the compounds $CH_3CX_iH_{3-i}$ (i = 1—3), from the analogous chloride, bromide, and iodide compounds which have been extensively studied.[1] It is only recently that fluoride pyrolyses have been successfully observed.[2-5]

We have studied the decomposition of CH_2CF_2 in a ball-valve type single-pulse shock tube, using techniques which have been previously described for the computation of reflected-shock temperature, reaction dwell time, and rate constant.[6] Even at moderate conversions ($\geqslant$10% reaction) the reaction is complex yielding some 18 volatile compounds including: C_2H_6, C_2HF, C_2F_4, C_2H_4, C_2H_2, CH_2CHF, $C_2H_3F_3$, and C_4H_2. Hydrogen fluoride, which is undoubtedly present, is not detectable in our apparatus.[4,5] However by working at low conversions ($\leqslant$5%) we have been able to observe the unimolecular elimination of HF from CH_2CF_2 as the dominant process.

Over the range 1290—1480K the variation of the first-order rate constant (which probably represents the high pressure limit rate constant, k_∞, under our conditions) with temperature is given by $\log_{10} k$ (k in s^{-1}) = 13·1 − (335/2·3 $\boldsymbol{R}T$), where $\boldsymbol{R}$ is in kJ mol^{-1} K^{-1}. Comparison with our previous results[4] for HF elimination from vinyl fluoride (Figure) indicates that increasing α-fluorination of $CH_2CF_iH_{2-i}$ (i = 1,2) leads to a marked decrease in the rate of HF elimination due mainly to an increase in the activation energy. This effect, which is contrary to a recent prediction,[7] has also been noted in the fluoroethanes $CH_3CF_iH_{3-i}$ (i = 1—3).

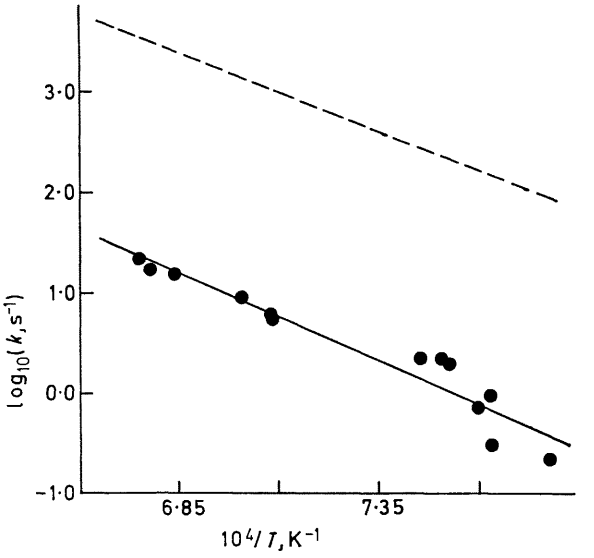

FIGURE. *Temperature dependence of first-order rate constant*; (———) *1,1-difluoroethylene*, (– – – –) *vinyl fluoride.*

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