Competitive αα- and αβ-Dehydrohalogenations from CH_3CDF_2 behind Shock Waves

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Summary An estimate of the extent of the αα-elimination of HF in 1,1-difluoroethane is obtained from a study of the shock-tube pyrolysis of the deuteriated isomer, CH_3CDF_2

IT has generally been accepted[1,2] that the pyrolytic dehydrohalogenations of halogeno-ethanes occur *via* a four-centre transition state so that elimination is an αβ-process involving substituents on adjacent carbon atoms. However, with the discovery of the formation of CD_2CDF in the decomposition of chemically activated CD_3CHF_2[3,4] the possibility of the occurence of concurrent αα-eliminations in halogeno-ethanes has to be considered. The αα-elimination involves the substituents on the same carbon atom and has been suggested[4,5] to occur *via* a three-centre transition state leading to a carbene intermediate, followed by the rapid rearrangement of the carbene to the olefin. On the basis of the results of the chemical activation experiments on CD_3CHF_2, Kim *et al.*[4] have concluded that the αα-elimination channel contributes *ca.* 10% to the total elimination in CH_3CHF_2. The present study of the pyrolysis of CH_3CDF_2 is the first report of a competition between αα- and αβ-eliminations occurring in a thermal system.

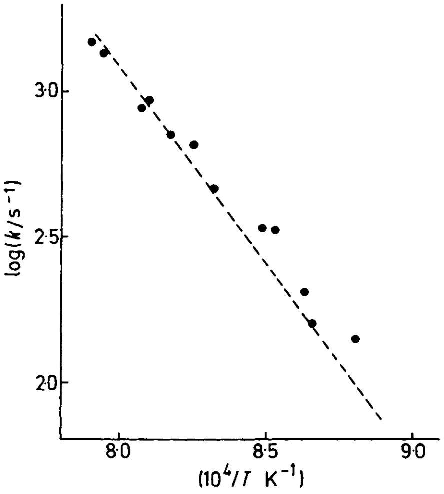

FIGURE. Temperature dependence of the overall rate constant for the HF and DF eliminations from CH_3CDF_2 (filled circles). Dotted line: data from ref. 7.

The decomposition was studied in a modified single-pulse shock tube.[6] The reflected-shock temperatures and the reaction dwell times were calculated using techniques which have been described previously.[6] The deuteriated reactant, CH_3CDF_2 was synthesised in two steps. In the first step, HI was added to CH_2CF_2 in a steel cylinder giving CH_3CF_2I which was then reduced with $LiAlD_4$ in ethereal solution. All kinetic experiments were performed on a well mixed, dilute (*ca.* 1%) mixture of the reactant in argon. Analysis for CH_2CDF *vs.* CH_2CHF of the shocked mixture was carried out using a g.c.-coupled mass spectrometer equipped with a Porapak Q column. A normal gas chromatographic analysis was also carried out to determine the total product to reactant ratios.

Over the range 1130—1270 K, the main products were CH_2CHF and CH_2CDF resulting from the elimination of DF and HF, respectively. Our preliminary results of the variation of the overall rate constant for the elimination ($k_{\alpha\alpha} + k_{\alpha\beta}$) with temperature are shown as filled circles in the Figure. The dotted line represents earlier detailed data of Tschuikow-Roux, *et al.*[7] for HF elimination from CH_3CHF_2. From the ratio $CH_2CHF:CH_2CDF$ in the shocked mixture, the rate constant ratio $k_{\alpha\alpha}k_{\alpha\beta}$ for CH_3CFD_2 is estimated to be 0·07. After correction for the isotope effect between HF and DF three-centre eliminations from CH_3CHF_2 and CH_3CDF_2, respectively, the αα-elimination channel is estimated to contribute *ca.* 13% to the total elimination in CH_3CHF_2.

(*Received, 26th November* 1973; Com. 1619.)

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