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COLLISIONAL ENERGY TRANSFER IN THE TWO-CHANNEL DECOMPOSITION OF 1,1,2,2-TETRAFLUOROCYCLOBUTANE AND 1-METHYL-2,2,3,3-TETRAFLUOROCYCLOBUTANE, I. GAS/GAS COLLISIONS

L. Zalotai, T. Turányi, T. Bérces and F. Márta

Central Reseach Institute for Chemistry,
Hungarian Academy of Sciences,
Pusztaszeri út 59-67, 1025 Budapest, Hungary

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The two-channel thermal decomposition of 1,1,2,2-tetrafluorocyclobutane (TFCB) and 1-methyl-2,2,3,3-tetrafluorocyclobutane (MTFCB) have been studied in the temperature range of 730-805 K at pressures varied from 1.1 Pa up to 4.6 kPa. In the pressure independent range, Arrhenius expressions were obtained for TFCB decomposition into 2 CH_2CF_2 (k_1) and C_2H_4 + C_2F_4 (k_2), respectively. The same kinetic equations were determined for the decomposition of MTFCB into $C_3H_4F_2$ + $C_2H_2F_2$ (k_3) and C_3H_6 + C_2F_4 (k_4). From the study of the pressure dependence of the homogeneous decomposition rates, the average downward energy transfer values of 1800±200 cm^{-1} and 1600±200 cm^{-1} were obtained for the TFCB and MTFCB molecules, respectively.

Akadémiai Kiadó, Budapest

INTRODUCTION

Study of vibrational energy transfer of polyatomic molecules offers many advantages as first recognized by Chow and Wilson [1].

In a recent paper [2] we have dealt with the two-channel decomposition of 2-methyloxetane and in this work we investigate gas/gas and gas/wall collisional energy transfer in the two-channel decomposition of TFCB and MTFCB. Thermal decomposition [3] and vibrational energy transfer [4] involving TFCB have been studied previously, however, neither MTFCB thermal decomposition nor gas/wall deactivation of TFCB and MTFCB has been investigated so far.

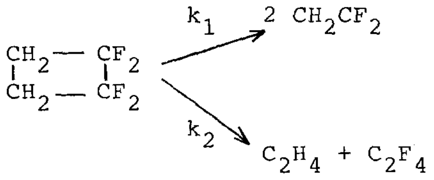
EXPERIMENTAL

TFCB and MTFCB were obtained by cycloalkylation method [5, 6], that is addition of tetrafluoroethylene to ethylene or propylene. The apparatus and procedure have been described earlier [7]. For the analysis of the experimental results the collision rate constant was calculated using the Lennard-Jones formula [8]

$$Z_{LJ}=N_A\sigma^2\Omega^{(2,2)}\ (8RT/\pi\mu)^{1/2}$$

RESULTS AND DISCUSSION

TFCB decomposed with a reproducible rate in a seasoned reaction vessel. The products of thermolysis were found to be ethylene, 1,1-difluoroethylene and tetrafluoroethylene. In agreement with previous investigations [3, 4], we found that under our experimental conditions the decomposition of TFCB can be adequately described by the concurrent reactions (1) and (2):



(1)

(2)

This is confirmed by the equivalence of the pressure change and the amount ethylene + 0.5 difluoroethylene determined by g.l.c. Reaction was carried out up to 5-25% conversion. The overall rate constant was calculated from the ratio of ethylene + 0.5 difluoroethylene and the unreacted TFCB concentrations which were obtained from analytical results. The rate constants for the concurrent paths producing ethylene + tetrafluoroethylene and difluoroethylene were calculated from the overall rate coefficients and the ratios of ethylene/difluoroethylene determined chromatographically.

Decomposition of TFCB was studied over the temperature range of 733-807 K at pressures of $p_o \geq 1.4$ kPa. A least-squares treatment of the high pressure rate constants data yields

$$\log(k_1^{\infty}/s^{-1}) = (15.45 \pm 0.09) - (293.7 \pm 1.4\ \mathrm{kJ\ mol^{-1}})/2.303\ RT$$

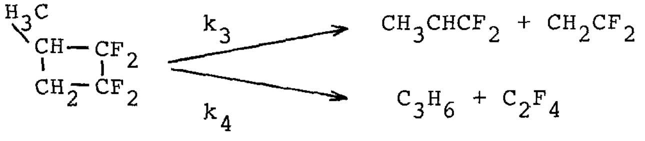
and

$$\log(k_2^{\infty}/s^{-1}) = (15.36 \pm 0.08) - (309.5 \pm 1.1\ \mathrm{kJ\ mol^{-1}})/2.303\ RT$$

where the quoted error limits are one standard deviation. We have used the log k-1/T data without any special weighting factors for the evaluation of the Arrhenius parameters. The rate parameters are in good agreement with the former work [3, 4].

The product distribution expressed by the ratio of individual rate coefficients is very much dependent on temperature as is shown in Fig. 1. This variation is reflected in the difference of activation energies between reactions (1) and (2).

The details of the thermal decomposition of MTFCB were closely similar to those of TFCB. From the preliminary experiments it seemed very probable, that the decomposition of MTFCB is a true unimolecular process and the pyrolysis could be represented by the following stoichiometry:



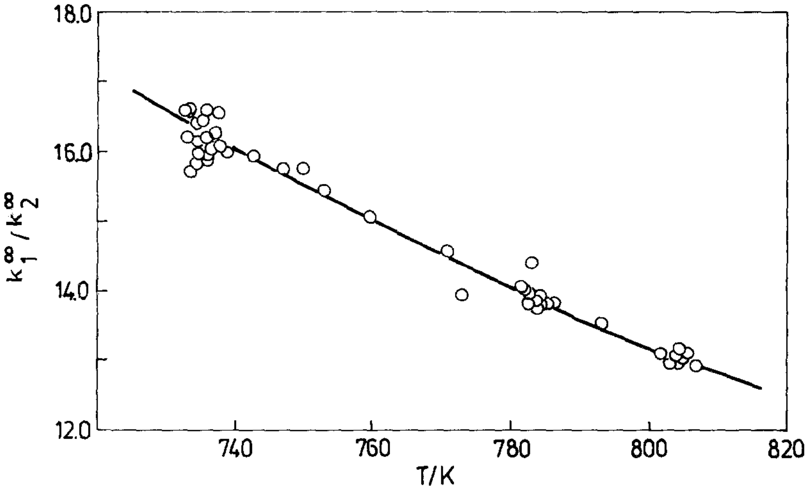


Fig. 1. Temperature dependence of the k_1^∞/k_2^∞ ratio

The overall first-order rate coefficient was calculated from the g.l.c. analysis of difluoropropylene, propylene and MTFCB, similarly to that of TFCB. From the individual rate constants the Arrhenius parameters were obtained by least squares

$$\log(k_3^\infty/s^{-1})=(15.24\pm0.08) - (294.0\pm1.1 \text{ kJ mol}^{-1})/2.303\ RT$$

and

$$\log(k_4^\infty/s^{-1})=(15.27\pm0.06) - (310.2\pm0.9 \text{ kJ mol}^{-1})/2.303\ RT$$

where the given error limits are one standard deviation.

The high pressure ratio of the individual rate coefficients is less dependent on temperature (Fig. 2) than that of TFCB.

The pressure dependences of the first-order rate coefficients have been studied in the fall-off region at three temperatures 769, 786 and 803 K. The series of experiments were

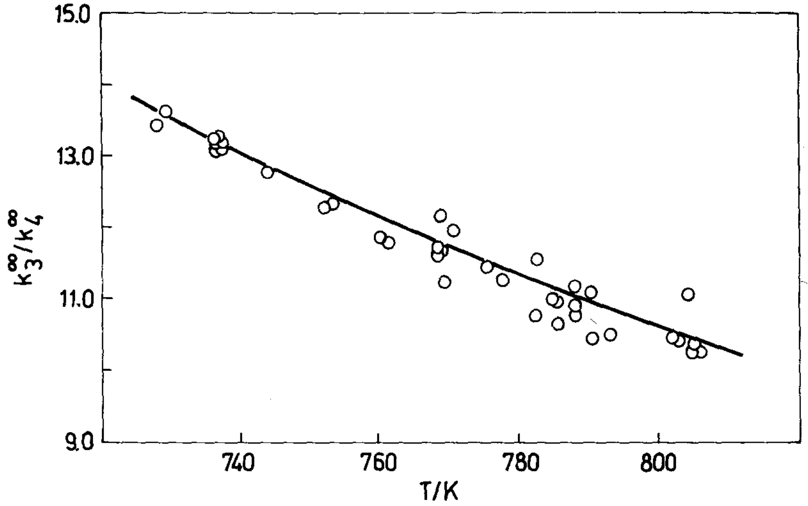


Fig. 2. Temperature dependence of the k_3^∞/k_4^∞ ratio

carried out with varying initial reactant pressures within the range of 0.001-4.6 kPa.

In order to extract energy transfer information from the experimental results, we performed master equation calculations [9] to determine the best values of the energy transfer step sizes $\langle\Delta E\rangle_d$ for collisions in the gas phase.

Plots of the channel ratio for TFCB decomposition vs collision rate, ω, is presented in Fig. 3. The results show that the ratio of the individual rate constants appears to change significantly as the pressure is lowered. The experimental k_1/k_2 ratios were fitted to a series of theoretical values calculated by the solution of the master equation.

The predicted ratio is sensitive to the choice of energy step size, so the ratio contains much useful information on the size of $\langle\Delta E\rangle_d$. The RRKM curve shows in Fig. 3 calculated with the assumption of strong collision hypothesis cannot describe the experimental results. By comparing the experiment with the

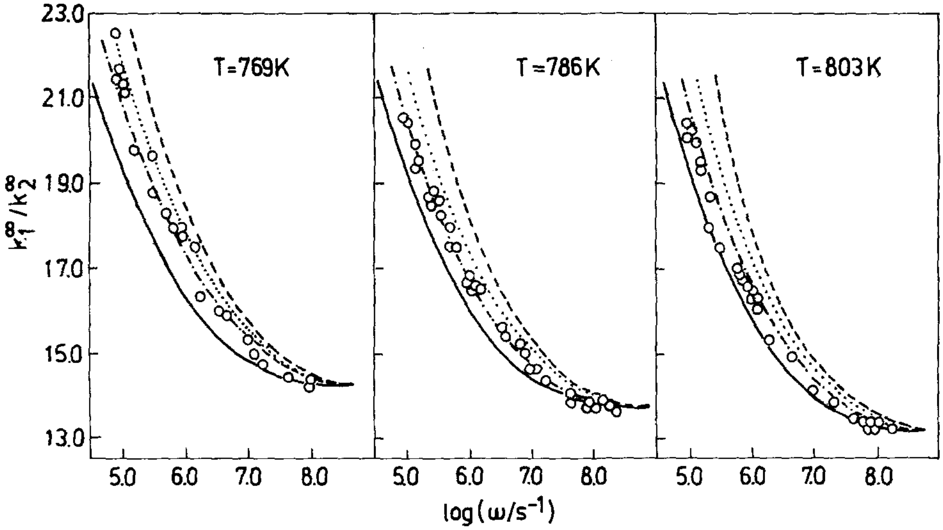


Fig. 3. Pressure dependent ratio of the two reaction channels for TFCB decomposition at 769, 786 and 803 K. 0 Experimental; (——) RRKM strong collision hypothesis; (---) RRKM stepladder model with $<\Delta E>_d=1200$ cm^{-1}; (···) $<\Delta E>_d=1500$ cm^{-1} and (-·-) $<\Delta E>_d=1800$ cm^{-1}

calculated curves, assuming stepwise deactivation, we can deduce the value of $<\Delta E>_d=1800\pm200$ cm^{-1} for the average energy transferred per collision without definite indication of temperature dependence. The energy step size derived is in good accord with previous determinations for TFCB [3, 4].

Results for MTFCB decomposition and calculated channel ratios for different average energies transferred per collision are shown in Fig. 4. As can be seen there is in this case a definite predominance of the path producing the difluorocompound with decreasing pressure as well. In the present system $<\Delta E>_d$ for the substrate was found to be 1600 200 cm^{-1} in the temperature range of 769-803 K. It could be seen that a multichannel

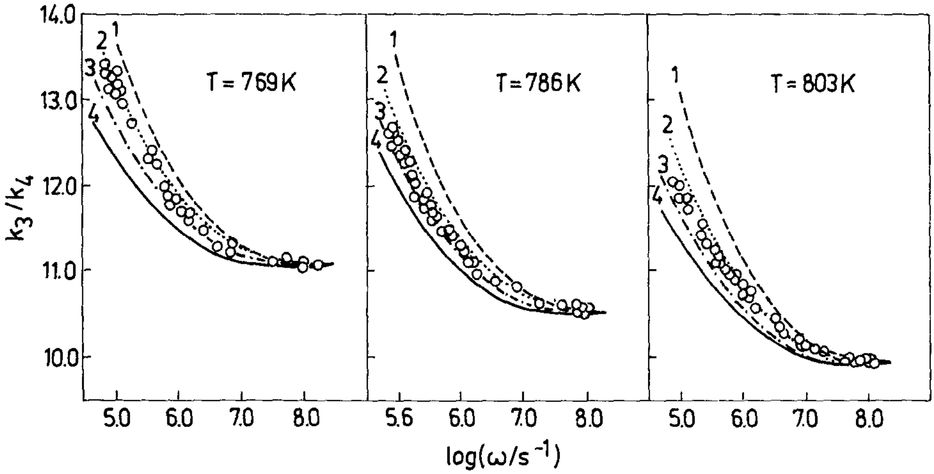


Fig. 4. Pressure dependent ratio of the two reaction channels for MTFCB decomposition at 769, 786 and 803 K. 0 Experimental; (——) RRKM strong collision hypothesis; (--) RRKM stepladder model with $\langle\Delta E\rangle_d$= 1200 cm^{-1}; (···) $\langle\Delta E\rangle_d$= 1500 cm^{-1} and (-·-) $\langle\Delta E\rangle_d$=1800 cm^{-1}

unimolecular reaction can provide a much more rigorous test of the applicability of RRKM theory. By making use of the ratios of the rates of different product channels, which are much more sensitive to the details of energy transfer model, the accuracy of the $\langle\Delta E\rangle_d$ values can be properly assessed.

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