React. Kinet. Catal. Lett., Vol. 51, No. 2, 409-414 (1993)

RKCL2366

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

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Received July 7, 1993
Accepted October 7, 1993

The efficiency of gas/wall vibrational energy transfer has been studied over the temperature range 800-1100 K by the "variable encounter" method. The average energies transferred per deactiviting collisions with the wall were determined at 800 K to be 3200 cm^{-1} and 2900 cm^{-1} for the 1,1,2,2-tetrafluorocyclobutane (TFCB) and 1-methyl-2,2,3,3-tetrafluorocyclobutane (MTFCB) molecules, respectively. This energy increased strongly with decreasing temperature. A comparison is made of $\langle\Delta E'\rangle$ with previous results for related molecules.

INTRODUCTION

The experimental investigation of thermal unimolecular reactions having two competitive reaction channels can provide valuable information on gas-gas and gas-wall vibrational energy transfer [1]. The thermal decomposition of TFCB and MTFCB (gas-gas collisions) have been described earlier [2].

EXPERIMENTAL

The apparatus used in this work was similar to that of previous studies [3]. The mean number of collisions (m) was calculated by a Monte Carlo method [4]. For the decomposition of TFCB and MTFCB, reactors having m values of 2.1, 3.5 and 10.5 were used. From the composition of reaction mixture apparent first-order rate constants for decomposition were calculated. The mean probability, $\bar{p}_c$ (m), for reaction per collision with the hot wall was obtained from the apparent first-order rate constant using simple kinetic theory of gases and the known reactor dimensions [4].

RESULTS AND DISCUSSION

The decomposition of TFCB and MTFCB was investigated over the temperature range of 800-1100 K. Experimental values for the ratio of the average probability of reaction per collision with the hot wall of the three reactors are shown in Figs 1 and 2 for TFCB and MTFCB decomposition, respectively.

The gas-wall energy transfer process theoretically can be calculated in terms of a probability matrix. The details of the construction of the probability matrix are described elsewhere [5].

Two different models have been used to characterize the probability p_{ij} of a downstep form energy E_j to E_i. Model E (flat exponential; i.e. $\langle\Delta E'\rangle$ independent of E_j) was: $p_{ij} = A_1\exp(-\Delta E'/\langle\Delta E_{mp}\rangle)$ for $0 \leq \Delta E/cm^{-1} \leq 9500$, and $p_{ij} = 0$ for $\Delta E >$ 9500 cm^{-1}. Model G (flat Gaussian; i.e. ΔE_{mp} independent of E_j) was: $p_{ij} = A_2\exp[-(\Delta E'-\Delta E_{mp})^2/2\sigma^2]$ for $0 \leq \Delta E/cm^{-1} \leq 9500$ and $p_{ij} = 0$ for $\Delta E' >$ 9500 cm^{-1}. The best fit seemed to be obtained with the flat Gaussian ($\sigma = 0.7\ \Delta E_{mp}$) model. For the Gaussian model, if $\sigma \ll \Delta E_{mp}$, then this effectively becomes a stepladder model and $\langle\Delta E'\rangle = \Delta E_{mp}$; if $\sigma \geq \Delta E_{mp}$, then there is a fairly large probability for elastic transitions.

The experimental points and the theoretical results of the computer simulation for TFCB are shown in Fig. 1. The solid

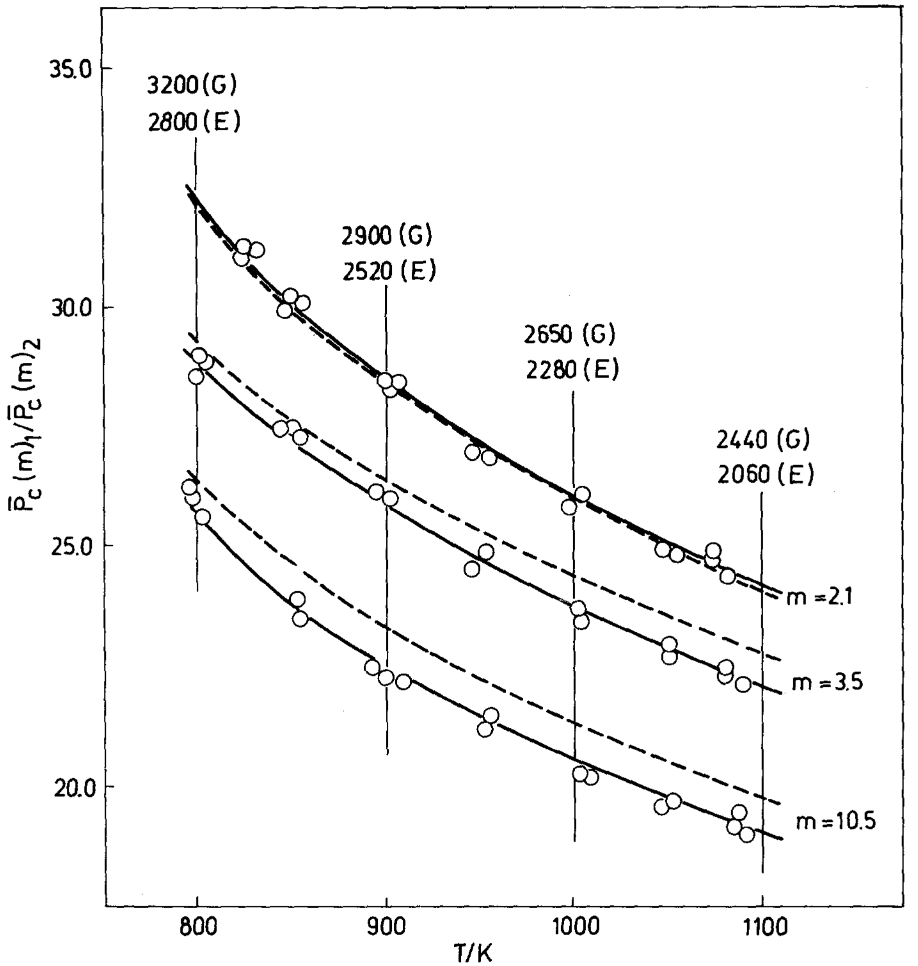

Fig. 1. Temperature dependence of the ratio of reaction probabilities for the two reaction channels in the TFCB decomposition. Transition probability models were Gaussian (——) and exponential (- - -) functions. <ΔE'> values are given at four different temperatures

and dashed curves were calculated using a Gaussian and exponential transition probability model, respectively. The flat Gaussian model gives the best agreement with our experimental data over the temperature range studied. It is seen that the average amount of energy transferred upon collision is large at lower temperatures and decreases at higher temperatures. We found that it was not possible to match the experimental data with exponential energy transfer function. Tardy and Rabinovitch suggest [6] that for a "strong collider" a Gaussian energy-transfer shape should be more appropriate than an exponential one.

The temperature dependent ratio of MTFCB decomposition probabilities and the fit obtained from the two models are shown in Fig. 2. The $\langle \Delta E' \rangle$ values here are significantly smaller than those found for TFCB decomposition.

The results of the gas-wall energy transfer experiments for TFCB and MTFCB molecules indicate the following: a) wall collisions are more efficient than gas-gas collisions; b) gas-wall collisional efficiency and $\langle \Delta E' \rangle$ values decline with increasing temperature in agreement with similar findings for the decomposition of small ring compounds.

Comparison with the previous results for four-membered ring molecules is summarized in Table 1.

If the reactant has more than one unimolecular reaction channel, then the observed temperature dependences of the ratio of reaction probabilities for the channels provide sensitive probes of the reactant-wall collision probability function.

Table 1
Values of $\langle \Delta E' \rangle$ for various four-membered ring compounds

Substrate	E_o (kJ/mol)	T(K) 800	900	1000	1100
Cyclobutane	263.6		2125	1925	1875
Oxetane	259.4	2970	2660	2400	2200
3-Methyloxetane	247.4	2570	2260	2000	1790
2-Methyloxetane	239.8	2460	2150	1890	1680
1,1,2,2-Tetrafluoro-cyclobutane	293.7	3200	2900	2650	2440
1-Methyl-2,2,3,3-tetrafluorocyclo-butane	294.0	2900	2600	2350	2140

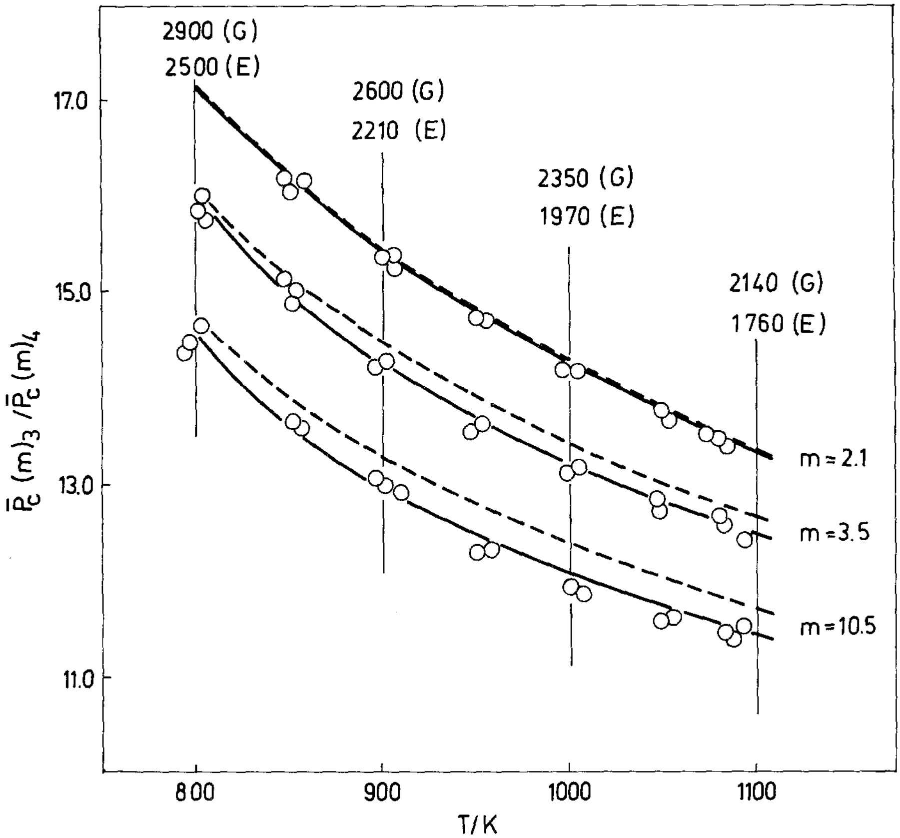

Fig. 2. Temperature dependence of the ratio of reaction probabilities for the two reaction channels in the MTFCB decomposition. Transition probability models were Gaussian (——) and exponential (---) functions. <ΔE′> values are given at four different temperatures

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