Isomerization of 1-Methylcyclobutene by Single Collision Activation at a Surface. Variation of Initial Energy

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The reaction probability per collision, P_c, for 1-methylcyclobutene activated at a hot seasoned fused silica surface has been measured under single collision conditions over the reactor temperature range T_r = 480–800 K. The initial thermal vibrational energy population distribution of the cyclobutene molecules was varied from T_c = 273 K to T_c 570 K. The reaction is isomerization to isoprene. Mixed samples of 1-methylcyclobutene and cyclobutene (which had been studied earlier) were used for internal comparison under the same conditions. These experiments provide a test of the relative suitability of various analytical forms for the collisional transition probability matrix **P**. Stochastic calculations with a Gaussian form provide the best overall fit to the data. The calculated average amount of energy ($\langle\Delta E'\rangle_{E_0}$) transferred from the hot molecules in a vibrational down transition from the reaction threshold energy level, E_0, declined from 7220 to 3890 cm^{-1} with increase in surface temperature from 600 to 800 K. The experimental collisional efficiency, β_1, declined from 0.39 to 0.035 over the combination temperature range T_r,T_c = 600,500 to 800,293. Strong collider behavior was observed with both 1-methylcyclobutene and cyclobutene for T_r less than 450 K.

Introduction

Gas–surface vibrational energy accommodation is being intensively studied, both experimentally and theoretically.[1-5] The variable encounter method (VEM) provides a simple technique for the study of collisional transfer of vibrational energy between gas molecules and a surface[4,6-9] at levels of excitation corresponding to homogeneous unimolecular reaction. By this technique, cold substrate molecules that are initially equilibrated at low temperature T_c experience a known and experimentally variable number of sequential collisions, m, with a hot reactor surface at temperature T_r before leaving the reactor and reequilibrating to their initial low temperature. Values of m between 2 and 30 have been conventionally used. Gas molecules describe a random walk along an energy coordinate until they reach an absorbing level, the critical reaction threshold E_0, characteristic of the homogeneous gas reaction. Such relaxation of nonequilibrium vibrational energy distribution was described theoretically a number of years ago by Rubin and Shuler,[10] Kim,[11] and Widom.[12]

Recently, single collision measurements (m = 1) by the VEM technique were described for the cyclobutene (CB) system.[13,14] Initial vibrational energy of CB was varied.[14] In the present communication, we have applied the single collision condition to the study of 1-methylcyclobutene (1-MCB) system for comparison with that of CB. The surface is a "seasoned" fused quartz finger. Although such a surface is not well defined, it is the conventional experimental surface of thermal kinetics.

The vibrational energy population vector of molecules after one collision, $\mathbf{N}_1$, is given by $\mathbf{N}_1 = \mathbf{P}\mathbf{N}_c^{eq}$, where **P** is a collisional transition probability matrix, and $\mathbf{N}_c^{eq}$ is the initial vibrational energy population vector that corresponds to the thermal Boltzmann distribution at the low temperature of the gas reservoir wall. Since no comprehensive theory of gas–surface collision interaction exists, at least for complex molecules on these surfaces, down-jump transition probability elements of the **P** matrix were constructed according to various assumed mathematical models; these have some plausible connections with physical reality. Up-jump transition probabilities were constructed from the down-jump transitions with use of the conditions of detailed balance and completeness.

The ring-opening unimolecular isomerization of 1-MCB to isoprene has a low E_0 (34.2 kcal mol^{-1}); that for CB[15] is 32.4 kcal mol^{-1}. The effect of the methyl substituent on the collisional reaction probability provides an interesting comparison. Previously, a similar comparison was made for the collisional relaxation of vibrational energy transients in the methylcyclopropane and cyclopropane systems with a VEM (m > 1) technique.[9]

Experimental Section

The 1-MCB sample was a mixture containing 14% of 3-MCB as impurity; it was not removed since it caused no complication and allowed a rough concurrent measurement for its own isomerization. A similar amount of cyclobutene was added as an internal standard. The reaction system apparatus used here was the same as that for previous single collision experiments.[13,14] The reaction vessel consisted of a 3-L spherical Pyrex reservoir flask that was provided with an internally heated, central fused-quartz

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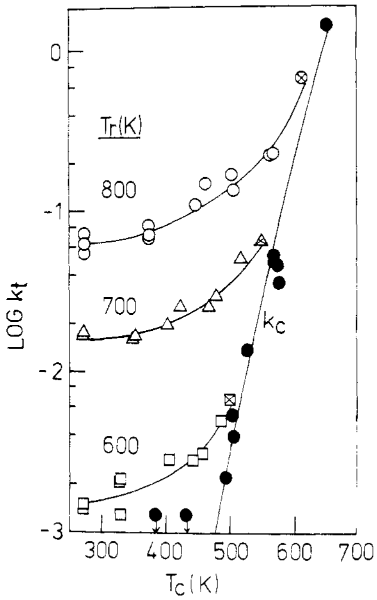

Figure 1. Observed isomerization rate constants of 1-methylcyclobutene to isoprene. Open and solid points represent the total rate constants, k_t, and the wall collisional rate constants, k_c. The crossed points were not used for the P_c calculations.

finger. The flask and the finger were heated independently. Two experimental series were used to measure the isomerization rate constants: (a) the surface temperature of the reactor finger was varied from 600 to 800 K, while the wall temperature of the flask reservoir was varied from 273 to 550 K; (b) the reactor temperature was varied from 480 to 800 K at constant wall temperature of 273 K. Temperature deviation of the finger surface was a maximum of ±5 K at 800 K, and that of the flask wall was ±10 K at 550 K. Before kinetic measurements were made, the reactor surface of fused quartz was "seasoned" at the highest temperature and the seasoning was maintained by exposure for a few hours to the mixture gas at a pressure of $\sim 5 \times 10^{-3}$ torr prior to each run.

The system was run in both static and flow modes in the pressure region between 10^{-4} and 10^{-3} torr, usually $\sim 2 \times 10^{-4}$ torr. For the flow mode, typical residence times in the reactor were 10 to 30 s. Duration of a flow run was several minutes. Detailed description of both modes was given earlier.[13] Pressure measurements were made with an MKS 146H capacitance manometer.

Product analysis was performed by gas liquid phase chromatography on a 5 ft × $^3/_{16}$ in. squalane column on Chromosorb P at 0 °C with FID detection.

Results and Discussion

Observed rate constants for 1-MCB isomerization to isoprene were calculated from the product yield. The total observed rate constant, k_t was a sum of reaction due to heating at the reaction finger, k_r, and at the reservoir wall, k_c, given by

$$k_t(T_r,T_c) = k_r(T_r,T_c) + k_c(T_c)$$

Independent measurements of $k_c(T_c)$ were made under the experimental condition, $T_r = T_c$, with use of a minor area correction for the relative surface area of the reactor finger and the reservoir wall (1:13). Both rate constants k_t and k_c are shown in Figure 1. Experimental values having a cross mark in Figure 1 were rejected, since correction for k_c amounted to $\simeq 50\%$ of the total rate k_t. The reaction probability per collision, $P_c(T_r,T_c)$, was calculated from the finger surface reaction constant $k_r(T_r,T_c)$

$$P_c(T_r,T_c) = k_r(T_r,T_c)/(A(8kT_c/\pi m)^{1/2}/4V)$$

where A is the reactor finger surface area, k is the Boltzmann constant, m is the molecular weight, and V is the volume of the reservoir flask. The values of the reaction probability are plotted as a function of T_c in Figure 2 and are listed in Table I. The experimental uncertainty in P_c is estimated to be $\sim 20\%$. Also listed is the collisional efficiency, β_1, defined as $\beta_1 = P_c(T_r,T_c)/P_c^{sc}(T_r)$; these quantities are the analogs of the conventional[16] homogeneous thermal collisional efficiency factor, β. The values of $P_c^{sc}(T_r)$ are calculated from the Boltzmann distribution population vector characteristic of T_r.

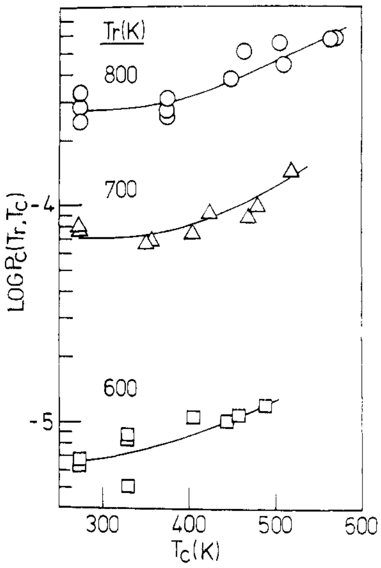

Figure 2. Plot of P_c vs. the initial temperature T_c.

TABLE I: Experimental Reaction Probability per Collision and Collisional Efficiencies in the 1-Methylcyclobutene System

T_r	T_c	273	400	500	550
800	P_c	2.8×10^{-4}	3.1×10^{-4}	4.5×10^{-4}	5.5×10^{-4}
	β_1[a]	0.035	0.039	0.056	0.068
700	P_c	7.0×10^{-5}	8.0×10^{-5}	1.2×10^{-4}	
	β_1	0.081	0.092		
600	P_c	6.5×10^{-6}	8.6×10^{-6}	1.25×10^{-5}	
	β_1	0.201	0.265	0.386	

[a] Collisional efficiency β_1 defined as $\beta_1 = P_c(T_r,T_c)/P_c^{sc}(T_r)$, where $P_c^{sc}(T_r)$ is the reaction probability for strong collider interaction of the molecule with the surface. T_r and T_c in units of K.

The mathematical forms used here for the transition probability distribution of *down*-transition energy jumps ΔE are exponential (E), Gaussian (G), a Boltzmann weighted exponential (BE), and Gaussian (BG) functions, given by eq 1–4. Here, $\langle \Delta E \rangle$, ΔE_{mp}, and σ are parameters

$$p^E(\Delta E) = C_1 \exp(-\Delta E/\langle \Delta E \rangle) \quad (1)$$

$$p^G(\Delta E) = C_2 \exp(-(\Delta E - \Delta E_{mp})^2/2\sigma^2) \quad (2)$$

$$p_{i \leftarrow j}^{BE}(\Delta E) = C_3 B_i p^E(\Delta E) \quad (3)$$

$$p_{i \leftarrow j}^{BG}(\Delta E) = C_4 B_i p^G(\Delta E); \qquad B_i = g_i \exp(-E_i/RT_r) \quad (4)$$

of the models, the C_i's are normalization constants, and B_i is a normalized Boltzmann distribution characteristic of the finger surface temperature, T_r, where g_i is the density

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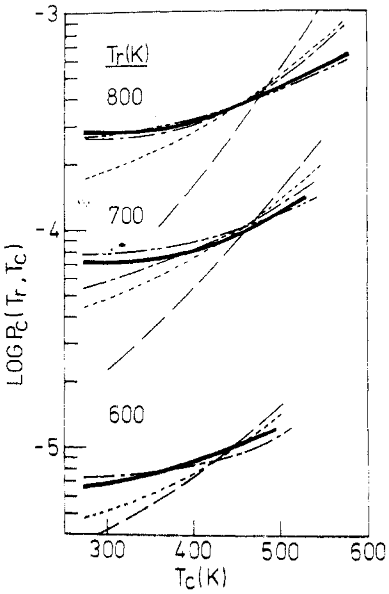

Figure 3. Calculated $P_c(T_r,T_c)$ plots for each finger surface temperature by least-squares fitting with use of the E (-·--), G (-----), BE(- - - -), and BG (---) models; the heavy solid line summarizes the experimental curve.

TABLE II: Energy Transfer Parameters[a] for E, G, BE, and BG Models Obtained by Least-Squares Fitting in the 1-Methylcyclobutene System

T_r, K	model	$\langle \Delta E \rangle$ or ΔE_{mp}	$\langle \Delta E' \rangle_{E_0}$	ΔE_{av}^+
800	E	3280	2850[c]	890
700		5820	3650[c]	800
600		b		
800	G	3890	4300[c]	630
700		4800	5180[c]	580
600		7220	6430[c]	580
800	BE	1790	3440	1130
700		1730	4780	910
600		1770	6850	690
800	BG	3570	5210	500
700		3570	6290	500
600		4160	7780	500

[a] The energy unit is cm^{-1}. [b] The E model could not be fitted to the 600 K curve in Figure 3. [c] Differ from column 3 due to truncation effects.

TABLE III: Average Energy of the Thermal Boltzmann Population in the 1-Methylcyclobutene System

T, K	273	400	500	600	700	800
$\bar{E}$, cm^{-1}	410	1080	1870	2860	4030	5320

TABLE IV: Average Energy Transfer ΔE_{av}[a] and Vibrational Energy Accommodation Coefficient α[b] for 1-Methylcyclobutene by Single Collision with a Seasoned Fused Quartz Surface

T_r, K	model	273	400	500	550
800	E	4910, 0.94	3630, 0.86	2600, 0.75	2090, 0.70
700		3460, 0.96	2470, 0.84	1540, 0.72	
600					
800	G	4670, 0.95	3950, 0.93	3120, 0.91	2640, 0.89
700		3580, 0.99	2870, 0.97	2030, 0.94	
600		2440, 1.0	1720, 0.96	910, 0.92	
800	BE	990, 0.20	960, 0.23	860, 0.25	780, 0.26
700		960, 0.27	860, 0.29	690, 0.32	
600		920, 0.38	730, 0.41	440, 0.45	

[a] $\Delta E_{av} = \bar{E}_f - \bar{E}_c$ (cm^{-1}). [b] $\alpha = \Delta E_{av}/(\bar{E}_r - \bar{E}_c)$.

of internal states at energy level E_i; σ is set equal to $0.7\Delta E_{mp}$ for the G and BG models. Transition probability values below $E = 0$ in a down transition from the energy level i were added to the element for elastic collisional transition probability, p_{ii}. The E and G models have been termed "flat"[6,7] since the distributions given by them are independent of the initial energy level. The microscopic rate constants at each reactive energy level were calculated by RRKM theory with use of the vibrational frequency assignment of Elliott and Frey;[15] these calculations were made with an energy grain size of 100 cm^{-1} that was also used to specify the transition probability matrix. Isomerization of excited molecules occurs during the average (collisionless) flight time between the reactor surface and the reservoir wall (9 cm). An average fraction, f_d, of molecules excited above E_0 that decompose during the flight time was calculated in order to estimate the dependence of the observed rate constant on the reaction probability. The most favorable experimental situation is obtained for $f_d = 1$, corresponding to $k/k_\infty \to 0$ in a homogeneous system; in this case, which holds for CB, reaction is governed only by the collisionally activated population distribution, and the need for RRKM calculations of $k(E)$, the specific reaction probability at internal energy E, with a postulated activated complex structure, is removed. In the present case, $f_d \sim 0.6$–0.65, so that the accuracy of the measurements was only moderately dependent on the accuracy of the RRKM calculational details. Clearly, as $f_d \to 0$, corresponding to $k/k_\infty \to 1$ in the $p \to \infty$ homogeneous case, no reliable information about energy transfer can be gained.

Results of the least-squares fitting to the experimental P_c curve for each reaction surface temperature (with use of $\langle \Delta E \rangle$, or ΔE_{mp}, as the parameter of fit) are shown in Figure 3 with use of four models. The corresponding parameters, the average down-transition energy $\langle \Delta E \rangle$ for E and BE, and the most probable energy ΔE_{mp} for G and BG, are listed in Table II. We have chosen to exhibit, and use, these average values rather than to enumerate a plethora of best-fit values for each value of T_c for a given T_r. Obviously, use of an average constant parameter for the whole T_c range cannot give as good fit at each T_c as would an optimized value. The calculated value of $\langle \Delta E' \rangle_{E_0}$ is the average amount of energy transferred in a down-transition from the threshold energy level E_0; $\langle \Delta E' \rangle$ is independent of E_0 for E and G but varies with initial level for BE and BG. Also listed is $\langle \Delta E^+ \rangle_{av} = [(\bar{E}_f)_{E_f > E_0} - E_0]$, the average amount of energy transferred in an up-transition to the levels above E_0. The average vibrational energy of 1-MCB molecules, $\bar{E}$, for the thermal Boltzmann distribution is given for the temperatures of interest in Table III. Another important quantity is the average energy transfer, ΔE_{av}, defined as $\Delta E_{av} = \bar{E}_f - \bar{E}_c$, where $\bar{E}_c$ and $\bar{E}_f$ are the average energies of molecules before and after single collision; ΔE_{av} is listed from results of E, G, and BE calculation in Table IV. The vibrational energy accommodation coefficient, α, is defined as $\alpha = \Delta E_{av}/(\bar{E}_r - \bar{E}_c)$, where $\bar{E}_r$ is the average energy $\bar{E}$ corresponding to $T = T_r$ and is given in Table IV.

Single collision experiments permit a more refined test of the correct form of **P** than do $m > 1$ experiments. In particular, an even more stringent criterion is realized here by changing the initial population vector $\mathbf{N}_c$. The features of the experimental P_c curves for all T_r in Figure 2 are similar to those for CB and also exhibit a foot for $T_c < 400$ K. The best fits at higher temperatures were obtained with the E and G models. The BE and BG models fail to agree with the data curve. At lower temperature ($T_r = 600$ K) where collisional interaction becomes stronger, the E model

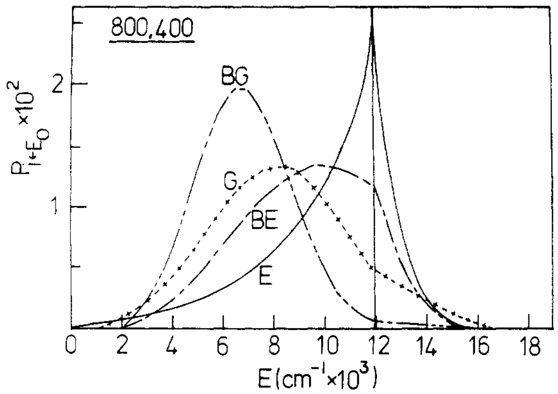

Figure 4. Plot of normalized transition probability distributions for down- and up-jumps starting from the vibrational energy level E_0 = 11950 cm^{-1}, calculated for the E, G, BE, and BG models for the temperature combination T_r,T_c = 800,400.

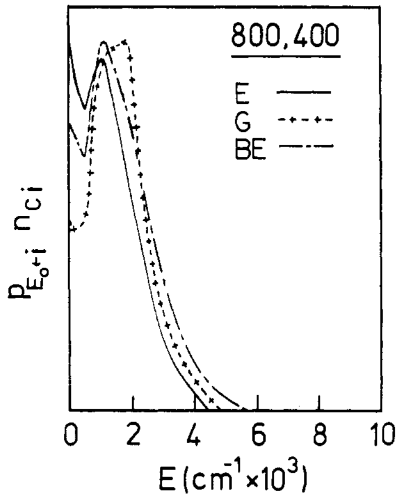

Figure 5. Curves showing relative contribution of the various elements of $\mathbf{N}_c$ to vibrational activation to the level E_0 in $\mathbf{N}_1$, given by $P_{E_0\leftarrow i}\, n_{ci}$. These illustrative plots were calculated for the reaction temperature combination (800,400) on the basis of the least-squares fitted parameters and are plotted with arbitrary units of the ordinate. Obviously, slightly different curves would result from a different temperature combination or different fitting procedure.

cannot be fitted to the experimental curve of T_r = 600 K for any reasonable parameter of $\langle \Delta E\rangle$. For each model, Figure 4 shows the normalized transition probability distribution $P_{i\leftarrow E_0}$ for up- and down-transitions from the level energy E_0 to the level i at a representative condition, T_r,T_c = 800,400 for the parameters obtained by the least-squares fitting.

It is of interest to examine the relative contribution of the various elements of $\mathbf{N}_c$ to the vibrational activation to the level E_0 in $\mathbf{N}_1$. The activation distribution, $p_{E_0\leftarrow i} n_{ci}$ vs. E, is shown for the temperature combination (800,400) in Figure 5 for the various model parameters fitted to experiment by least squares. The activation functions are mainly distributed around the initial energy 2000 cm^{-1}. The maxima would be shifted to higher energies if $\langle \Delta E'\rangle_{E_0}$ values were smaller as was illustrated previously[14] for CB.

The various transient population vectors $\mathbf{N}_1$ that arise after single collision are shown in Figure 6 for the E, G, and BE models. For E and G, the $\mathbf{N}_1$ population elements are distributed close to those for T_r = 800 K in the energy range below $E = 10^4$ cm^{-1}, while those for the BE model are much below the strong collider curve. The relative population in the energy range below E_0 provides the main criterion for the average amount of energy transferred on collision, ΔE_{av}, and for the accommodation coefficient α. Thus, the BE model gives relatively small values of ΔE_{av} and α for the (Table IV). The same situation was found in the CB system.[14]

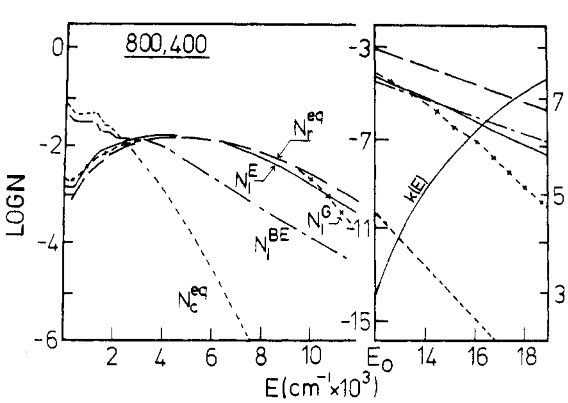

Figure 6. Relative population distribution vector vs. energy E. $\mathbf{N}_c^{eq}$ and $\mathbf{N}_r^{eq}$ represent the Boltzmann distribution curves characteristic of the initial temperature, T_c = 400 K, and the reactor surface temperature, T_r = 800 K, respectively. $\mathbf{N}_1$ superscripted E, G, and BE represent the transient distribution curve after one collision with the surface, the two left ordinates apply. The $k(E)$ curve is the RRKM isomerization rate constant to which the right side ordinate applies.

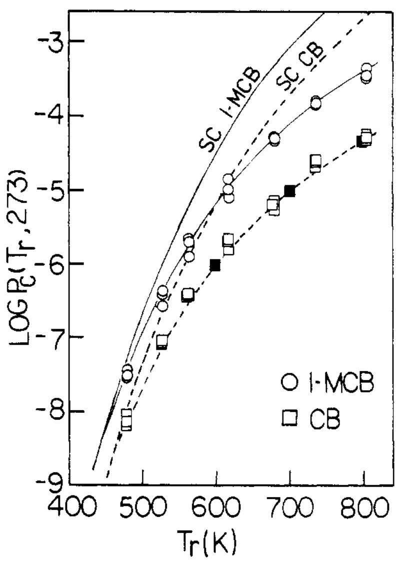

Figure 7. Plots of experimental values of $P_c(T_r,273)$ vs. T_r for 1-MCB (—) and CB (----) substrates measured by internal comparison in the same reaction system. Also shown are the calculated strong-collider $P_c^{sc}(T_r)$ curve. Solid squares represent earlier experimental values.[14]

By contrast, P_c values are determined by the reacting state population above E_0, in the $\mathbf{N}_1$ vector, and which derives from the product of the up-transition probability to states above E_0 with the state populations of the $\mathbf{N}_c$ vector below E_0. And although α(BE) is smaller than α(G) or α(E), it is evident from Figure 6 that the BE model is relatively very efficient in transferring molecules to levels above E_0. Indeed, it gives rise to too-large values of P_c at higher temperatures. As discussed in our earlier CB study, the models for $\mathbf{P}$ that fit the experimental P_c values are not necessarily adequate to predict α. It is clearly evident that measurements of α and P_c are both desirable in order to deduce the most apt form of $\mathbf{P}$.

Plots of $P_c(T_r,273)$ obtained by simultaneous measurements of gas mixtures containing both 1-MCB and CB are shown in Figure 7. Filled squares represent the P_c values from the earlier CB experiment.[14] Good reproducibility for CB is evident and supports the presumption of a negligible role of catalytic reaction on the fused quartz surface.

Strong collider behavior is found for both CB and 1-MCB molecules curves at T_r < 450 K. This behavior for

TABLE V: Some Comparisons of 1-Methylcyclobutene with Cyclobutene in Single Collision Systems

	CB[14]	1-MCB[a]
$P_c(800,400)$	4×10^{-5}	3×10^{-4}
$P_c(600,400)$	1×10^{-6}	9×10^{-6}
E_0, kcal mol^{-1}	32.4	34.2
k(E),[b] s^{-1}	$\sim 10^5$	$\sim 10^3$
f_d	1	0.64 (800,500)[e] 0.60 (600,273)[e]
$\bar{E}_{400}$,[c] cm^{-1}	760	1080
$\langle \Delta E' \rangle_{E_0}$[d]	4090	4300

[a] Present work. [b] The isomerization rate constant by RRKM theory at several 100 cm^{-1} above E_0. [c] Average thermal energy at 400 K. [d] Average down-transition energy from the level of energy E_0, given by the G model for T_r = 800 K. [e] Calculated by G model.

TABLE VI: Energy Transfer Parameters[a] Fitted to Experimental $P_c(T_t,273)$ with the G Model in the 1-MCB and CB Systems

T_r, K		600	700	800
$\langle \Delta E' \rangle_{E_0}$	CB	5595	4580	4070 (2490)[b]
	1-MCB	6325	5350	4630 (2870)[b]
ΔE_{av}	CB	1620	2420	3200 (2480)[b]
	1-MCB	2400	3590 (3450)[b]	4740 (4640)[b]
α	CB	0.96	0.96	0.94 (0.73)[b]
	1-MCB	1.0	0.97 (0.96)[b]	0.97 (0.95)[b]
β_1	CB	0.13	0.044	0.021
	1-MCB	0.21	0.084	0.036

[a] In units of cm^{-1}. [b] Parenthetic calculation made with the least-squares fitted E model.

CB has been shown in earlier CB studies.[7,13,14] This trend is related to the fact that, as T_r is lowered, the time that molecules spend trapped in the gas–surface potential well increases.

Some comparison of 1-MCB with CB for the single collision conditions are given in Table V. The relatively larger experimental values of P_c for 1-MCB seems to result from the difference in molecular vibrational eigenstate densities, as illustrated by the mean vibrational energies at 400 K: 1-MCB, $\bar{E}_{400}$ = 1080 cm^{-1}; CB, $\bar{E}_{400}$ = 760 cm^{-1}.

The least-squares fit values of $\langle \Delta E' \rangle_{E_0}$ for the G model, for 1-MCB and CB, are listed in Table VI.

In the previous VEM studies ($m < 1$) of $P_c(T_r,273)$, comparison[9] of methylcyclopropane with cyclopropane and of[17] cyclopropane with cyclopropane-d_6 was made with use of the best fitted E model in the reactor temperature range above T_r = 800 K. It was found that $\langle \Delta E' \rangle_{E_0}$ decreased with an increase in the vibrational heat capacity of each pair of molecules. The energy transfer (m = 1) parameters for 1-MCB and CB fitted to the experimental $P_c(T_r, 273)$ values are listed with use of the G model in Table VI. The more complex 1-MCB molecule appears to exhibit somewhat stronger collider behavior, unlike the methylcyclopropane and the cyclopropane systems where the smaller molecule gave larger $\langle \Delta E' \rangle$ values. The same trend is observed in the $\langle \Delta E' \rangle_{E_0}$ values calculated with use of the best fit E model to the T_r = 800 curve, and in the collisional efficiency β_1. We must leave this effect of structure for future resolution.

The G model leads to $\alpha \sim$ 0.9–1.0 for all T_r used (Table IV).

Note: A referee has raised a valid question regarding the exponential distribution function for mean free paths in a gas with respect to molecules that leave the hot finger. Thus, at 2×10^{-4} torr, roughly 10% of these molecules experience a collision with another molecule within a distance of 1.4 cm from the hot surface. He has questioned whether such molecules have been thermally equilibrated at T_c before experiencing another collision with the reactor finger. In fact, this concern had been tested pragmatically by us over a range of a factor of 10 in pressure extending from 10^{-4} to 10^{-3} torr (see Experimental Section). No change in the experimental result within experimental error was found: in effect, the fraction of molecules of concern that are backscattered and hit the finger is minor, and those that are have been adequately cooled (recall that the area of the cold reservoir wall is much larger than that of the finger).

Acknowledgment. We thank Professor H. M. Frey for the gift of a sample of 1-MCB. This work was supported by the Office of Naval Research.

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