Surface–Gas Energy Transfer in the Cyclopropane/Cyclobutane Isomerization Systems by the Variable Encounter Method

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The isomerization of cyclopropane to propene has been investigated in three different reactors using VEM under conditions identical with those used in a previously reported study on cyclobutane. In order to establish the relative collision efficiency of the wall vis-a-vis these two substrates, we also studied the simultaneous reaction of cyclobutane in the largest reactor. The treatment of the transients in the vibrational energy distribution is amplified in this paper. The distribution functions $f(n)$ for numbers of collisions in each reactor are displayed, as are the contributions to reaction $R(n)$ as a function of the number of consecutive collisions n. The present data are compared with those obtained by Kelley et al.; the average size of an internal energy down transition ($\langle\Delta E'\rangle$) for cyclopropane molecules colliding with a hot surface is a little lower than previously estimated. The increasing efficiency of the surface in deactivating energized molecules as the surface temperature decreases is confirmed ($\langle E'\rangle = 2550$ cm^{-1} at ~1100 K). The surface acts as a somewhat stronger collider for cyclopropane than for cyclobutane and is also a more efficient collider for cyclopropane than are gas–gas cyclopropane collisions.

Introduction

The variable encounter method (VEM) is a new and simple technique whereby studies can be made of energy transfer between a hot surface and gaseous substrate molecules in the transient region; an initial vibrational energy distribution of the molecules is transformed into the distribution characteristic of the surface temperature by a series of collisions with the surface.

Studies of the isomerization of cyclopropane to propene by Barton et al.[1] gave average probabilities of reaction per collision with the hot surface somewhat *higher* than those previously reported by Kelley et al.[2] for 1,1-cyclopropane-d_2 using this same technique; the disagreement was most pronounced at lower temperatures (900 K). In addition, a VEM study of the decomposition of cyclobutane with the same reactor as was employed in ref 1 has been reported[3] in which the average energy transferred per collision with the wall for down transitions of cyclobutane was somewhat *less* than that found for cyclopropane-d_2 at a similar temperature (e.g., 1850 and 2600 cm^{-1} at 1100 K for cyclobutane and cyclopropane, respectively, with use of a Gaussian model for the energy transfer probabilities).

In order to clarify the situation with respect to the above observations, we found it desirable to restudy cyclopropane in the same reactor and under the same conditions of seasoning and of surface as had been used for the cyclobutane study and, if possible, to study the two systems simultaneously. The results of such a study are reported here together with a detailed calculational treatment of the transient behavior of the contribution to reaction by substrate molecules, due to some (variable) number of collisions with the surface, due to their changing vibrational energy distribution.

Experimental Section

The entire reaction and analytical system was similar to that described previously.[3] The initial temperature of molecules before encounter with a reactor was ~350 K. The reactors used provided mean numbers of collisions, m, that a gas molecule suffered with wall per encounter with the reactor, of 27.2, 8.5, and 2.6.

Cyclopropane (99.9% with 0.08% propene as the major impurity) and cyclobutane (99.8% with propene and butene-1 the major impurities) were thoroughly degassed before use.

Before all kinetic runs, the reactor was aged by pyrolyzing cyclopropane (or cyclopropane plus cyclobutane) at a pressure between 3×10^{-4} and 3×10^{-3} torr for prolonged periods at a temperature equal to the highest temperature used for that reactor. Aging of the $m = 27.2$ reactor occurred readily; reproducible rates resulted from aging for 24–48 h. Cyclopropane formed no products other than propene and trace amounts of methane in this reactor. Aging of the 8.5 and 2.6 reactors proved more difficult. In the latter instance, up to 1–2 weeks was required before reproducible rates were obtained; the reaction rate slowly declined during the aging period. At the highest temperatures investigated in this reactor, the formation of acetylene was also observed. Aging also continuously reduced acetylene yields. The rate of formation of propene converged to a constant rate faster than the rate for acetylene and the rate constant for propene formation was found to be independent of the rate of formation of acetylene. The relative amount of acetylene formed decreased rapidly with decrease of temperature and at 1000 K in a seasoned reactor acetylene yields had already dropped to less than 3% of the propene yields.

The reaction rate was measured by adding aliquots of either cyclopropane (initial pressure ~1.6×10^{-4} torr) or an equimolar mixture of cyclopropane and cyclobutane (total initial pressure ~3.2×10^{-4} torr) to the reaction vessel for known times, and quantitatively trapping reactants and products which were then analyzed by gas chromatography on a 6 ft × 1/8 in. diameter 28% squalane on 60–80 mesh Chromosorb P column at room temperature with use of fid. A trapping time correction (~10 s) was added to the measured pyrolysis time used to calculate rate constants.

Results and Dicussion

Although the isomerization of cyclopropane to propene has been one of the most widely studied unimolecular

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(1) B. D. Barton, D. F. Kelley, and B. S. Rabinovitch, *J. Phys. Chem.*, 84, 1299 (1980).

(2) D. F. Kelley, B. D. Barton, L. Zalotai, and B. S. Rabinovitch, *J. Chem. Phys.*, 71, 538 (1979); D. F. Kelley, L. Zalotai, and B. S. Rabinovitch, *Chem. Phys.*, 46, 379 (1980).

(3) M. C. Flowers, F. C. Wolters, B. D. Barton, and B. S. Rabinovitch, *Chem. Phys.*, 47, 189 (1980). Note the following erratum in this reference: The right ordinate of Figure 5 should carry the legend $P(n) \times 10^4$.

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TABLE I: Probabilities of Reaction of Cyclopropane (and Cyclobutane) per Collision ($\bar{P}_c(m)$) for Various Reactors

			$m = 27.2$			
T, K	1080	1034	959	890	843	789
$\bar{P}_c(m) \times 10^7$	42.4	15.7	2.56	0.47	0.090	0.021
	745[a]	331[a]	75.4[a]	13.8[a]	3.53[a]	0.51[a]
			$m = 8.5$			
T, K	1080	1033	959	880	842	786
$\bar{P}_c(m) \times 10^7$	17.9	7.52	1.47	0.30	0.074	0.021
			$m = 2.6$			
T, K	1141	1078	999	928	852	
$\bar{P}_c(m) \times 10^7$	1.06	0.35	0.095	0.021	0.0072	

[a] Cyclobutane values.

reactions, and, in conventional thermal studies, appears to be a homogeneous reaction without significant contributions from surface reactions, the present study suggests that in addition to the homogeneous reaction, a very minor wall reaction that produces acetylene, may also occur. Fortunately, the reaction giving rise to propene was unaffected by this side process. The continuing slow decline in acetylene yields with further aging (while propene yields remained constant) indicates that these products result from different processes.

The isomerization of cyclopropane to propene was investigated over the temperature range 786–1141 K. In the m = 27.2 reactor, which closely approaches steady-state conditions ($m = \infty$), it was possible to study the cyclopropane and cyclobutane reactions simultaneously. However, because of the higher rate of cyclobutane decomposition compared to cyclopropane isomerization in the transient regime, coupled with the formation of small amounts of propene from cyclobutane, it was not possible to study the two molecules simultaneously in the smaller m reactors.

At each temperature, first-order plots for loss of cyclopropane were accurately linear and passed through the origin; for runs in the m = 27.2 reactor with a cyclopropane–cyclobutane mixture, a small propene correction was made for known amounts that arose from cyclobutane. The extent of reaction at not less than five different reaction times was determined at each temperature.

The average probability, $\bar{P}_c(m)$, for isomerization of cyclopropane to propene per collision with the hot wall was calculated from the apparent first-order rate constants with use of simple kinetic theory and the known reactor dimensions. Values of $\bar{P}_c(m)$ are shown in Table I, and values of log $\bar{P}_c(m)$ vs. temperature are plotted in Figure 1.

The distribution function for numbers of collisions and hence the fraction of molecules f(n) remaining after n collisions was determined by Monte Carlo calculation of a large number (5×10^3–20×10^3) of individual molecular trajectories (Figure 2). This distribution was then used in an iterative simulation of the encounter process. The details of these calculations are given in ref 2.

Two different models for the probability of a down transition ΔE were used: (exponential): $P_{\Delta E} = A \exp(-\Delta E/\langle\Delta E\rangle)$ for $0 \leq \Delta E \leq 9000$ cm^{-1}; $P_{\Delta E} = 0$ for $\Delta E > 9000$ cm^{-1}; (Gaussian): $P_{\Delta E} = A' \exp\{-(\Delta E - \Delta E_{mp})^2/2\sigma^2\}$ for $0 \leq \Delta E \leq 9000$ cm^{-1}; $P_{\Delta E} = 0$ for $\Delta E > 9000$ cm^{-1}. Here, A and A' are normalization constants: $\langle\Delta E\rangle$, ΔE_{mp} (mp signifies most probable) and σ are parameters of the model; $\langle\Delta E\rangle$, ΔE_{mp} were taken as constant, independent of the initial energy level ("flat" models), and σ was set equal to $0.7\Delta E_{mp}$. The truncation, $\Delta E < 9000$ cm^{-1}, is a practical computational feature to limit the transition probability matrix to more tractable dimensions. Detailed balance and completeness were maintained. It should be noted that because of the truncation at 9000 cm^{-1}, and also at zero energy in the case of the Gaussian model, the effective average down transition size, called $\langle\Delta E'\rangle$, is not equal to $\langle\Delta E\rangle$ or ΔE_{mp}, except when the latter quantities and σ are small; $\langle\Delta E'\rangle$ may be significantly different from $\langle\Delta E\rangle$.

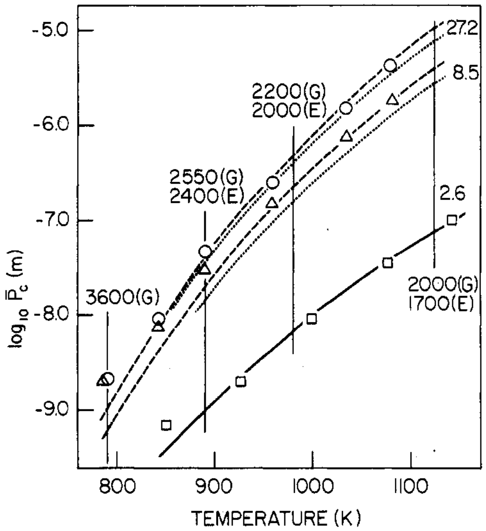

Figure 1. Plots of experimental values of log $\bar{P}_c(m)$ vs T(K) for each of the three reactors. Also shown are curves calculated on the basis of Gaussian (G),----, and exponential (E),····, models. The values of down jumps $\langle\Delta E'\rangle$ required to fit the m = 2.6 (or m = 8.5 at 790 K) curve are given for Gaussian and exponential models.

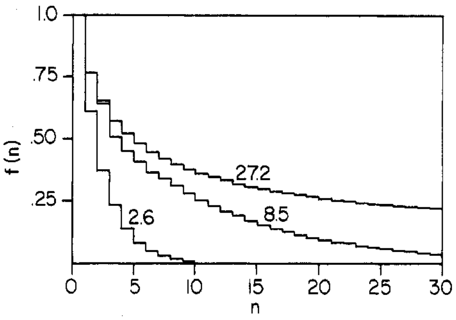

Figure 2. Calculated histograms of the fraction of molecules remaining in the reactor after n collisions, $f(n)$, vs. n, for the three reactors.

The microscopic rate constants for the isomerization of cyclopropane to propene, which are required in the computer simulation, were calculated from RRKM theory. The molecular and transition state frequencies, reaction path degeneracy, and critical energy of the reaction were the same as previously adopted for this reaction.[4]

The results of the computer simulation are included in Figure 1 for both models. In each case, a value of $\langle\Delta E'\rangle$ was found that produced a fit to the experimental data for the smallest (m = 2.6) reactor. The curves for two larger reactors were then calculated by using the same values for $\langle\Delta E'\rangle$. This approach was adopted since the value of $\bar{P}_c(m)$ for the reactor with the smallest mean collision number is the most sensitive to changes in $\langle\Delta E\rangle$.

One may also define a relative collisional efficiency similar to the quantity used in steady-state thermal unimolecular systems, as

$$\beta_c = P_c(\text{steady state})/P_c(\text{strong collider})$$

The values of β_c found in this study are given in Table II.

As noted in ref 2, very little reaction takes place in the first few collisions, i.e., $P(n)$, defined as the probability of

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[4] E. Kamaratos, J. F. Burkhalter, D. G. Keil, and B. S. Rabinovitch, *J. Phys. Chem.*, 83, 984 (1979).

TABLE II: Values of β_c in the Cyclopropane VEM System

T, K	790	890	980	1123
β_c	0.79	0.64	0.54	0.43

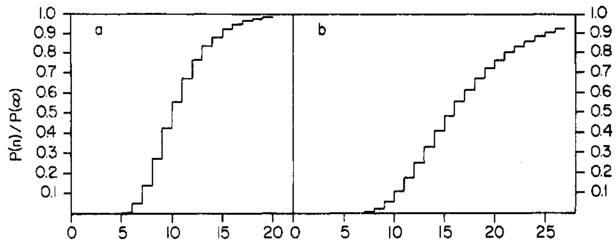

Figure 3. Histograms of the calculated sequential reaction probability $P(n)$ vs. n, the number of consecutive collisions. Calculations were performed with a Gaussian model at (a) 890 and (b) 1123 K.

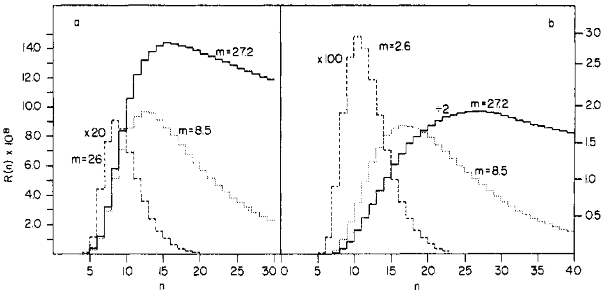

Figure 4. Histograms of the sequential reaction probability $R(n) = P(n)f(n)$ vs. n, the number of consecutive collisions. Calculation for the different reactors was performed with a Gaussian model at (a) 890 and (b) 1123 K.

reaction per collision per remaining molecule, after n collisions, is approximately zero for $n \leq 4$ (Figure 3). Hence, in the small m reactors, it is only those molecules which experience a number of collisions significantly greater than m that make a nonnegligible contribution to the amount of reaction $R(n) = f(n)P(n)$. This is seen in Figure 4, where the function $R(n)$ is plotted. The transients that occur in the vibrational level population vector with increasing n have been sketched in ref 2 and 3.

Data obtained in this study for $m = 27.2$ and 8.5 give comparable (just slightly lower) values of $\bar{P}_c(m)$ to those obtained in the earlier study[2] of 1,1-cyclopropane-d_2 in reactors of closely like m values ($m = 22$ and 10.5). However, values for the $m = 2.6$ reactor were lower than those obtained earlier in a $m = 2.3$ reactor. The consequence of this is that the values of $\langle \Delta E' \rangle$ that fit the experimental data are somewhat lower than those reported in ref 2, e.g., for a "flat" Gaussian model at ~1100 K, $\langle \Delta E' \rangle = 2030$ cm^{-1} in this work, but $\langle \Delta E' \rangle = 2580$ cm^{-1} previously; and at ~900 K, $\langle \Delta E' \rangle = 2510$ cm^{-1}, and was 3100 cm^{-1} previously. However, the values for $\langle \Delta E' \rangle$ found in the present study are still higher than those found for cyclobutane with this same experimental system and, in the case of data for the 27.2 reactor, than was found for cyclobutane in experiments in which cyclopropane and cyclobutane were pyrolyzed together. (This latter finding, especially, assures us that the difference in wall efficiency found here between cyclopropane and cyclobutane is real and is not an artifact due to a difference in experimental conditions.) For the Gaussian model, $\langle \Delta E' \rangle$ is ~1850 and 2125 cm^{-1} at 1123 and 900 K, respectively, for cyclobutane (Table II).

The Gaussian model fits cyclopropane data somewhat better than the exponential model. At the lowest temperature investigated in each case, values of $\bar{P}_c(m)$ in all three reactors were higher than would be expected on the basis of extrapolation of the data obtained at higher temperatures (Figure 1). This is particularly evident for the $m = 2.6$ reactor. It would seem that surface reactions begin to contribute significantly to the reaction rate at the lowest temperature. Such behavior was absent for cyclobutane.[3] We conclude that the variations between the present study and that of Kelley et al. are minor in character and that both reveal substantially the same behavior. The study by Barton et al. gave higher values of $\bar{P}_c(m)$, and hence of $\langle \Delta E' \rangle$, especially at 900 K ($\Delta E' = 4900$ cm^{-1} (Gaussian)); nonetheless, it also reveals the same basic characteristic features of this new data on the transients in energy transfer. The reason for the high values by Barton et al. was, undoubtedly, insufficient appreciation of the need for more prolonged aging of the reactor.

TABLE III: Values for $\langle \Delta E' \rangle$ in Recent VEM Studies[a] (cm^{-1})

molecule	model[b]	825	900	1000	1100	ref
		T, K				
cyclopropane	G		4900	3275	2700[c]	1
cyclopropane-1,1-d_2	G	3500	3100	2875	2580	2
	E	~6500[d]	3035	2750	2280	
cyclopropane	G	2950	2500	2170	2040	this work
cyclobutane	E	2020	1780	1600	1480	3
	G	2420	2125	1925	1875	

[a] Some values by slight interpolation. [b] G = Gaussian; E = exponential. Probability distribution model given is the one that fits the data better; behavior is intermediate between Gaussian and exponential in ref 2; exponential is better for cyclobutane (ref 3) but Gaussian model values are also given for easier comparison with cyclopropane values. [c] 25-deg extrapolation. [d] Large magnitude suggests strongly that the exponential model is not physically realistic for describing the more efficient transfer behavior observed at lower temperature; this value calculated with truncation of probability matrix at 18000 cm^{-1}.

Finally, the general trend of an increasing efficiency for deactivation of energized molecules by surface collisions as the temperature is decreased, observed previously in VEM studies of both the isomerization of dideuteriocyclopropane[2] and of the decomposition of cyclobutane,[3] is borne out in this study; the value of $\langle \Delta E' \rangle$ rises to 3600 cm^{-1} at ~800 K, on a Gaussian model from the value of 2030 cm^{-1} at 110 K (Table II). It also accords with the decrease in efficiency with increase of temperature found previously in homogeneous bath gas studies on cyclopropane-d_2.[5]

The latter comparison also confirms[1-3] that the wall is a stronger collider than is the parent substrate molecule. Thus, the value at 973 K measured here for gas-wall collisions is $\langle \Delta E' \rangle = 2275$ cm^{-1}, on a Gaussian model. By comparison, the gas-gas value for neat cyclopropane-d_2 measured at the same temperature by Klein and Rabinovitch[5] is 1850 cm^{-1} and by Krongauz et al.[6] is 1625 cm^{-1}. This relative behavior accords with the general increase of collision efficiency that attends increase of molecular complexity (increasing chain length) in gas-gas collisions.[7]

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(7) Y. N. Lin, S. C. Chan, and B. S. Rabinovitch, *J. Phys. Chem.*, **72** 1932 (1968).