($\gtrsim$10%), secondary reactions begin to noticeably influence reaction kinetics as noted by the formation of excess toluene and diphenylmethane and the darkening of the pyrolysis mixture. Further work is needed to clarify the reactions responsible for this behavior.

We find that use of thermochemical kinetics techniques, developed for gas-phase reactions, leads to consistent and useful predictions for the chemistry of high-temperature, liquid-phase reactions. In one sense, agreement between the computer-model predictions and observed product formation rates is made possible by use of "adjustable" rate parameters. However, the point of the present analysis is to show that these rate parameters all fall within the often narrow range of values consistent with thermochemical kinetics calculations and existing rate data. Such modeling also serves the purpose of clearly indicating aspects of the reaction that are not yet understood.

Application of the approach used in the present studies to other systems should lead to consistent sets of rate parameters for all common classes of elementary reactions in liquid pyrolysis and to the development of a firm understanding and predictive ability of chemical mechanisms in these reactions.

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Supplementary Material Available: Appendixes I and II, giving a detailed description of the reasons for choosing specific rate-constant values and of the associated reaction thermochemistry (12 pages). Ordering information is given on any current masthead page. A computer listing of the reaction model, including concentrations of all intermediates, is available upon request from the authors.

Transients in Thermal Isomerization of Cyclobutene by the Variable Encounter Method. Vibrational Energy Transfer and Relaxation at Lower Temperatures

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Vibrational energy transfer and relaxation in the thermal isomerization of cyclobutene to 1,3-butadiene has been studied over the temperature range 429–778 K by using the variable encounter method (VEM). Reactors characterized by various mean numbers of collisions, m, per encounter of a substrate molecule with the reactor (m = 2.6, 5.9, 8.5, and 27.2) were used. Strong collider behavior in collisions of substrate with a seasoned fused quartz wall was observed at lower temperatures (below 450 K) as evidenced by the coincidence of values of the probability of reaction per collision, $\bar{P}_c(m)$, obtained in VEM reactors having different m values. The average energy transferred to the wall per deactivating collision, $\langle \Delta E' \rangle$, increased strongly as temperature decreased, from $\langle \Delta E' \rangle$ = 2150 cm^{-1} at 764 K to >6000 cm^{-1} at 460 K. Various forms of models for the probability of energy transfer in down transitions were applied to data.

Introduction

The variable encounter method (VEM) has been shown to be a technique whereby studies can be made of energy transfer between a hot surface and gaseous molecules in the transient region. Investigations have been reported previously on cyclopropane-d_2,[1] cyclobutane,[2] cyclopropane,[3,4] and methylcyclopropane.[5] The efficiency for deactivating energized molecules has been found to decrease significantly with increase of temperature in the range 750–1150 K.

The isomerization of cyclobutene to 1,3-butadiene has been studied in conventional thermal systems in the temperature range 400–450 K.[6] The high-pressure first-order rate constant was found to be given by the expression $k(\mathrm{s}^{-1}) = 2.5 \times 10^{13} \exp(-32900/1.987T)$. The reaction is unaffected by surface catalysis and, coupled with its low critical threshold energy, seemed ideal for the purpose of applying VEM at temperatures much lower than were feasible in the previous work. In this paper we present the results of our work with this molecule studied on a seasoned quartz surface over the temperature range 429–778 K. A preliminary account has appeared.[7]

Experimental Section

The reaction system, reactors and procedure, were identical with those described previously;[2] these reactors were characterized by mean numbers of collisions per encounter, m, of 27.2, 8.5, and 2.6. In addition, an m = 5.9 reactor was also used. Reactor temperatures were controlled to ±1 °C. Temperature gradients for the 27.2 and 8.5 reactor varied between ±6 °C at the highest temperature to ±2 °C at the lowest temperature used. For the

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TABLE I: Mean Probabilities for Reaction of Cyclobutene per Collision with the Reactor Wall, $\bar{P}_c(m)$

reactor i, m = 27.2	temp (K)	643	577	512	461	429	
	$10^7\bar{P}_c(m)$	477	46.8	2.06	0.0995	0.0112	
reactor ii, m = 8.5	temp (K)	665	585	516	463		
	$10^7\bar{P}_c(m)$	736	53.7	2.28	0.112		
reactor iii, m = 2.6	temp (K)	778	731	668	585	523	469
	$10^7\bar{P}_c(m)$	1930	844	230	21.0	1.91	0.122

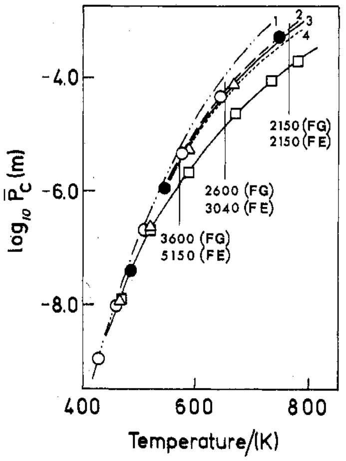

Figure 1. Plot of calculated and experimental values of log $\bar{P}_c(m)$ vs. temperature for cyclobutene. Experimental data: (○) m = 27.2; (△) m = 8.5; (●) m = 5.9; (□) m = 2.6. Calculated data: curve 1, strong collider; curve 2, model FG, m = 27.2; curve 3, model FE, m = 27.2, and model FG, m = 8.5, which coincide; curve 4, model FE, m = 8.5. All models were fitted to the m = 2.6 data. Values of $\langle \Delta E' \rangle$ (the model used is indicated in parentheses) used to fit the curves to the experimental data are indicated at three temperatures.

2.6 reactor, temperature gradients at the highest temperature were ±10 and ±4 °C at the lowest temperature. In order to test the assumption that the temperature gradients near the tops of the reactors were negligible and to verify that the average temperatures used were correct, we replaced the stainless-steel heater block with a stirred oil bath at 476 ± 0.2 K. The observed reaction rates were identical with those obtained by using the heater block. In an experiment designed to simulate a much worse temperature gradient than any encountered, the oil-bath level was lowered from its original level (2–3 mm above the top of the m = 2.6 reactor) to a level ~1–2 mm below the top of the reactor. The decrease in the observed reaction rates was less than 20%. After trap-to-trap distillation, cyclobutene showed no impurity greater than 0.05% upon analysis by gas chromatography. Before kinetic runs, the cyclobutene reactant was thoroughly degassed. The reactors were aged by pyrolysis of cyclobutene at ~4 × 10^{-4} torr for 24–48 h at the highest temperature used for that reactor. Additional aging at even higher temperature, e.g., 1100 K for the m = 2.6 reactor, had no effect.

The reaction rate was measured by adding aliquots of cyclobutene from a gas buret to the reaction vessel, pyrolyzing the reactant for measured times, and then rapidly freezing the reaction mixture in a glass-wool-packed trap cooled to 77 K. A measured freeze-down time correction of ~10 s was added to the measured pyrolysis times which varied upward from 1 min. Good straight-line relationships (cf. Figure 2 of ref 2) were obtained in the plots of log fraction unreacted vs. time.

Analysis of the reaction mixture was accomplished by gas chromatography with use of a 6-ft $^1/_8$-in. i.d. column of 28% squalane on 60–80-mesh fire brick and flame ionization detection.

Results and Calculations

The isomerization of cyclobutane to 1,3-butadiene was investigated over the temperature range 429–778 K at an initial pressure of ~1.7 × 10^{-4} torr of cyclobutene. 1,3-Butadiene was the only detectable product. A mass balance to better than 95% was observed.

At each temperature first-order rate plots were accurately linear and went through the origin. From these plots, which normally composed the result of at least seven different run times, an apparent first-order rate constant was determined. The standard deviation of the slope of these plots was typically 1%.

The rate constants were converted into the mean probability of reaction per collision with the reactor wall, $\bar{P}_c(m)$, in the manner described previously.[1] Values of $\bar{P}_c(m)$ are given in Table I for m = 2.6, 8.5, and 27.2. A plot of log $\bar{P}_c(m)$ vs. temperature is given in Figure 1 along with some more limited data obtained in the m = 5.9 reactor. A stochastic computer simulation procedure of the collisional processes has also been described previously.[1] Various pragmatic forms for the probability of a given down transition, p_{ij}, of an energized molecules of energy E_j going to energy E_i, were investigated: model FE ("flat" exponential), $p_{ij} = c_1 \exp(-\Delta E/\langle \Delta E \rangle)$; model FG ("flat" Gaussian), $p_{ij} = c_2 \exp\{-(\Delta E - \Delta E_{mp})^2/(2\sigma^2)\}$; model LG ("linear" Gaussian), $p_{ij} = c_3 \exp\{-(\Delta E - \Delta E_{mp})^2/(2\sigma^2)\}$, where ΔE_{mp} (cm^{-1}) = 100 + αE_j; model EB (exponentially weighted Boltzmann), $p_{ij} = c_4 N(E_i) \exp[-E_i/(RT)] \exp(-\Delta E/\langle \Delta E \rangle)$; model GB (Gaussian weighted Boltzmann), $p_{ij} = c_5 N(E_i) \exp[-E_i/(RT)] \exp\{-(\Delta E - \Delta E_{mp})^2/(2\sigma^2)\}$. The c's are normalization constants; $\langle \Delta E \rangle$, ΔE_{mp} (mp signifies most probable), α, and σ are parameters of the models; $\langle \Delta E \rangle$, ΔE_{mp}, was constant in all cases except for model LG; σ was set equal to 0.7ΔE_{mp}; $N(E_i)$ is the density of states for a cyclobutene molecule of internal energy E_i. An early computational feature (desirable to limit the probability matrix **P** to tractable dimensions) imposed a limit of 9000 cm^{-1} on ΔE (=$E_j - E_i$); then p_{ij} = 0 for ΔE > 9000 cm^{-1}. Detailed balance and completeness were maintained. Because of the limitation in the size of **P**, the values of $\langle \Delta E \rangle$ and ΔE_{mp} are related to, but not necessarily equal to, the *effective* average down transition size $\langle \Delta E' \rangle$; (note: $\langle \Delta E' \rangle$ for some models varies with the initial energy of the cyclobutene molecule, and in these cases the value of $\langle \Delta E' \rangle$ at the critical reaction threshold energy (E_0) has been used to characterize the size of the down step). Later calculations were made with a limit on ΔE of 18 000 cm^{-1}; the value of $\langle \Delta E' \rangle$ is found to be substantially invariant.

Models EB and GB have functional forms which, in the limit of very large average amounts of energy transferred per collision, approach strong collider behavior more closely than do models FE, FG, and LG. True strong collider behavior will not be precisely observed owing to the limitation on the size of **P**.

The microscopic rate constants for the isomerization of cyclobutene molecules were calculated from RRKM theory using the frequency assignments of "Model C" of Elliott and Frey,[6] but with removal of the exact commensurability employed by them to simplify the calculation. Variation of k_E with E is shown in Figure 2 along with corresponding plots for cyclopropane and cyclobutane. The fraction of

TABLE II: Calculated Mean Probabilities for Reaction of Cyclobutene Molecules per Collision with the Reactor Wall, $\bar{P}_c(m)$, for Various Energy-Transfer Models

					$-\log \bar{P}_c(m)$				
					$m = 27.2$		8.5		
temp K	model	$\langle \Delta E \rangle$ ΔE_{mp}, cm^{-1}, or α	$\langle \Delta E' \rangle$, cm^{-1}, at E_0	SC[a]	calcd	exptl	calcd	exptl	2.6[b]
571	FE	6400	5150		5.47		5.54		
	FG	3300	3600		5.44		5.50		
	LG	0.40	4500	5.30	5.44	5.44	5.51	5.53	5.90
	EB	1100	5850		5.40		5.48		
	GB	1750	3700		5.39		5.45		
652	FE	3200	3040		4.29		4.37		
	FG	2350	2600		4.24		4.32		
	LG	0.32	3950	4.00	4.20	4.20	4.30	4.30	4.81
	EB	1120	4500		4.17		4.27		
	GB	1600	2950				4.26		
764	FE	2400	2150	2.75	3.20		3.29		3.78
	FG	1960	2150		3.12		3.21		

[a] Limiting strong collider value. [b] The calculated value for each model was adjusted to fit experiment for $m = 2.6$; see text.

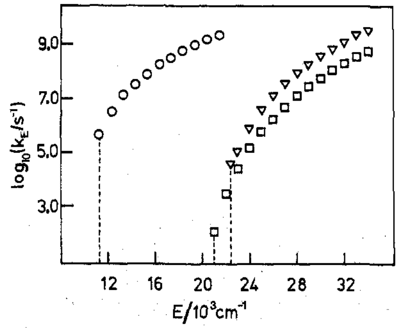

Figure 2. Calculated plots of the microscopic reaction rate constants, k_E, vs. energy (cm^{-1}) for (O) cyclobutene (E_0 = 11400), (▽) cyclopropane (E_0 = 22300), and (□) cyclobutane (E_0 = 20800).

molecules excited to energy levels above E_0 which undergo reaction is >98% for cyclobutene, compared to ~75% and 20% for cyclopropane and cyclobutane, respectively, at 1100 K. Thus, cyclobutene is virtually in the second-order region where the critical energy threshold constitutes an ideal absorbing barrier.

The results of the computer-simulation calculations are included in Figure 1, and the model parameters that fit the experimental data are listed in Table II. As in previous work,[1] a value of $\langle \Delta E' \rangle$ was found at each temperature by fitting the calculations to the experimental data for the $m = 2.6$ reactor. It should be noted that the calculated curves in Figure 1 have been shifted by 14 K to lower temperatures and by 0.10 log units to higher values of log $\bar{P}_c(m)$. These shifts bring the calculated value of $\bar{P}_c(m)$ for a strong collider and the experimental value of $\bar{P}_c(m)$ at the lowest temperature in the $m = 27.2$ reactor into agreement. The required shifts are not large and reflect the combined experimental and theoretical uncertainties. For example, a decrease in the true value of the activation energy of the reaction by 300 cm^{-1} (an amount easily within the experimental uncertainty), with concomitant reduction of the preexponential factor from 2.5×10^{13} to 1.3×10^{13} s^{-1}, is equivalent to shifting the calculated curves to lower temperatures by ~10 K. Also, anharmonicity effects, while unimportant (partially self-compensating) when estimating unimolecular rate constants near the high-pressure limit, are much more important at the low-pressure limit. Anharmonicity effects increase the fraction of molecules that reach the critical energy for reaction. In the present instance, we consider that an increase in the low-pressure rate of 20–25% due to anharmonicity effects is quite reasonable (for example, the rate constant for isomerization of methyl isocyanide was estimated to increase by 25–40% when anharmonicity effects were taken into account[8]); this is equivalent to a shift of the calculated values by 0.10 log units along the log $\bar{P}_c(m)$ axis.

Included for comparison in Figure 1 is the calculated curve for strong collider behavior. This curve is essentially the same for all values of m (it would be identical if the free-flight times (between wall collisions) were the same for all reactors, or if the system were in the second-order region rather than in the falloff region. Model FE is the most difficult to fit to data that approach strong collider behavior at the lowest temperature.

Discussion

The experimental results shown in Figure 1 are qualitatively in total accord with previous work.[1-5] As before, the data for the reactor with $m = 27.2$ may be considered as effectively representing steady-state limiting behavior. The data for the reactor with smallest mean collision numbers, $m = 2.6$, deviate most from strong collider and from steady-state behavior, while the deviation decreases with decreasing temperature. This indicates that the surface behaves as a progressively stronger collider as the temperature is decreased. Thus, the present results at the lowest temperatures: the values of $\bar{P}_c(m)$ become virtually independent of the mean collision number, and the curves of $\bar{P}_c(m)$ vs. temperature become coincident at temperatures below ~400–450 K. This behavior graphically demonstrates that at the lowest temperatures the surface is behaving as an ideal strong collider: each collision with the surface effectively brings the molecule into thermal equilibrium with the wall. This significant conclusion is independent of calculational models, parameters, or detailed deconvolution of the data.

Incubation times[1] are 4.4 at 778 K for both models FE and FG and decrease to 3.5 and 3.1 at 585 K for FE and FG, respectively.

In previous work with cyclopropanes[1,3,4] stochastic modeling of the energy-transfer processes resulted in model FG, as well as a linear exponential model, LE (i.e., model FE but with $\langle \Delta E \rangle$ = constant + αE_j), providing the best fit; however, for cyclobutane[2] and methylcyclopropane,[5] where wall collisions were found to be weaker than in the cyclopropane system, model FE provided the best fit, although the fits of model FG and model LE were also reasonable. From the curves in Figure 1, it can be seen

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that both models FE and FG give quite good fits to the cyclobutene data in the higher-temperature region that overlaps the lower-temperature portion of the cyclobutane study. The values of $\langle \Delta E' \rangle$ resulting from the calculations vary from 2150 cm^{-1} for both models, at 778 K, to 5150 and 3600 cm^{-1} for models FE and FG, respectively, at 585 K (Table II). For comparison, the value for cyclobutane[2] at 778 K was $\sim$2290 cm^{-1} (model FE). At comparable temperatures, therefore, the difference between cyclobutane and cyclobutene is not great, even though the critical energy for the former reaction (20 700 cm^{-1}) is approximately twice that of the latter (11 300 cm^{-1}). It could be tempting, therefore, to conclude that the correct model for energy transfer probably is one in which the average amount of energy transferred did not vary greatly with the energy content of either of these highly energized species. However, in the present study (Table II), it can be seen that *all* of the models of energy transfer used give an adequate fit to the cyclobutene data, while models LG, EG, and GB are such that $\langle \Delta E' \rangle$ *does* vary with molecular energy content. We have applied models LG, EB, and GB to the cyclobutane data,[2] and they are found to give worse fits than models FE and FG.

It is evident that, for a clearer distinction to be made between the various models for energy transfer, it would be desirable, but difficult, to obtain data at much higher temperatures than those which have been investigated. For the case of efficient collisions, data obtained at low temperatures do not provide adequate distinctions, although they do suffice here to illustrate the failure of a simple exponential model (FE), a conclusion that now has long standing[9] from steady-state work.

Finally, it is evident from the present and earlier VEM work that the assumption frequently used in very low pressure pyrolysis (VLPP) that strong collider behavior adequately described gas–wall encounters at temperatures as high as 1200 K in many cases[10] is incorrect. The comparative insensitivity of conclusions with respect to the model in VEM work appears to arise from the circumstance that it integrates collisional efficiencies over a wide range of nominal energies from the low to high region; compensating features tend to prevail. We agree in this with a recent conclusion by Gilbert and King.[11]

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Photoassisted Hydrogen Production from Titania and Water

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When TiO_2, reduced by H_2 or CO, is placed in an ambient of gas-phase water and illuminated with band gap light, H_2 is evolved. Adding a small amount of O_2 completely retards this reaction. A dark reaction of reduced TiO_2 with water to form H_2 also occurs at temperatures above 200 °C. These results show that H_2 evolution is not the result of catalytic water photolysis but a photoassisted reaction of water with oxygen vacancies produced by the reduction.

Introduction

The photodecomposition of water over heterogeneous catalysts containing compound semiconductors has recently received considerable attention. Some works involve the use of semiconductors alone for achieving this and the results and their interpretation are the subject of some disagreement. Schrauzer and Gath[1] concluded that water adsorbed on TiO_2 or Fe_2O_3-doped TiO_2 was catalytically photolyzed in their system, whereas Van Damme and Hall,[2] on the basis of finding only a trace of H_2, concluded that H_2 formation arose from the noncatalytic photodecomposition of hydroxyl groups originally present on TiO_2. Kawai and Sakata,[3] on the other hand, found that D_2 was formed in the dark when gaseous D_2O was contacted with TiO_2 reduced by CO under UV irradiation. The evolution of D_2 was accelerated by illumination and continued even after evacuating D_2O, but no O_2 was observed. The acceleration was ascribed to the photodecomposition of D_2O over TiO_2 on the assumption that oxygen formed was held at the TiO_2 surface. This assumption is based on the fact that O_2 as well as H_2 was formed by the addition of RuO_2, a good electrode material for O_2 evolution, to TiO_2. Rao et al.[4] have recently reported that H_2 and H_2O_2 are produced when reduced TiO_2 (in flowing H_2 for $\sim$6 h at 700–800 °C) is suspended in liquid water and illuminated in bubbling N_2. Unreduced TiO_2 produces neither H_2 nor H_2O_2.

We have already reported that platinized TiO_2 is a suitable catalyst for the photolysis of water to H_2 and O_2 but TiO_2 alone is not.[5] Moreover, we found that reduced TiO_2 produces H_2 when illuminated in the presence of gaseous or liquid water as observed by Kawai and Sakata[3] and Rao et al.,[4] but we concluded, in agreement with Van Damme and Hall,[2] that this H_2 production is noncatalytic. However, our results require somewhat different interpretation. This brief paper presents the experimental results and our interpretation of them, the latter relying

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