A Crucial Demonstration of Strong Collision Behavior of Vibrational Energy for Gas-Surface Collisions

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The Variable Encounter Method was applied to the study of the transient region in vibrational accommodation of reacting cyclobutene at surfaces. Collision efficiency declines with rise of temperature. Surface collisions are more efficient than binary gas phase encounters and, at temperatures below 450K, the wall behaves like a theoretical strong collider.
A CRUCIAL DEMONSTRATION OF STRONG COLLISIONAL BEHAVIOR OF VIBRATIONAL ENERGY FOR GAS-SURFACE COLLISIONS

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Abstract

Application of the VEM technique has been made to the thermal cyclobutene decomposition system. Vibrational energy transfer in the cyclobutene - seasoned quartz surface system has been studied. The occurrence of strong collisions is demonstrated in crucial manner at temperatures below 450K.
A new, simple technique has been recently described [1], the Variable Encounter Method (VEM), that enables the study to be made of energy transfer between a hot seasoned quartz surface and gaseous molecules in the transient region. VEM depends on the random entry of cold molecules into a hot zone under molecular flow conditions. The apparatus for VEM consists simply of a large, degassed bulb, usually fused quartz, with several attached quartz cylindrical "reactor fingers" of varying dimensions. These reactors are blown on at convenient places on the surface of the flask and can be heated independently. The bulb is connected to a gas-handling system. Entrance area to a reactor is restricted to \( \geq 1/50 \) of the bulb area. Dimensions of the reactors used in work to date have provided mean wall collision numbers, \( m \), from 2 to 100, per encounter; \( m \) is the mean number of wall collisions experienced by a molecule between entry to and exit from the reactor finger (an encounter). For a given \( m \), the distribution of wall collisions may be found by Monte Carlo calculation. Molecules that return to the bulb are cooled by collisions with the bulb wall before experiencing another encounter with the reactor.

Studies have been reported with cyclopropane [1] and cyclobutane [2] using this technique, and the efficiency for activating/deactivating energized molecules was found to increase significantly with decreasing temperature. At the lowest temperatures investigated, and using a gaussian model for energy transfer, the amount of vibrational energy transferred per collision with the wall was found to be \( \sim 3500 \text{ cm}^{-1} \) for cyclopropane (825K) and \( \sim 2800 \text{ cm}^{-1} \) for cyclobutane (750K), for down transitions. The corresponding values obtained for these two molecules at 1100K had declined to 2600 cm\(^{-1}\) and 1850 cm\(^{-1}\), respectively. However, even at \( \sim 800\text{K} \), the collisional efficiency of the wall is substantially below that for strong-collider behavior in these two systems.

It seems likely that the wall efficiency for energy transfer would continue to increase at even lower temperatures. No previous experimental study on gas-
surface systems has been reported that would enable successive measurements of the energy transfer efficiency, collision-on-collision, to be made in this low temperature regime. The very slow rate of reaction of cyclopropane and cyclobutane at temperatures below those already studied using the VEM technique precludes their employment in extending the temperature range to lower temperatures.

Cyclobutene isomerizes to 1,3-butadiene with an activation energy of 32.9 kcal mole$^{-1}$ and a pre-exponential factor of $2.5 \times 10^{13}$ s$^{-1}$ [3]. The reaction has been studied in conventional thermal systems in the temperature range 400K-450K, and, like cyclobutane [4], it has been shown to be a reaction unaffected by surface catalysis and hence ideal for study using VEM. Our own work on cyclobutane [2], and the present work on cyclobutene, has substantiated this premise.

We have investigated this reaction using the VEM in reactors with mean collision numbers, $m$, per encounter (i.e., the average number of collisions a molecule experiences with the hot wall of the reactor between entering and leaving) of 27.2 and 2.6. In previous work [1,2] it was demonstrated that the steady state is substantially attained in the $m = 27$ reactor. Values of the average probability of reaction per wall collision, $P_c(m)$, for encounters with reactors of different $m$ were measured. Values of $P_c(m)$ are plotted as a function of temperature in Fig. 1.

The curves for the two reactors can be seen to converge at the lowest temperatures. Such convergence demonstrates that at the lowest temperatures the surface is behaving as a strong collider and that the values of $P_c(m)$ do not depend on the number of collisions a molecule suffers with the surface; each collision effectively brings the molecule into thermal equilibrium with the wall. As the temperature of the surface is increased, the efficiency of vibrational energy accommodation with the wall decreases and the curves for the two reactors begin to diverge. Such divergence continues progressively at still high temperatures [1,2].
Extension of the measurements and, especially, stochastic modelling of these energy transfer systems \([1,2]\) will be undertaken in future work. But the behavior displayed is a graphic demonstration of the satisfaction of the theoretical, as opposed merely to operational, requirements for strong collision behavior for this system at temperatures below \(400\)K. This conclusion is independent of calculational models, parameters or detailed deconvolution of the data. Satisfaction of the operational requirements for strong collider behavior for vibrational energy transfer in reacting polyatomic molecules has previously been demonstrated at lower temperatures in a number of steady state homogeneous systems \([5]\), but such practical demonstration has depended on operational criteria which were much less severe than have been satisfied in the present work.
References

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5. D. C. Tardy and B. S. Rabinovitch, Chem. Revs. 77 (1977) 369
Fig. 1  Average probability of reaction per surface collision as a function of surface temperature for isomerization of cyclobutene to 1,3-butadiene for two reactors, $m = 2.6$ and $27.2$. 