

rate into each of the remaining energetically accessible channels? In other words, what is so special about the 0^0 channel? Unfortunately, the model in its present form cannot explain why the 0^0 channel is the only large energy gap channel observed experimentally. Neither does the model account directly for the initial mode selectivity of the VP branching ratios (although the existence of mode selectivity comes as no surprise). It is possible that both effects depend sensitively on the exact energetic relationships of the various levels depicted schematically in Figure 6, and on the details of the coupling matrix elements responsible for the level mixing. Future experiments on isotopically substituted pDFB-Ar complexes should help shed light on these questions. If the 5^1 and 6^2 VP branching ratios are determined by "accidental" overlaps of specific energy levels, then large changes in these

branching ratios might be observed in isotopically substituted samples.

Despite these unresolved questions, we believe that the basic premise and conclusion of the model are correct. Namely, we have argued that mixing can occur between initially pumped intramolecular vibrational levels and near-isoenergetic combination levels involving large amounts of van der Waals stretching (and bending) excitation; and we have shown that even small amounts of mixing can dramatically increase the probability of VP channels involving large energy gaps.

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Registry No. *p*-Difluorobenzene, 540-36-3; argon, 7440-37-1.

Vibrational Energy Transfer at a Liquid Gallium Surface. Activation of Unimolecular Cyclobutene Isomerization

D. A. Oswald, W. B. Nilsson,[†] and B. S. Rabinovitch*

Department of Chemistry BG-10, University of Washington, Seattle, Washington 98195

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Single-collision vibrational energy transfer for a canonical ensemble ($T = 300$ K) of cyclobutene molecules at a heated liquid gallium surface has been studied from 450 to 700 K. Transport above the reaction threshold for isomerization to butadiene ($E_0 = 32.4$ kcal mol⁻¹) was used as the criterion for efficiency of vibrational energy accommodation. The efficiency was found to fall below strong collider behavior above 625 K. Evidence of surface catalysis became important below 525 K. The observed behavior is reminiscent of that found previously for other liquid (Sn) and solid (Au) metal surfaces.

Introduction

Conventional thermal energy transfer between gases and solids is an area that has undergone much experimental and theoretical scrutiny. Studies of translational and rotational energy transfer by molecules at well-characterized surfaces and specific sites may be found in the literature.¹⁻⁴ Recently, some attention has been given to energy transfer with somewhat ill-defined solid surfaces (polycrystalline materials in the low vacuum region). These studies have been concerned with the change in internal energy of an ensemble of molecules initially at a well-defined (lower) temperature, after they have interacted with a solid surface of higher temperature. Reports of the magnitudes of vibrational accommodation coefficients have varied. Foner and Hudson⁵ used a molecular beam technique to estimate $\alpha_v = 0.05$ for *n*-C₄H₁₀ on a Pt filament at 1273 K. Rosenblatt and co-workers⁶ obtained translational and internal energy accommodation coefficients for a series of paraffins measured at relatively high pressures on a variety of polycrystalline surfaces. Their lower limit estimates for vibrational accommodation at room temperature on Fe were 0.36, 0.72, and 0.90 for CH₄, *n*-C₄H₁₀, and *n*-C₈H₁₈, respectively. Amorebleta and Colussi using a technique basically similar to that utilized in our laboratory found $\alpha_v = 0.47$, 0.58, and 0.52, respectively, for *n*-butane, *n*-octane, and 1-chlorobutane on silica surfaces at 350 K.⁷ They also found that relaxation for these same compounds was more efficient on Pt (by a factor of 1.4-1.8 in α_v) and appeared to be quasi-independent of surface temperature between 350 and 700 K.

Until recently, virtually no data existed for vibrational energy transfer at solid surfaces by polyatomic molecules at high levels of vibrational excitation. Such energy-transfer studies conducted in this laboratory have utilized the variable encounter method

(VEM) in which a controlled variable number of sequential collisions of gas molecules at some initial lower temperature is allowed to occur with a hot surface. The method has been fully described.⁸ The single-collision ($m = 1$) version has been used to show a decrease of α_v with temperature.⁹ In these systems, the criterion for collisional energy transfer is transport of reactant gas molecules above their reaction threshold. In our studies, done first on fused Pyrex and quartz, the surfaces have usually been deliberately seasoned with the reactant (deactivation of "hot spots" and deposition of a mono- or multimolecular layer) in order to reduce surface catalytic effects and to provide reproducible results.^{9,10} Deliberate seasoning of the surface with reactant has been a long-time common procedure in gas kinetic studies. Nonetheless, we have shown that such seasoning does not completely obscure effects due to the nature of the original underlying matrix.¹¹ Work on cyclobutene isomerization to butadiene on

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[†] Present address: National Fish, Meal and Oil Association, c/o Northwest and Alaska Fisheries Center/URD, Seattle, WA 98112.

these glass surfaces provided evidence for strong collider behavior at temperatures up to ~ 425 K. A study by Yuan and Rabinovitch¹¹ showed strong collider behavior persisted up to 550–600 K for cyclobutene on variously treated, gold wire and plane surfaces; they found that preadsorbed O_2 enhanced the efficiency of energy transfer. This concurred with reports by Somorjai and co-workers.¹² Metals may behave as stronger colliders than Pyrex and silica due to possible relaxation mechanisms that are unique to metals.

Energy accommodation between gases and liquids has received much less attention. The earliest work appears to be that of Alty and co-workers¹³ who examined accommodation coefficients for several covalent liquids and their own vapors, as well as for Hg and its vapor. In all cases, except for water, penetration and absorption into the liquid rather than reflection was found. Thomas and Petersen¹⁴ looked at accommodation of He on a K-coated tungsten filament, just above and below the melting point of K, and found $\alpha_v(338\text{ K}) = 0.095$ and $\alpha_v(328\text{ K}) = 0.089$. No discontinuity was observed at the melting point.

Very recently, Nilsson and Rabinovitch¹⁵ reported on vibrational energy transfer between cyclobutene and liquid tin at temperatures up to 800 K. Strong collider behavior was observed up to 550 K. They found that the Sn surface, which most likely consisted of small islands of tin(II) oxide floating on liquid Sn,¹⁶ was strongly reminiscent of oxygen-processed gold surfaces investigated by Yuan and Rabinovitch.¹¹ They also observed no discontinuity in the vibrational accommodation coefficient at the melting point. Liquid tin is known to exhibit structure resembling that of solid β -tin.

The present study extends our work to a liquid gallium surface. The choice of suitable surfaces, in this case of metals, is limited greatly by the requirements of nonreactivity and low vapor pressures, for work at higher temperatures. Like Sn, Ga seems to be unreactive at the temperatures used here. It has the longest liquid range known of any metal. Its vapor pressure is reported to be 10^{-6} torr at the highest temperature used in this study.¹⁷ Cyclobutene has a low reaction threshold ($E_0 \sim 32$ kcal mol⁻¹) for isomerization to 1,3-butadiene¹⁸ and therefore is favorable for use as a subject molecule at moderate temperatures. Moreover, it is known to be relatively clean and uncomplicated as an experimental example of a thermal unimolecular reaction. At the reactant pressures used in the current study, this reaction is close to the low-pressure falloff region so that virtually all molecules that are energized to levels above E_0 decompose. Our previous studies done on Pyrex, silica, crystalline gold, and liquid tin surfaces showed no catalytic behavior for cyclobutene isomerization. While some catalytic behavior is observed in the present system at the lower temperatures used, this does not negate the general import of the behavior observed at higher temperatures. The present technique affords a specific test of vibrational energy transfer at high energy levels (above E_0), in contrast to conventional bulk energy accommodation studies.

Experimental Section

Cyclobutene was synthesized according to the procedure of Fadel et al.¹⁹ GLC and GCMS analysis showed that it contained less than 0.05% 1,3-butadiene as an impurity. The sample was therefore used without further purification. The gallium (original purity > 99.9%) was further treated as follows: the metal was melted and liquid beneath the surface was drawn up into glass

tubes and allowed to harden. The tubes were then cracked to yield clean rods of solid Ga.

The reaction chamber consisted of a 5-L Pyrex bulb, the lower part of which was sealed to a 4-cm i.d. flat-bottom quartz well containing the liquid sample which was heated in a bath. The volume of Ga used was the minimum amount necessary to cover the bottom of the well. The liquid sample was not stirred; our previous experiments done on liquid Sn showed no difference in the observed rate of isomerization with rate of stirring.¹⁵ This greatly simplified the experimental design. The surface of the liquid Ga, while not a perfect mirror, was in general shiny, with slowly accumulating small gray patches of dross, especially at the perimeter edges of the surface; the surface was cleaned from time to time.

The quartz walls just above the level of the hot Ga (as well as the bulb itself) were maintained at or near room temperature. This was accomplished by wrapping the quartz well with $3/8$ -in. copper tubing and circulating cold water through it. At the highest temperature used (700 K) the temperature of the walls never exceeded 325 K. Molecules that leave the liquid surface accommodate with the cold bulb wall before restriking the hot surface.

A molten salt bath (53% KNO_3 , 7% $NaNO_3$, 40% $NaNO_2$) was used. The bath was contained in a stainless steel dish that had four cartridge heaters symmetrically encased within the bottom wall of the dish. The dish was wrapped in asbestos tape to minimize heat loss to the surrounding environment. For the majority of runs made in the temperature range 600–700 K (excluding those at 629.5, 631.5, and 665.5 K) an alternate heat source was also used. A two-piece spherical heating mantle filled with sand replaced the cartridge heaters. The stainless steel dish was sunk in the sand up to its top edge. This allowed for uniform heating of the entire salt bath.

Temperature measurement was made by a 40-gauge chromel–alumel thermocouple probe that extended through the top of the Pyrex bulb downward directly into the surface of the metal in the center of the well. Temperature measurements made on the molten salt bath showed the temperature fluctuation within the bath to be less than 5 K.

In a typical run, the Pyrex bulb was pumped down to $\sim 10^{-6}$ Torr prior to the introduction of the substrate. Sample pressures in the range $(2\text{--}6) \times 10^{-4}$ Torr were employed. The duration of exposure of the cyclobutene sample to the hot Ga was varied in order to keep the percent reaction less than 15% and usually below 5%. The reaction gas was then transferred for analysis. Products were analyzed by using a liquid support coated open tubular squalane column at 0 °C with He as the carrier gas. A flame ionization detection system was employed.

Results and Discussion

The reaction probability per collision P_c (i.e., the measure of transport of reactant molecules above the reaction threshold after a single collision with the hot surface) was calculated from the following expression:

$$P_c = 4kV/S\bar{c}$$

where k is the apparent first-order rate constant, V is the volume of the reaction vessel, S is the surface area of the liquid Ga, and \bar{c} is the average translational velocity of the reactant molecules which have equilibrated with the cold wall prior to collision with the hot surface.

Initially, a series of runs (data set I) was made which established the general trend of the data for P_c vs. T for this system. These runs showed strong collider behavior above 525 K but greater than strong collider at temperatures below this, suggesting a contribution from surface catalysis (this behavior has previously been observed and can be corrected (in whole or in part) by pretreatment (seasoning) of the surface¹¹). As is well-known, e.g. from very low-pressure pyrolysis experiments,²⁰ the importance of low activation energy surface catalysis/free radical contributions to the mechanisms of homogeneous gas-phase unimolecular re-

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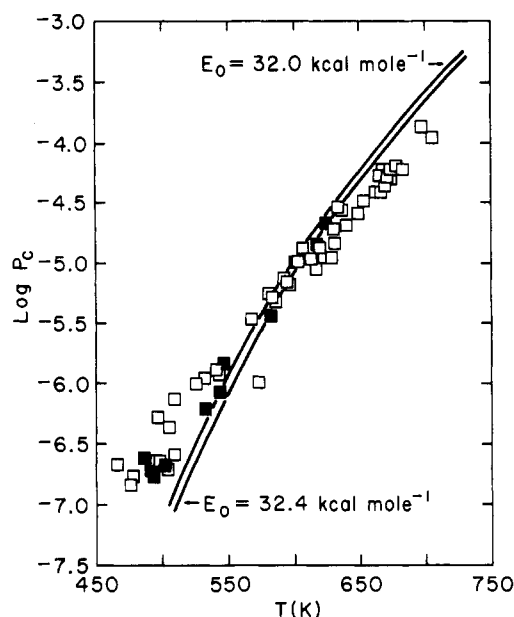


Figure 1. Plot of experimental values of P_c vs. T ; ■ and □ represent values from data sets I and II, respectively (see text). The solid lines are strong collider curves ($E_0 = 32.0$ and 32.4 kcal mol $^{-1}$).

action diminishes with increase of temperature. The second set of data (data set II) was another investigation of the behavior of this system made after a lapse of time and with minor alterations to the apparatus and reactor. These experiments confirmed the results previously obtained. While showing the same trend in the variation of P_c with temperature, the second data set showed a small systematic deviation from the first. This was taken to be indicative of a small discrepancy in the temperature measurement. The apparent temperature discrepancy is due to a difference in the presence and absence of a thin-wall glass tip at the end of the thermocouple in the two sets together with some difference in positioning of the thermocouple probe in the liquid Ga. Any repositioning of the thermocouple probe resulted in a small variation in the temperature measurement. In order to clean off any dross, i.e. oxide,²¹ that had formed on the surface due to traces of oxygen, removal of the thermocouple probe was necessary. As this procedure was carried out between data sets I and II, the above explanation seems the most likely cause of a systematic temperature variation. The relative temperature of the later runs was estimated to be low by ~ 7.5 K.

Figure 1 is a plot of experimental results of P_c vs. T . The solid curves show strong collider behavior ($E_0 = 32.0$ – 32.4 kcal mol $^{-1}$). Unlike the Sn studies which conform to simple strong collider behavior at low temperatures, the results here for runs made below ~ 525 K show evidence for some catalysis. Defect from strong collider behavior was observed to occur above 625 K, analogous to the behavior with Sn. In general, the results conform to strong collision behavior over the middle range. This concurs with studies of cyclobutene vibrational accommodation not only on liquid Sn, but also on seasoned gold and on O_2 -processed gold surfaces.¹¹

Transport above the reaction threshold for isomerization of butadiene is used as the criterion for efficient vibrational energy accommodation. This is a more severe test than measurement of the average energy of the final distribution as a whole, as in conventional accommodation coefficient measurements. In such cases, relatively large deviations from strong collider behavior for transitions at higher energy may not greatly alter the average energy of the distribution.²² The same behavior, however, can significantly alter the population above E_0 and therefore lead to more sensitive determinations of the high-energy collisional efficiency.⁹ The new population vector N^1 after a single collision is related to the population vector corresponding to the Boltzmann

distribution at the original gas temperature, N^0 , by $N^1 = PN^0$, where P is the transition probability matrix. In this work, strong collider behavior was present below 625 K. This corresponds to complete vibrational accommodation in a single collision. N^1 , therefore, is simply the Boltzmann distribution characteristic of the surface temperature. The value of the accommodation coefficient, α_v , deduced above 625 K depends on the form of P which is currently unknown. Studies in this laboratory have sought to ascertain the correct analytical form of P using both single- and multicollision variations of the variable encounter method.^{22–25} P can be partitioned at E_0

$$P = \begin{vmatrix} P_I & P_{III} \\ P_{II} & P_{IV} \end{vmatrix}$$

P_I concerns transition probabilities between levels below E_0 . These transitions contribute heavily to N^1 and therefore to the average energy change ΔE_{av} . Knowledge of P_I is most helpful for deducing values of α_v . This information can be indirectly obtained by the variable encounter method when $m > 1$. P_{II} contains transition probability elements from levels below E_0 to those above and is probed by single-collision studies. P_{III} is ascertained from detailed balance. The two variants ($m = 1, m > 1$) of the VEM technique can give complementary information about the correct analytical form of P .^{22–24}

The results of the present study concur with those of Nilsson and Rabinovitch,¹⁵ suggesting substantial accommodation on the surface and that the liquid Ga surface also behaves much like a solid metal surface with respect to energy transfer by polyatomic gas molecules. Interpretation of the structural properties of liquid Ga has led to the conclusion that a marked analogy exists between the short-range order in liquid Ga and in the metastable monoclinic form β -Ga,²⁶ which usually forms when supercooled Ga crystallizes at low temperatures. The structure of liquid Ga has been studied by X-ray,²⁷ neutron,²⁸ and electron²⁹ diffraction. Early results suggested the presence of "pseudo" molecules of Ga_2 with an interatomic distance of ~ 2.44 Å separated from each other by 2.7–3.3 Å; this was explained as covalent short binding in liquid Ga similar to that found in orthorhombic α -Ga.³⁰ More recent studies, however,^{26,31} make the analogy with the less stable β -Ga. Regardless of which hypothesis is valid the various studies agree that liquid Ga has some of the structural characteristics of a solid form.

Relatively long residence time of gas molecules and accommodation at the surface need not imply and does not here mean that reaction takes place on the surface. Expressed otherwise, the strong collision behavior of Figure 1 represents the prediction of the Boltzmann distribution and not the Tolman distribution. Our early results on seasoned silica surfaces with cyclopropane, where strong collider behavior was found at lower temperatures, first showed that ensuing reaction was characterized as low-pressure homogeneous gas-phase behavior.⁸ The time scale for unimolecular reaction in Lindemann theory is here much longer than the residence time on the surface.

Is it possible that the "catalysis" noted earlier above at lower temperatures is not chemical in nature but represents highly extended lifetimes on the surface? Our earlier work on Au¹¹ and

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Sn¹⁵ surfaces, as well as on silica surface,⁹ wherein the experimental curves *did* follow the strong collider curve at the same lower temperatures, indicates otherwise. The predicted magnitude of fractional surface coverage θ in such case would be only $\theta \sim 10^{-5}$ and virtually independent of temperature.

Finally the higher α_v values found in this work on metal surfaces

relative to studies in other laboratories⁷ may be explained by the high temperature seasoning of the surface that occurs in our work.

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Methyl Isocyanide Isomerization Kinetics: Determination of Collisional Deactivation Parameters following C-H Overtone Excitation

Deanne L. Snavely,[†] Richard N. Zare,*

Department of Chemistry, Stanford University, Stanford, California 94305

James A. Miller, and David W. Chandler

Combustion Research Facility, Sandia National Laboratories, Livermore, California 94550

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The isomerization of methyl isocyanide (CH₃NC) to acetonitrile (CH₃CN) was studied by excitation of the $5\nu_{C-H}$ (726.6 nm) and $6\nu_{C-H}$ (621.4 nm) overtone states, which lie about 1 and 8 kcal/mol, respectively, above the isomerization barrier. Product yields were measured as a function of pressure and collision partner. A Stern-Volmer plot (yield⁻¹ vs. pressure) shows that (1) deactivation by collision with pure CH₃NC is more rapid than with C₃H₆, SF₆, or Ar, (2) the collisional deactivation efficiencies decrease in going from C₃H₆ to SF₆ to Ar, and (3) the single-collision deactivation approximation (strong collider approximation) fails for both the $6\nu_{C-H}$ and $5\nu_{C-H}$ data. With the use of a master equation solution, assuming an "exponential down" energy-transfer function, the average energy transferred in a deactivating collision, $-\langle\Delta E\rangle_{\text{down}}$, is extracted from each data set, as well as the average energy transferred per collision, $-\langle\Delta E\rangle$. It is concluded that the isomerization yield depends markedly on the collision partner and on the average energy transferred per collision, $-\langle\Delta E\rangle$, even though the single-collision deactivation approximation might have been expected to have its greatest validity in this energy regime.

Introduction

The role of collisional deactivation in unimolecular processes continues to be controversial. Major questions remain unanswered as to (1) the magnitude of the average amount of energy transferred in a collision (or in a deactivating collision),¹ and (2) the energy dependence of $-\langle\Delta E\rangle$.^{2,3} The thermal isomerization of methyl isocyanide (CH₃NC) to acetonitrile (CH₃CN), extensively investigated by Rabinovitch and co-workers,⁴ has long served as a classic model for the study of unimolecular dynamics. Beginning in 1977, Reddy and Berry^{5,6} used direct C-H stretch overtone excitation as a means of extending these isomerization studies beyond thermal energies and of specifying the energy content of the activated molecule with more precision. Their emphasis was on (1) the determination of the rate of unimolecular decomposition, based on the strong collider approximation in which it is assumed that single-collision deactivation applies, and (2) on the comparison of such rates with those derived from statistical models (RRKM theory).⁷⁻⁹

In this study, the isomerization of CH₃NC by overtone excitation is revisited, but with an emphasis on the role of collisional deactivation. Chandler and Miller¹⁰ have modeled the overtone-induced dissociation of *tert*-butyl hydroperoxide (*t*-BuOOH) via a master equation, and have shown that the product yield resulting from overtone excitation is sensitive to the energy-transfer parameters used in the master equation. The yield was found to vary significantly with the average energy transferred in a deactivating collision. Their best fit to the data of Chandler, Farneth, and Zare,¹¹ for overtone excited *t*-BuOOH collisions with room temperature *t*-BuOOH, implied an average energy transfer per collision of about -1700 cm^{-1} . More recently, Baggott¹² has used a master equation formalism to analyze his data on the

overtone-induced isomerization of cyclobutene and has extracted similar parameters. From his studies, as well as those presented here, it is clear that product yield following overtone excitation is a sensitive function of the details of the collisional deactivation process, even when the molecule is excited just above the reaction barrier and would be expected to be in a "strong collider" regime.

The product yield, which is the observable in these studies, results from the competition between three rates: (1) the specific rate of reaction, $k(E)$, averaged over the distribution of internal energies, denoted by k_u ; (2) the rate of collisional deactivation, k_d ; and (3) the rate of photoactivation, k_a .

In this study, we assume that the RRKM model adequately describes the dynamics of the overtone excited CH₃NC and use it to calculate $k(E)$. The rate of photoactivation, k_a , is determined from the experimental condition (laser power, absorption cross section, path length etc.). Having both $k(E)$ and k_a , we further assume a single exponential down model for the shape of the energy-transfer function. This means that the probability of a

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