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# A Molecular Beam Study of Isomerization and Dehydrogenation of Butene on a Mica Surface

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By means of a Recycling Molecular Beam Reactor (RMBR) we have determined for 1-butene incident on a mica surface the reaction probabilities for: (1) isomerization to *cis*-2-butene, (2) isomerization to *trans*-2-butene, and (3) dehydrogenation to 1,3-butadiene. The probabilities for each of these reactions is determined entirely by the temperature of the surface which can be considered as amorphous silica–alumina. The translational and vibrational energies of the incident reactant molecules have no apparent effect on the reaction rates. The reaction probability in each case can be fitted by an equation of the form $P = A \exp(-E/RT)$. For reactions (1), (2), and (3), respectively, $A$ is $2.9 \times 10^{-3}$, $1.2 \times 10^{-2}$, and 0.2 and $E$ is 41.9, 48.1, and 48.2 kJ/mol. These results strongly suggest that the reactions are truly catalytic on the surface and that there is no energy barrier to adsorption. Similar conclusions were reached from some cursory studies of the dehydrogenation of *cis*-2-butene on mica and the hydrogenation of propylene on rhodium.

## I. INTRODUCTION

Molecular beam methods have often been applied in the study of gas–solid reactions but only occasionally has true heterogeneous catalysis been involved (*1*). Of previous studies perhaps the one most relevant to the present work was the investigation by McCarroll and Thomson of the displacement of ethylene by acetylene from a palladium surface (*2*). This reaction is one of the few studied by beam methods which could be considered at all typical of the relatively complicated reactions of organic molecules encountered in the industrial practice of heterogeneous catalysis. The objective of McCarroll and Thomson was to ascertain the effect on reaction rate of the temperatures of the surface and the incident beam molecules, independently varied. They encountered a difficulty common to most experiments in which beam molecules are reactively scattered from a surface, namely a relatively low sensitivity for the detection of product molecules. Using ethylene-$^{14}$C and following its displacement by acetylene by monitoring surface radioactivity, they were able to measure a reaction probability of $1.75 \times 10^{-2}$. That is to say, about one of every hundred acetylene molecules incident upon the surface resulted in the displacement of an adsorbed ethylene. More often mass spectrometers are used to detect product molecules in the flux from the surface. In general, these detectors also restrict one to the study of relatively fast reactions, i.e., those with reaction probabilities greater than about $10^{-5}$.

Isomerization reactions, which are often used as diagnostic test reactions in fundamental catalysis research, cannot readily be studied in conventional beam systems.

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Not only do they feature relatively low reaction probabilities, but they also defy analysis by mass spectrometric detectors, especially when there may be only one product molecule in every $10^4$ or more reactant molecules. To overcome these difficulties we have developed an RMBR (Recycling Molecular Beam Reactor) in our laboratory. This apparatus, described in detail elsewhere, provides continuous recycling of reactant gas through the reaction zone (*3*). The molecules from an uncollimated free jet molecular beam undergo a single collision with an appropriate target surface. They then merge with background gas which is removed from the reaction chamber by a system of pumps, recompressed and returned to the nozzle source. This recycling permits integration over long periods of time, i.e., many collisions of each molecule with the surface, so that detection of relatively small conversions per pass (reaction probabilities) becomes possible. Nozzle pressures can be maintained at high enough levels to allow sampling for analysis by gas chromatography which can easily distinguish quantitatively between structural isomers. By integrating conversion over many cycles and by using a flame ionization detector on the gas chromatograph we have been able to measure reaction probabilities as small as $10^{-7}$ to $10^{-8}$ with little difficulty. With care, the sensitivity might reach $10^{-9}$ or $10^{-10}$ (*3*). Of course, these advantages cost something. The RMBR does not provide any information on the angular distribution of product flux from the target surface. Nor does it allow the determination of velocity distribution of product molecules.

Nozzle sources provide beams of substantially higher intensity and thus higher effective pressure than can be obtained with effusive sources. Moreover, by means of the so-called seeding technique, they make possible a much wider variation in translational energy of reactant species incident on a target surface than can be achieved by changes in the source temperature. In this technique the reactant species is dispersed in an inert carrier gas whose molecular weight determines the final velocity of the molecules after expansion in the source jet (*4*). Even more important is the fact that for some molecules vibrational energy does not relax during expansion (*5*). Their vibrational energy, when they strike the target, is characterized by the source temperature. Consequently, seeding in conjunction with changes in source temperature makes possible the independent variation of translational and vibrational energies of reactant molecules incident upon a target surface. When this independent variation can be achieved it makes possible the determination of the relative effectiveness in promoting reaction by translational and vibrational components of the energy of the reactant molecules. This ability to distinguish between the efficiency of different energy modes in promoting reaction will generally be of interest in reactions where there may be incomplete accommodation to the surface temperature before reaction occurs, in reactions for which the rate limiting step is adsorption to which there is an activation barrier, and in reactions that occur by an Eley–Rideal mechanism. For example, the rate of exchange between molecular hydrogen and hydrogen atoms adsorbed on copper is determined by the rate of dissociative adsorption of molecular hydrogen on the copper surface. Using molecular beam methods Balooch *et al.* showed that the normal component of translational energy of hydrogen molecules incident upon the surface is a significant factor in determining the exchange rate (*6*).

With our RMBR we recently investigated the isomerization of cyclopropane to propylene on a mica surface (*7*). In contrast to the case of hydrogen exchange on copper we found that translational energy had little or no effect on reaction probability but that the surface temperature and the vibrational energy of the incoming molecules were very important. In interpreting these results we concluded that the overall rate of the surface reaction was limited by the adsorption step and that 235 kJ/mol of vibrational energy was required to overcome the barrier to adsorption. This relatively high apparent activation energy suggests that the cyclopropane molecule forms an activated complex involving some sort of an adsorbed biradical configuration. At constant vibrational energy there was an apparent activation energy associated with the surface temperature which amounted to only 88 kJ/mol. We associate this energy with the reaction steps following adsorption, including desorption of propylene product. In conventional batch experiments where the temperature is the same for the surface and for all the energy modes of the gas molecules, only the high activation energy can be observed and little can be said about the surface reactions.

In this communication we report results obtained with the RMBR on the isomerization of *n*-butenes on a mica surface. There have been extensive previous studies of butene isomerization over a number of catalysts at atmospheric pressure. References (*8*) through (*16*) relate to representative studies on alumina and silica–alumina surfaces, which, as we will show, have much in common with the mica surface we used. Objectives of our investigation were to obtain accurate values of the reaction probability per collision and to determine its dependence on the temperatures of the gas and the surface, each of which could be independently varied.

## II. EXPERIMENTAL METHOD

The apparatus has been previously described in detail (*3*). We will here simply recite some features and procedures specifically relevant to the present study. A 40-ml STP volume of 1-butene (Matheson C.P. grade) was admitted to the system after it had been evacuated. The gas was recirculated with the nozzle at the desired temperature and the target at room temperature until a steady state was reached. Samples were then withdrawn and analyzed to determine the amount of background reaction, i.e., in the nozzle and elsewhere in the system. After approximately 2 hr the target heater was turned on to start the surface reaction. When the desired temperature was reached, as indicated by the target thermocouple, samples were withdrawn every 20 min and analyzed. Each sample was 0.3 ml and was extracted with a gas syringe (Hamilton 1.0 ml). When sufficient variation in composition had occurred to establish the effective rate, the target temperature and/or the nozzle temperature were changed to new values and another round of sampling was effected. Analysis was by a gas chromatograph whose column packing comprised 10% dimethyl-N,N-oxamate on 100/120 acid washed Chromosorb (Supelco, Inc.) Flame ion detection was used. The catalyst surface was an (001) plane of natural mica cleaved in air.

Figure 1 shows a plot of mole fraction of *trans*-butene-2 product as a function of time. The source temperature was held constant at 600 K. During the first 2 hr while the target surface was at 300 K there was little or no reaction. When the surface temperature was increased to 737 K the mole fraction of product started to increase. Although the RMBR is essentially a batch reactor and the reaction is probably first order, the rise in mole fraction of product is linear with time because the total conversion was always small, i.e., we essentially measure the initial differential rate (*11*, *15*). Thus, the slope $k$ of the straight line is analogous to a first-order rate constant with units of reciprocal time. The reaction probability can be cal-

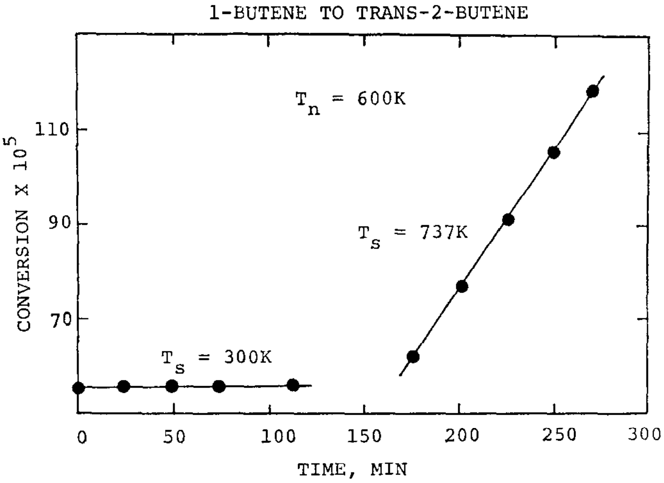

FIG. 1. Conversion of 1-butene to *trans*-2-butene versus time for a source temperature $T_n$ of 600 K at surface temperatures $T_s$ of 300 K and 737 K.

culated from the relation

$$p = (r/f)k, \quad (1)$$

where $r$ is the recycle time and $f$ is the fraction of the beam molecules intercepted by the target surface. For our geometry a value of 0.74 is appropriate for $f$ (*7*). Recycle times measured by means of the helium tracer technique described in Ref. (*3*) were found to be of the order of 1 min. They increased slightly with higher nozzle temperatures. In all cases the source pressure was 400 Torr (1 Torr = 133.33 N m$^{-2}$).

Earlier we made reference to the ability of nozzle beams to provide independent control over translational and vibrational energies of reactant molecules incident upon a target surface. It is appropriate to describe briefly the basis for this control. During free jet expansion of a gas mixture the initial enthalpy of the source gas becomes transformed into streaming kinetic energy of a component $i$ in accordance with the steady flow energy equation:

$$m_i v^2/2 = (m_i/\bar{m})\int_T^{T_0} \bar{C}_p dT, \quad (2)$$

where $T_0$ is the source temperature, $m$ is the molecular mass, $C_p$ the constant pressure specific heat capacity, $v$ is the streaming velocity at the local temperature $T$, and the bar indicates mean values for the mixture. The extent to which the expansion occurs, or the final value of $T$ before transition to free molecule flow, depends upon the source Reynolds number, i.e., diameter of the nozzle together with the temperature, pressure, and viscosity of the source gas. Actually, in most cases the final temperature is very low so that little error is made in assuming it to be zero. When $\bar{m}$ is made very small by dilution of reactant gas with a light carrier gas such as helium, the kinetic energy of the reactant gas can be higher than its enthalpy in the source by a factor which in the limit of infinite dilution approaches the ratio of the molecular weight of the reactant to the molecular weight of the carrier. In the case of butenes in helium, the limiting value of this factor is 14. Conversely, by dilution with a heavy carrier gas, the reactant kinetic energy can be decreased. Of course, proper account must be taken of contribution by the carrier gas to $C_p$ as well as to $m_i/\bar{m}$. Indeed, we could decrease the translational energy of butene by adding argon. Even though the molecular weight of argon is less than that of butene, its specific heat capacity is substantially less so that $\bar{C}_p$ is decreased more than $m_i/\bar{m}$ is increased.

Clearly, the translational energy of the butene molecules can be controlled by appropriate combinations of $T_0$ and $\bar{m}$ (dilution with carrier gas). What about internal energy? In considering Eq. (2) we have tacitly assumed an equilibrium value for $C_p$, i.e., that vibrational, rotational, and translational temperatures remained equal throughout the expansion so that energy from the internal degrees of freedom contributed their fair share to the increase in streaming kinetic energy. In fact, because the rate of expansion is so rapid in free jets from small nozzles the internal degrees of freedom do not remain in equilibrium with translation and a phenomenon known as heat capacity lag is encountered. The extent of this lag, which is to say the amount of internal energy which does not relax but is retained in the internal modes, depends on the source Reynolds number which determines the number of collisions which each molecule undergoes during expansion. In addition, the lag depends upon the effectiveness of these collisions in transferring energy from internal modes to translation. The average collision effectiveness is reflected in the so-called characteristic relaxation rate which varies widely from species to species and from mode to mode in any particular species. In the case of rotational energy the relaxation rate is generally very rapid with the notable exception of hydrogen. Consequently, it is a reasonable approximation to assume that the rotational temperature remains in equilibrium with the translational temperature during expansion. Vibrational relaxation rates, on the other hand, are usually much slower than rotational relaxation rates. Therefore, substantial fractions of the initial vibrational energy can be retained internally giving rise to vibrational excitation in the final beam molecules. The extent of this excitation must be determined by experiment unless values of the relaxation rate are well enough known to permit calculation of the final state of the beam molecules.

In this velocity analysis of beams from nozzle sources Gallagher found that in cyclopropane none of the initial vibrational energy relaxed during the expansion (*5*). Thus, the vibrational energy of cyclopropane molecules incident on a target was the same as it was under equilibrium conditions at the source temperature. This absence of vibrational relaxation made it possible for us to determine the effect of vibrational energy on the isomerization probability of cyclopropane molecules on a mica surface (*7*). In the case of *n*-butenes, the reactants of interest in the present study, Gallagher found that the vibrational modes which were excited at room temperature relaxed completely during expansion but that those modes which required higher temperatures for excitation did not relax during expansion. Thus, in our experiments as the source temperature was increased above room temperature, there were increasing amounts of vibrational energy retained in the butene molecules incident on the target surface, most likely in the higher frequency bending and stretching modes. Note that Gallagher's measurements were made with pure gases and cannot be directly applied to the mixtures used in some of our experiments. We doubt that there was more relaxation in these cases because it seems unlikely that helium or hydrogen would be more effective than butene in absorbing vibrational energy during a collision. At a source temperature of 600 K Gallagher found that roughly half of the initial vibrational energy did not relax. We made no attempt to arrive at a more quantitative estimate of the extent and nature of vibrational energy of the reactant butene molecules. Nor did we attempt to apply corrections to the nozzle thermocouple readings even

TABLE 1

Energy States of 1-Butene Beam Molecules (in kJ/mol)

| Symbol | $T_0$(K) | Total enthalpy[b] | Vibrational energy[c] | Translational energy | Translational velocity (in cm/sec × $10^5$) |
|---|---|---|---|---|---|
| □ | 330 | 17.4 | 0.0 | 17.4 | 1.11 |
| ● | 600 (90% Ar)[a] | 53.0 | 14.3[d] | 22.0 | 1.25 |
| ⬓ | 600 | 53.0 | 14.3 | 38.6 | 1.66 |
| ■ | 680 | 65.2 | 20.8 | 44.2 | 1.78 |
| ○ | 600 (90% He)[a] | 53.0 | 14.3[d] | 99.4 | 2.66 |

[a] Carrier gas used to accelerate or decelerate 1-butene.

[b] From Ref. (*17*).

[c] Calculated from data reported in Ref. (*5*).

[d] We assume that the extent of relaxation in the seeded beam is the same as measured for pure 1-butene at the same source temperature and pressure.

though we know that the effective source gas temperature was less than the thermocouple value. The reasons for this apparently somewhat cavalier treatment of what might seem an important parameter will emerge when we examine the results.

As we have already mentioned, the target surface was a natural mica (Ruggles Mine, Grafton, New Hampshire) cleaved in air. Analysis by X-ray photoelectron spectroscopy showed potassium, silicon, aluminum, and oxygen as major components with traces of carbon as an impurity. Comparison with $\alpha$-$Al_2O_3$ and quartz standards indicated that the Al/Si ratio was near unity. In the infrared spectrum only a single OH stretching frequency at 3628 $cm^{-1}$ was observed, indicative of a dioctahedral mica, muscovite, for which the ideal composition can be represented by the formula $KAl_2Si_3AlO_{10}(OH)_2$ (*19*). At temperature above 600°C for short periods and at even lower temperatures for long periods, muscovite decomposes; it loses potassium and the surface becomes enriched in silica. In one sample which had been heated above 873 K and used in the reactor for several weeks, the surface Al/Si ratio was 0.60 or 33% $Al_2O_3$ by weight. The structure of our mica surface is not known but the large changes in surface stoichiometry suggest that it is no longer crystalline.

## III. RESULTS AND DISCUSSION

Most of our measurements were made with 1-butene as the reactant gas for surface temperatures ranging between 650 K and 850 K. The main products were *cis*-2-butene, *trans*-2-butene and 1,3-butadiene. Cracking products $C_1$, $C_2$, and $C_3$ were observed in small amounts. Table 1 shows the vibrational and translational energies of the beam molecules incident on the target surface as obtained by the indicated combinations of source temperature and composition. The vibrational energies were calculated from Gallagher's data (*5*). The translational energies were computed from Eq. (2). It should be noted that the indicated translational velocities are the most probable or streaming values around which there was a spread of only a few percent because the terminal local or static temperature in each case was only a few degrees Kelvin. Also shown in Table 1 are the symbols by which each combination of conditions can be identified in the figures.

Figure 2 shows an Arrhenius plot for the dependence of reaction probability for the formation of *trans*-2-butene on surface temperature. Despite the fairly wide variation in translational and vibrational energy the points all fall reasonably close to a single straight line. The apparent message is that the amount and distribution of energy in the incident butene molecules has little or no effect on the reaction probability. All the data in Fig. 2 can be correlated with an equation in Arrhenius form where $T$ is surface temperature:

$$P = A \exp(-E/RT). \tag{3}$$

Values for $A$ and $E$ obtained by a least-squares fit to the data in Fig. 2 are shown in Table 2. Entirely similar results were obtained for the temperature dependence of reaction probabilities to form *cis*-2-butene and 1,3-butadiene. The data are shown in Figs. 3 and 4 and can also be described by Eq. 3. The appropriate values of $A$ and $E$ are also given in Table 2.

It seems clear that the probabilities for all of these reactions depend largely on the surface temperature, hardly at all on the energy of the 1-butene molecules incident upon the surface. The obvious conclusion is that the reactions take place after the molecule has been adsorbed and become thermally accommodated to the surface. It would also appear that there is no activation barrier to the adsorption step. In view of the fact that the homogeneous thermal isomerization and dehydrogenation of 1-butene have activation energies in excess of 250 kJ/mol, the relatively low values of $E$ summarized in Table 2 further suggest that the reactions we observed are truly catalytic (*18*). It should also be noted that even for runs of low conversion such as the one exhibited in Fig. 1, the number of molecules converted per surface site is in excess of 300 if we assume $10^{15}$ sites per square centimeter. Moreover, the same mica was used for many experiments with no significant change in catalytic activity. It is noteworthy that our activation energies are within experimental error, the same as those obtained by Gerberich and Hall (*9*). They found a value of 12 ± 1 kcal/mol (50 kJ/mol) with a commercial silica–alumina catalyst (Houdry, M-46, 12.5% $Al_2O_3$) independent of the hydroxyl content.

TABLE 2

Rate Parameters for Reaction of 1-Butene on Mica[a]

| Reactant | 1-Butene | |
|---|---|---|
| | $A$ | $E$ (kJ/mol) |
| *cis*-2-Butene | $2.9 \times 10^{-3}$ | 41.9 |
| *trans*-2-Butene | $1.2 \times 10^{-2}$ | 48.1 |
| 1,3-Butadiene | 0.2 | 68.2 |

[a] Compare Eq. 3.

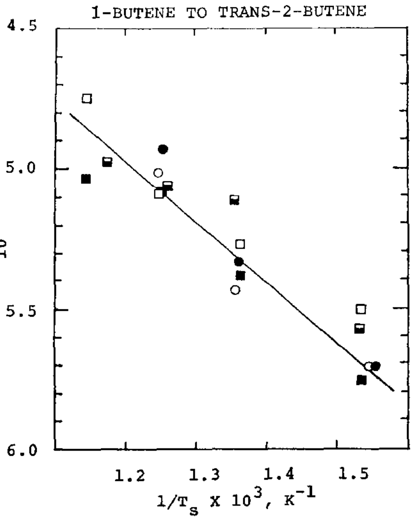

FIG. 2. Surface temperature dependence of reaction probability for isomerization of 1-butene to *trans*-2-butene on mica for various variational and translational energies of reactant molecules. See Table 1 for interpretation of symbols.

Comparison of our results with those obtained by others is not entirely straightforward. Most previous studies have been at temperatures some 250 K lower than ours. We could not make meaningful measurements at such low temperatures because the reaction probabilities would have been too small. We can use Eq. 3

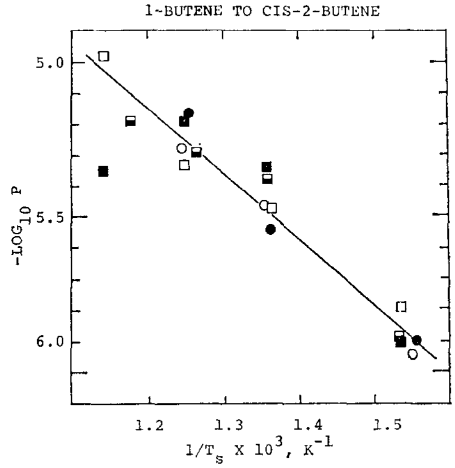

FIG. 3. Surface temperature dependence of reaction probability for isomerization of 1-butene to *cis*-2-butene on mica for various variational and translational energies of reactant molecules. See Table 1 for interpretation of symbols.

and calculate a rate at lower temperatures from our values of $A$ and $E$. Assuming an activation energy of 50 kJ/mol for the overall disappearance rate of 1-butene we calculate a rate of $1.8 \times 10^{-5}$ mol atm$^{-1}$ sec$^{-1}$ m$^{-2}$ at 385 K. Gerberich and Hall found values from 0.16 to $1.73 \times 10^{-7}$ at this temperature. At first glance there appears to be little agreement but we note that their values were obtained after 40 hr of reaction. Their catalyst showed a marked decrease in activity during the first few hours of reaction, presumably due to the formation of a residue of some sort at the relatively low temperatures used (*11*). In a pulse experiment at 323 K over silica–alumina pretreated at 823 K the rate during the sixth pulse was found to be $8 \times 10^{-8}$ mol atm$^{-1}$ sec$^{-1}$ m$^{-2}$. Extrapolation to the first pulse gives a value of $6 \times 10^{-7}$ in the same units (see Ref. 7, Table 4 and Fig. 1). It we use Eq. 3 to extrapolate our data to this temperature we obtain a value of $9 \times 10^{-7}$. Thus, if we can assume that the high temperature used in our experiments keeps the surface free of the residue which apparently can deactivate a catalyst at low temperatures, we can conclude that our rates are very nearly the same as those measured in more conventional reactors and that our mica has catalytic properties similar to those of conventional alumina–silica formulations despite the higher alumina content and the presence of potassium. A comparison of mica with the zeolites might appear to be more appropriate than with silica–aluminas. We did not attempt such a comparison because we suspect that the active surface of the mica we used has lost its crystallinity and the reported activation energy for butene isomerization on zeolites is much higher than we observe (*20*).

We did a few experiments on the isomerization and dehydrogenation of *cis*-2-butene on mica and the hydrogenation of propylene on a rhodium surface. The results in both cases were similar to those obtained with 1-butene. Rates were determined by surface temperature, not by the energy state of the reactant molecules.

In sum, the isomerization and dehydrogenation of butenes on a nonstoichiometric mica surface and the hydrogenation of

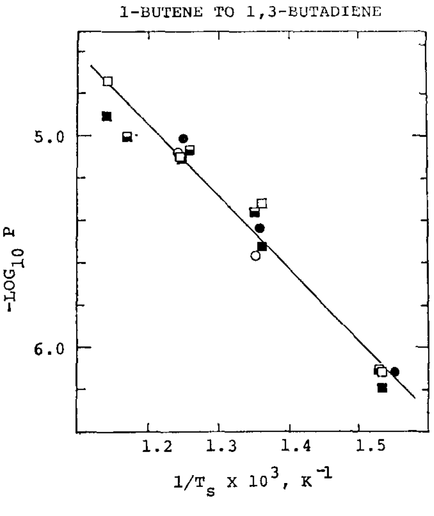

FIG. 4. Surface temperature dependence of reaction probability for dehydrogenation of 1-butene to 1,3-butadiene on mica for various vibrational and translational energies of reactant molecules. See Table 1 for interpretation of symbols.

propylene on rhodium can be added to that class of surface-induced reactions whose rates do not depend upon the energy state of the incident reactant molecules. The oxidation of ethylene and acetylene on platinum are previously reported examples of this class (*21*). The more interesting class of surface reactions, whose rates are governed by the initial energy of the incident molecules, include hydrogen–deuterium exchange on copper, nickel, and platinum (*1*, *6*), oxidation of deuterium on platinum (*22*), and the isomerization of cyclopropane on mica (*7*). In some cases, as in the hydrogen deuterium exchange on copper, translational energy is the important factor. In others, as in the isomerization of cyclopropane on mica, vibrational energy is the key component of apparent activation energy. As yet, there has been no reported case in which rotational excitation has emerged as the important variable. Indeed, because rotation in gas phase molecules is nearly always in equilibrium or near equilibrium with translation, experimental resolution of any effect due to rotational energy may be difficult to achieve. That vibrational energy can play such a vital part in reaction dynamics is no longer as noteworthy as it once might have been. The advent of the laser has long since made clear the importance of vibrational energy in promoting unimolecular and bimolecular reactions in the gas phase. Elucidation of its analogous role in surface reactions is of more recent origin but promises to be of at least equal interest and importance.

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