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Effect of Incident Translational Energy on the Surface-Induced Isomerization of Cyclopropane

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A supersonic free jet of cyclopropane molecules in the free molecular flow regime was intercepted by a heated mica surface. The resulting interaction isomerized a small fraction of the incident molecules to propylene. Previous studies had shown that reaction probability depended strongly on the temperature of the source gas, which determined the extent of vibrational excitation in the incident cyclopropane molecules. There was also a somewhat weaker dependence of reaction probability on surface temperature. We report here some experimental results on the effect of incident translational energy on reaction probability. With source temperature fixed the translational energy of the cyclopropane was varied by aerodynamic acceleration with helium or deceleration with argon or krypton. At each of five translational energies from 9 to 65 kJ/mol of cyclopropane we determined the surface temperature dependence of reaction probability to arrive at an apparent "surface activation energy" from the slope of an Arrhenius plot. It emerged that the sum of the translational and apparent surface activation energies had a constant value of about 105 kJ/mol. One model that explains these results assumes a high barrier to adsorption that is surmounted most effectively by vibrational energy in the incident cyclopropane molecule. Incident translational energy determines the sticking probability and thus affects the reaction rate. The resulting intermediates become transformed into a product propylene molecule and desorbed from the surface.

Introduction

For at least the time since Arrhenius it has been recognized that there is a barrier to many chemical reactions that can be surmounted only by those reactant molecules that have sufficient energy. In the early days of chemical kinetic studies the height of this barrier was obtained from experimental measurements of the dependence of reaction rate upon the temperature of a reacting mixture that was at or near thermal equilibrium. Such determination of the barrier height could not generally distinguish the relative importance of translational, rotational, and vibrational components of the activation energy necessary to cross the barrier. Separation of these variables has become experimentally possible with the advent of lasers and molecular beam techniques so that some general features of potential energy surfaces have been resolved for a number of gas-phase reactions. In those reactions for which the barrier is encountered early along the reaction coordinate, translational energy is more effective than vibrational energy in promoting reaction. When the barrier occurs late along the reaction trajectory, i.e. in the "exit channel", vibrational energy plays a more important role.[1]

Gas–surface reactions have not yet been as extensively studied with the still relatively new laser and molecular beam techniques. Moreover, even with these new techniques it is experimentally more difficult to resolve the dynamics of reactions that take place at least in part on surfaces that are concrete as opposed to abstract, i.e., solid or liquid. Consequently, potential energy surfaces for such reactions comprise, for the most part, unknown terrain with unmapped topography but it is to be expected that these surfaces will contain features similar to those governing gas-phase reactions. For many important cases it has been fairly well established that the critical steps for the reaction of interest take place between species that are adsorbed on and in thermal equilibrium with the material surface. When there is an energy barrier to be surmounted in such cases it is clear that with respect to the barrier height for the surface reaction the energy state of an incident molecule before it has become adsorbed and thermally accommodated is irrelevant. On the other hand, if there is an energy barrier to the adsorption step then the energy state of an incident reactant molecule is very relevant. Such "activated adsorption" has long been suspected and often invoked but was difficult to identify by classical experiments in which the surface and reactant gas were generally in thermal equilibrium with each other. In the experiments that led to and were continued in the present study, the temperatures of the surface and incident gas molecules were made independent of each other by molecular beam methods. We found that cyclopropane molecules required about 235 kJ/mol of vibrational excitation in order to isomerize when they hit a heated surface.[2] On the other hand, the isomerization and dehydration probabilities of 1-butene were independent of the energy content of the incident molecules.[3] The former case clearly involved an activated adsorption step, the latter did not. About that same time Bass and Fanchi reported that the reaction probability of nitrous oxide on a copper surface was enhanced by laser excitation of vibrational energy in the incident molecules.[4] Since then the activation of reactant by laser photons has been increasingly applied in the study of molecule surface interactions.[5]

Until recently the role of translational energy in gas-surface reactions has received much less attention. Balooch et al. found that translational energy of hydrogen incident on a copper surface had an effect on the adsorption probability. A subsequent Monte Carlo analysis with classical trajectories suggested that vibrational energy may be even more important in this process.[6] Amirav and his colleagues have accelerated iodine molecules to energies as high as 9 eV by seeding them into a free jet of helium or hydrogen and thus achieved dissociation during single collisions with a target surface.[7,8] They have also dissociated propyl iodide by the same method.[9] In some more closely related experiments Greene and his co-workers have decomposed several chlorinated hydrocarbons, dioxtene, and carbonyls of tungsten and molybdenum by surface collisions at hyperthermal energies using aerodynamic acceleration.[10,11] Auerbach and his colleagues found that aerodynamically accelerated nitrogen upon striking a tungsten surface gave rise to an adsorbed state substantially different from the state obtained at incident energies in the thermal range.[12] More recently Rettner et al. have found strong effects of incident

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translational energy on the adsorption of hydrocarbons by metal surfaces.[13] In addition, they have found that vibrational and translation energy were of equivalent effectiveness in promoting the dissociative adsorption of methane on tungsten and rhodium.[14] Also noteworthy was their finding that increasing translational energy enhanced the vibrational excitation of incident NO molecules but not as much as did increasing the temperature of the surface.[15] In an interesting extension of Green's results de la Mora had repeated some of the experiments at higher nozzle Reynold numbers and obtained quantitative data on the reaction probability. For tungsten carbonyl, it ranged from 5×10^{-5} to 5×10^{-3} and had a very steep velocity dependence near a threshold value slightly below 1.2 km/s, somewhat lower than the value found by Greene's group.[16]

During our earlier study of cyclopropane isomerization we did indeed take a perfunctory look at the effect of incident translational energy on reaction probability. At fixed values of surface and source temperature we accelerated the reactant molecules with helium and decelerated them with argon. Finding only modest difference in the probability of isomerization at three different translational energies we concluded that translational energy played no significant role. Somewhat uneasy about this conclusion we performed some more critical experiments and obtained the results that we here report.

Experimental Apparatus and Procedure

The recycling molecular beam reactor (RMBR) and the procedures for its use have been set forth previously in some detail and will be only briefly summarized here.[2,3,17] The reactor comprised a chamber maintained at a background pressure of about 0.013 Pa by a 15-in. mercury diffusion pump. In this chamber the free jet from a quartz nozzle (throat diameter of 90 μm) was intercepted by a circular mica target 3.8 cm^2 in area located 1.0 cm downstream from the nozzle exit. Because the jet was uncollimated the angle of incidence of molecules on the target varied from 0° (relative to the surface normal) at the target center to 45° at its edge. As a result the normal component of incident translational energy at the edge was only half its centerline value. Because the target area was very small relative to the surface area of the reactor chamber only an extremely small minority of the jet molecules had more than one collision with the target before they were removed by the diffusion pump. The exhaust flow from that pump at a pressure of about 25 Pa entered a mercury jet booster pump whose outlet pressure was about 4 kPa, sufficiently high so that three reciprocating bellows pumps in series could raise the flow of recycled gas to the nozzle source pressure of about 55 kPa. At a sampling port in the line from the bellows pumps to the nozzle, samples were withdrawn periodically through a septum into a syringe and injected into a gas chromatograph for analysis.

In a typical experiment about 40 cm^3 (STP) of reactant mixture comprising cyclopropane, with or without a carrier gas, were charged into the reactor. With the surface cold and the nozzle at a desired temperature, typically between 700 and 750 K in these experiments, the background conversion was measured over a period of about 2 h. The rate of conversion with a hot surface was then measured over a comparable period. Because in most experiments the total conversion did not exceed 1% the rate could be determined from a simple plot of conversion vs. time. It had been previously established that both the background and surface reactions are first order even when carried to high total conversions.[2] In those experiments the measured rates for fixed nozzle and surface temperature remained constant for many hours indicating that surface reactivity was also constant and uneffected by the presence of reaction products in the flux incident on the surface. It is also noteworthy that except for experiments in which traces of oxygen leaked into the system only trace amounts of species other than cyclopropane, propylene, and carrier gas could be detected. When even trace amounts of oxygen were present, the propylene formation rate vanished and cracking products including methane and hydrogen appeared. The apparent rate in the hot surface experiment was corrected for the background rate due to any reaction in the hot nozzle and converted to a reaction probability from the product of known values for the recycle flow rate and the fraction of jet flow intercepted by the target (0.69). The recycle time and thus the flow rate were determined by monitoring a nitrogen tracer when the reactor was charged with argon. For charges of different composition the recycle time can be calculated by taking advantage of the fact that flow is sonic at the nozzle throat and computing the speed of sound for the mixture relative to that for argon. For such a computation it is appropriate to assume that vibrational modes do not contribute to the effective heat capacity because the characteristic flow times in free jet expansions from such a small nozzle are short relative to most vibrational relaxation times.

TABLE I: True Source Temperature T_0 from Homogeneous Reaction Rate (Eq 1) for Various Mixtures at T_0 (Thermocouple) 750 K

reactant mixture, % rare gas	k min^{-1} × 10^5	T_0 calcd from obsd rate, K
0	4.30 ± 0.19	728
83.2 Kr	4.32 ± 0.22	728
83.3 Ar	3.26 ± 0.24	723
66.7 He	3.42 ± 0.19	724
83.3 He	2.53 ± 0.43	720

Reported surface temperatures are those measured by a thermocouple in contact with the surface of the mica near the center of the target. Estimated corrections for radiation and conduction losses were small. The nozzle temperature was more difficult to determine. A thermocouple sheathed in quartz was placed on the centerline of the nozzle body about midway between the ends of the annular resistance heater. The strong radiation exchange with the heater resulted in the thermocouple's indicating a temperature somewhat above the true gas temperature as estimated by so-called pneumatic thermometry based on measurements of the mass flow through the nozzle. Because the temperature dependence of the homogeneous isomerization rate of cyclopropane is so large, a more satisfactory measure of gas temperature could be obtained with the expression:

$$-\ln [(1 - x)/(1 - x^0)] = ktv \qquad (1)$$

where $k = 10^{15.5} \exp(-65600/RT)$/s, the known rate constant for the homogeneous gas-phase isomerization of cyclopropane to propylene.[18] Also, $x - x^0$ is the change in mole fraction of propylene in t seconds and v is the volume fraction of total gas charged that is in the heated part of the nozzle. For most experiments the nozzle temperature as indicated by the thermocouple was held constant at 750 K, about 20 K higher than the temperature obtained from the above equation.

As already mentioned the translational energy was varied by aerodynamic acceleration (or deceleration) in what has come to be known as the "seeded beam" technique.[19] Carrier gases were helium (Air Products C.P. grade, 98.0%), argon (Matheson U.H.P. grade, 99.999%), and krypton (Matheson Research purity, 99.995%). The cyclopropane (Matheson C.P., 98.8%) typically contained 0.18% propylene and 0.02% propane. The sampling procedure and analysis by gas chromatography were the same as previously reported.[2] Rate constants measured at various surface and source temperatures for different reactant–carrier mixtures were fitted by the method of least squares to the logarithmic form

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of the Arrhenius equation for which log K is a linear function of $1/T$. The experimental uncertainties in the rate constants were not equal throughout the measured temperature range. For example, the signal-to-background ratio goes from $^1/_3$ at low temperature to $^3/_1$ at high temperature. Therefore, in the linear least-squares-fitting program, instead of minimizing the simple sum of the squares of the deviations we weighted each term of the sum with a factor proportional to its rate constant.

Results

Tabulated in Table I are the background pseudo rate constants for the homogenous isomerization of cyclopropane in the nozzle when the target surface was cold. In every case the nominal thermocouple temperature for the nozzle was 750 K but the variation in apparent rate constants clearly indicated that the thermocouple temperature was always higher than the temperature computed from the rate constant and shown in the last column. The variation in effective nozzle temperature with source gas composition is just what one might expect from the relative heat transfer characteristics of the rare gas diluents.

Previous work in our laboratory had shown that vibrational energy in cyclopropane does not relax during free-jet expansion from nozzles as small as the one used in this study which was only 90 μm in diameter.[20] Consequently, the vibrational temperature of the cyclopropane molecules striking the target was the same as the nozzle temperature. Because of the strong dependence of reaction probability on vibrational temperature, conveniently expressed as a vibrational activation energy of 235 kJ/mol, the apparently small variations in nozzle temperature shown in Table I are not insignificant. It is appropriate to note that this activation energy was obtained from an Arrhenius plot of reaction probability against the inverse of the source temperature which was varied over the range from 700 to 800 K. The source gas was neat propane so that the translational energy increased from 23.3 to 26.6 kJ/mol in that same interval. The question is whether an appreciable contribution to the apparent vibrational activation energy could be attributed to the translational energy.

In principle, the translational energy could have been maintained constant in the face of source temperature changes by judicious adjustment of the source gas composition with argon and/or helium. In practice such adjustment is difficult because of the effect of source gas composition on true nozzle temperature as shown in Table I. To reassure ourselves on this point we repeated the experiments using a constant source gas composition of 16.7% cyclopropane and 83.3% helium. The resulting activation energy was 220 kJ/mol, very close to the value of 235 kJ/mol obtained with neat propane, even though the translational energy was three times as great. It went from 65.0 to 74.3 kJ/mol as the source temperature increased from 700 to 800 K. In the unaccelerated case (neat cyclopropane) the incident translational energy was only 23.2 kJ/mol at 700 K and 26.6 kJ/mol at 800 K. Indeed, because the experimental accuracy was substantially less when the cyclopropane was highly diluted, the 15-kJ difference between the two measurements can be entirely attributed to experimental uncertainty in the dilute gas results. Consequently, we conclude that the high value of activation energy based on source temperature variation is due largely to the effect of vibrational energy though we cannot completely rule out a small contribution from translational energy.

In order to pursue further the possible effects of translational energy we did a series of experiments in which we determined apparent surface activation energy (from the slope of semilog plots of *reaction probability against reciprocal surface temperature*) with five different mixtures of reactant cyclopropane in helium, argon, and krypton. The results are summarized in Table II.

TABLE II: Surface Activation Energies for Various Translational Energies at a Thermocouple Source Temperature of 750 K

reactant, % rare gas	adjusted source temp (eq 1), K	E_{tr}, kJ/mol	E_{sa}, kJ/mol	$E_{sa} + E_{tr}$
0	728	23.3	82 ± 6.7	105.3 ± 6.7
83.3 Kr	728	8.8	99 ± 14	107.8 ± 14
83.3 Ar	723	16.7	88 ± 9.2	104.7 ± 9.2
66.7 He	724	44.0	62 ± 7.1	106.0 ± 7.1
83.3 He	720	65.0	34 ± 8.1	99.0 ± 8.1
				av 105 ± 11

TABLE III: Effect of T_0 (Vibrational Excitation) on E_{tr} and Apparent E_{sa} (Slope of ln P_r vs. $1/T_s$)

T_0, K (eq 1)	E_{tr}, kJ/mol	E_{sa}, kJ/mol
714	22.8	60 ± 9.2
728	23.3	82 ± 6.7
750	24.0	119 ± 12

The last column in Table II reveals a remarkable correlation between the translation energy E_{tr} of incident cyclopropane molecules and the apparent surface activation energy E_{sa}. Over an energy range of more than sevenfold for E_{tr} and nearly threefold for E_{sa} the sum of the two is constant within about 3%. This correlation invites comment but for the moment we note only that it raises the question of a possible correlation between E_{sa} and E_{va}, the vibrational activation energy obtained from the dependence of reaction rate on source temperature. It will be recalled that we found virtually no apparent relation between E_{va} and E_{tr}. Consequently, we ran some experiments in which we attempted to determine E_{sa} at several values of source temperature T_0. Unfortunately, there are some problems with such experiments because of the narrow range of source temperatures that can be used. When T_0 is 700 K the surface temperature T_s must be above 800 K in order for its effect on reaction rate to be clearly distinguishable from the contribution due to homogeneous reaction in the nozzle. As T_0 increases the situation gets worse because the dependence of homogeneous reaction rate on T_0 (activation energy = 273 kJ/mol) is much greater than its dependence upon T_s ($E_{sa} + E_{tr}$ = 105 kJ/mol). Even so we obtained the results shown in Table III by averaging data from some 200 measurements.

Although the uncertainty is large there seems to be a clear trend toward higher values for apparent surface activation energy as vibrational energy (T_0) increases. This trend is in contrast to the case of increasing translational energy which resulted in a decrease in surface activation energy.

In our earlier study we found in a somewhat perfunctory experiment that the reaction probability P_r at fixed source and surface temperatures decreased somewhat with increasing incident translational energy. It seemed appropriate to check this observation with data obtained in the present study which covered a wider range of translational energies. For this purpose we note in Figure 1 that for each translational energy the relation between reaction probability P_r and surface temperature T_s has the form:

$$\ln P_r = \ln a - b/T_s \qquad (2)$$

As already noted the slope b of each straight line is E_{sa}/R where E_{sa} is the apparent surface activation energy to which the data in Table II accord the value $(105 - E_{tr})$ kJ/mol. The intercept ln a represents the value of ln P_r when b/T_s vanishes and corresponds to the situation in which P_r is not at all limited by any activation barrier on the surface after initial adsorption of reactant takes place. In Figure 2 we have plotted ln a against the translational energy E_{tr}. The resulting straight line has the form $\ln a = c - mE_{tr}$ and clearly indicates an exponential decrease in a with E_{tr}. In order to make the last term dimensionless it will be convenient to normalize the slope m of the line in Figure 2 by RT_0 to give $\ln a = cnE_{tr}/RT_0$. Fitting this expression to the data plotted in Figure 2 gives n a value of 1.05 which will be used later. For now we content ourselves with rewriting eq 3 to give at constant T_0

$$P_r \propto (\exp c)[\exp(-nE_{tr}/RT)][\exp(-E_{sa}/RT_s)] \qquad (3)$$

Further, as we have pointed out, the data for all combinations of T_s and E_{tr}, show that ln P_r is linear in E_{va}/RT_0 where E_{va} represents a vibrational activational energy. Consequently, an additional term, $\exp(-E_{va}/RT_0)$, can be added to eq 3.

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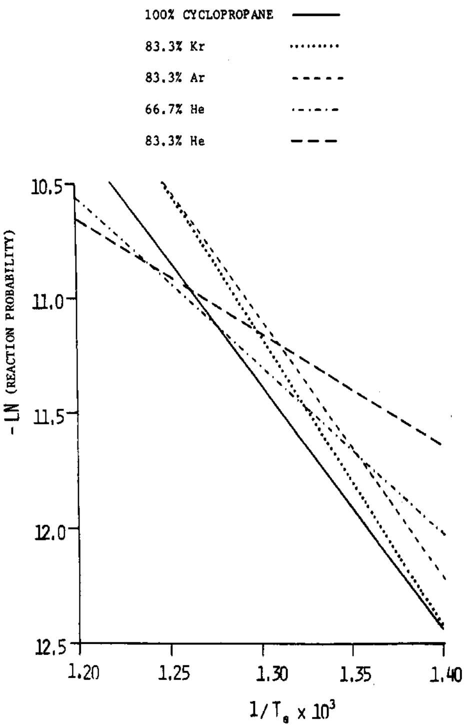

Figure 1. Arrhenius plots for varying T_s at fixed source temperature, T_0, and fixed translational energy, E_{tr}, from which the apparent surface activation energies were calculated.

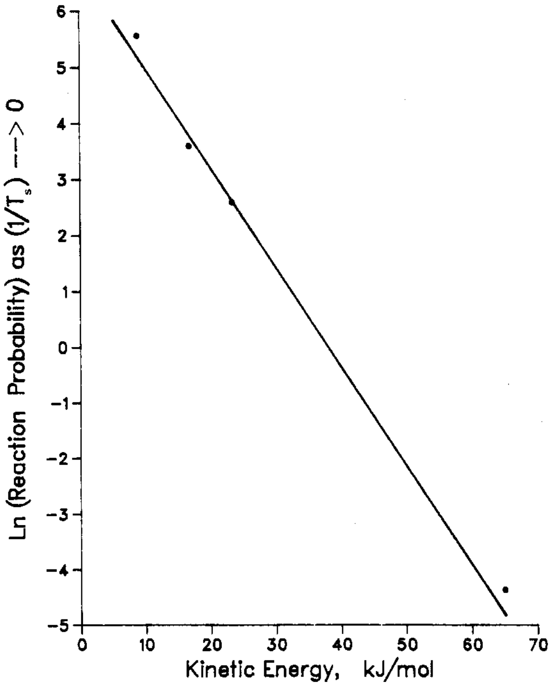

Figure 2. ln (reaction probability) extrapolated to $1/T_s = 0$, see Figure 1, plotted against the translational energy, E_{tr}.

Finally, we address the implications of the data in Table III which show that E_{sa}, the apparent surface activation energy, increases substantially with increasing T_0, the nozzle source temperature. This effect can be accommodated by an additional factor, $\exp(-B/RT_s)$ where B depends upon T_0. Using the data in Table III for fitting we obtain the simple relation: $-B = (1007 - 1.61T_0)$ kJ/mol. The physical significance of this purely empirical expression is not obvious but it does reproduce the three values in Table III to within a couple of percent. With the addition of these two factors to account for the effect of source temperature T_0, eq 3 becomes

$$P_r = A[\exp(-E_{va}/RT_0)][\exp(-nE_{tr}/RT_0)][\exp(-B/RT_s)] \times [\exp(-E_{sa}/RT_s)] \quad (4)$$

We recall that $E_{va} = 235$ kJ/mol, $n = 1.05$, $-B = (1007 - 1.61T_0)$ kJ/mol, and $E_{sa} = (105 - E_{tr})$ kJ/mol, and insert these values in eq 5 to obtain

$$P_r = A[\exp\{-(235 + 1.05E_{tr})\}/RT_0] \times [\exp\{-(1.61T_0 - 902 - E_{tr})\}/RT_s] \quad (5)$$

In these two equations the nominal frequency factor A incorporates exp c along with other constants and surface properties as well as steric factors. Within the ranges of independent variables that we have obtained data, A does not seem to show a significant dependence on either T_s or T_0, but we have not rigorously established the absence of such dependence. Because the data on which the exponential terms are based comprise a potpourri of results obtained by several investigators over a period of some years with a number of different surfaces we have not attempted to assign a numerical value of A.

Discussion

In effect eq 4 asserts that the overall reaction probability P_r is the product of several component probabilities for each of which there is a term in eq 4. The first term is governed principally by the source temperature T_0 and represents the probability that an incident cyclopropane molecule will become adsorbed on the surface. It is characterized by a vibrational activation energy E_{va} that has the value 235 kJ/mol which is just sufficient to break a C–C bond in cyclopropane. We conclude that the active intermediate is a diradical that readily bonds to the surface where it subsequently rearranges to the product propylene which desorbs. The appearance of E_{tr} in the second term is less easily understood. It may simply reflect a decrease in sticking probability of the diradical with increasing incident translational energy, reminiscent of the recent observations of Tang et al. on the sticking probability of CO on a Ni surface although Rettner et al. have found that the dissociative adsorption of CH_4 of tungsten and rhodium increases with increasing translational as well as vibrational energy.[21] The difference may simply be that translational energy of impact is more effective in exciting C–H bonds than C–C bond.

The third term in eq 4 seems to introduce a dependence on source temperature for the surface process or processes because it emerges expirically that B depends upon T_0 but is divided by T_s so as to affect the surface temperature dependence of P_r. We find it a bit difficult to understand why T_0 should have any influence upon processes that occur after absorption has occurred because surely the reactant molecules have "forgotten" the source temperature by the time they have sufficiently accommodated to the surface to become intermediates that respond to surface temperature. We seem to be faced with a rather bizarre situation in which surface temperature does not affect the dependence of reaction probability on source temperature but source temperature does affect the dependence of reaction probability on surface temperature. We have not yet conjured up a mechanism to rationalize this empirically based "one way" interaction.

The last term in eq 4 seems at first glance to be a straightforward embodiment of an Arrhenius activation energy relating to the surface reaction and/or desorption after the diradical adsorbs on the surface. But, as we have noted, E_{sa} is stongly dependent upon E_{tr} being equal to the quantity $(105 - E_{tr})$ kJ/mol. One possible rationale is that E_{sa} relates to the desorption process and that kinetic energy of incident molecules is just as effective in overcoming surface bonding of product as is thermal energy from the surface. Though superficially plausible this mechanism would require that the overall rate be second order with respect to incident cyclopropane (or carrier molecules of equivalent energy). All the experimental evidence indicates that the reaction is first order. Thus, we still seek an explanation for this remarkable apparent interchangeability of incident translational energy and thermal activation energy from the surface.

An important result of this study is the demonstration that even without lasers molecular beam methods in the study of surface-

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induced reactions can simply and effectively separate the experimental variables which include translational and vibrational energies in reactant molecules as well as surface temperature. Moreover, the recycling feature of this novel reactor makes possible such separated-variable studies for reactions with much smaller cross sections than those which can be effectively studied in single pass experiments. Even so, though our investigation has revealed many new features of this much-studies isomerization of cyclopropane it is clear that much more remains to be learned before we fully understand its mechanism.

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Registry No. Cyclopropane, 75-19-4.

Theoretical Study of the Interaction of CO with Pd Clusters: Relations between Surface and Organometallic Chemistry[†]

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The results of a pseudopotential configuration interaction investigation of the electronic structure of small Pd clusters interacting with CO are reported. The Pd clusters chosen can be considered as models of on top, bridge, and three-hollow sites on the (111) Pd surface. The results provide some insight into the nature of the Pd–CO bonding, confirming the repulsive nature of the σ interaction and the essential role of the π-back-donation mechanism for the formation of the Pd–CO bond. Some interesting similarities between Pd_n–CO clusters and CO chemisorbed on a Pd (111) surface have been found. In particular, the three-hollow position is found to be the preferred interaction site and the MO spectra qualitatively reproduce the photoelectron spectra of CO on Pd. However, the adopted theoretical method predicts the existence of weak bonds among the Pd atoms which retain much of their d^{10} character. For this reason, small bare Pd clusters are probably not "optimal" models of Pd surfaces. On the other hand, the Pd_n–CO clusters considered provide interesting information about the nature of the bonding in organometallic Pd clusters. The analysis of the bond in these systems indicates that Pd–carbonyl clusters, where the Pd atoms formally are in the zero-oxidation state, are held together mainly through interaction with the bridging CO ligands, since the metal–metal bonds are rather weak.

Introduction

Metal clusters have been proposed as possible models for the study of chemisorption phenomena because of the analogies found between reactions on catalytically active metal surfaces and on inorganic clusters[1] and because of the similarity in the ligand stereochemistry on clusters and surfaces.[2]

The belief that the cluster–surface analogy is correct, at least to a first approximation, has stimulated the theoretical modeling of chemisorption processes with small metal clusters. The results obtained up to now are considered encouraging and seem to confirm the basic assumption that chemisorption processes can be described as local phenomena involving only few nearest neighbors to the adsorbate on the metal surface.[3]

The use of metal clusters in studying chemisorption still represents a challenge for the theoreticians. Catalysis occurs mainly on transition-metal surfaces, and most of the experimental studies of chemisorption deal with these systems. Unfortunately, at the present, the theoretical treatment of transition elements at the same level of accuracy as the light atoms is computationally very hard.

In particular, large computational problems are connected with the study of Pd clusters due to the dimensions of the systems and to the presence of the heavy Pd atoms. Few theoretical studies of CO chemisorption on Pd clusters have been reported, and the methods adopted range from extended Huckel,[4] to $X\alpha$,[5] local spin density,[6] and Hartree–Fock[7] approximations. In this paper we present the results of pseudopotential configuration interaction (CI) calculations on small Pd_n clusters ($n = 2, 3, 4$) interacting with the CO molecule. Preliminary results of this study have been reported.[8] Here we emphasize the methodological aspects which, although tedious, are extremely important to assess the quality of the calculations and the reliability of the results obtained.

The discussion of the results has been divided into three parts. First, we analyze the nature of the metal–metal bond in small bare Pd clusters and we discuss their similarity with the corresponding bulk metal. Then the mechanism of Pd–CO bonding is described

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