J. Am. Chem. Soc. **2001,** *123,* 929−940

Trapping-Mediated Dissociative Chemisorption of Cycloalkanes on Ru(001) and Ir(111): Influence of Ring Strain and Molecular Geometry on the Activation of C−C and C−H Bonds

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Received July 6, 2000

Abstract: We have measured the initial probabilities of dissociative chemisorption of perhydrido and perdeutero cycloalkane isotopomers on the hexagonally close-packed Ru(001) and Ir(111) single-crystalline surfaces for surface temperatures between 250 and 1100 K. Kinetic parameters (activation barrier and preexponential factor) describing the initial, rate-limiting C−H or C−C bond cleavage reactions were quantified for each cycloalkane isotopomer on each surface. Determination of the dominant initial reaction mechanism as either initial C−C or C−H bond cleavage was judged by the presence or absence of a kinetic isotope effect between the activation barriers for each cycloalkane isotopomer pair, and also by comparison with other relevant alkane activation barriers. On the Ir(111) surface, the dissociative chemisorption of cyclobutane, cyclopentane, and cyclohexane occurs via two different reaction pathways: initial C−C bond cleavage dominates on Ir(111) at high temperature ($T > \sim 600$ K), while at low temperature ($T < \sim 400$ K), initial C−H bond cleavage dominates. On the Ru(001) surface, dissociative chemisorption of cyclopentane occurs via initial C−C bond cleavage over the entire temperature range studied, whereas dissociative chemisorption of both cyclohexane and cyclooctane occurs via initial C−H bond cleavage. Comparison of the cycloalkane C−C bond activation barriers measured here with those reported previously in the literature qualitatively suggests that the difference in ring-strain energies between the initial state and the transition state for ring-opening C−C bond cleavage effectively lowers or raises the activation barrier for dissociative chemisorption via C−C bond cleavage, depending on whether the transition state is less or more strained than the initial state. Moreover, steric arguments and metal−carbon bond strength arguments have been evoked to explain the observed trend of decreasing C−H bond activation barrier with decreasing cycloalkane ring size.

I. Introduction

Due to the enormous potential of hydrocarbons as fuel sources and petrochemical building blocks, the design of catalysts for the commercial reforming of hydrocarbons with consistently higher product yields and selectivities is a perpetual goal in the field of heterogeneous catalysis.[1] A successful catalyst for these applications must be one that selectively activates the strong C−C and C−H bonds in the alkanes used as process feed streams. Because of the economic and scientific importance of such advances in catalysis, much attention has been devoted over the past few decades to understanding the elementary C−H and C−C bond activation reactions of alkanes on catalytically important transition metal surfaces. One specific research area that has provided particularly valuable contributions toward elucidating the initial elementary reaction mechanisms and quantifying the kinetics of these individual reaction steps on catalytically important transition metal surfaces is the study of the activation of alkanes on well-defined single-crystalline transition metal surfaces under ultrahigh-vacuum (UHV) conditions.[2] The goal of these studies has been to provide accurate mechanistic and kinetic data which describe the *intrinsic* reactivities of a variety of catalytically active transition metal surfaces concerning the *initial* C−H or C−C bond cleavage reactions of alkanes. The accurate determination of the reaction mechanisms and kinetic parameters describing *initial* alkane bond cleavage reactions on these surfaces is extremely important since the initial elementary C−H or C−C bond cleavage step is usually rate limiting. Because of this, the mechanistic and kinetic information obtained from these studies can be used in the design of better catalysts for specific reactions of interest[3] involving the initial activation and subsequent conversion of alkanes.

To date, the vast majority of UHV alkane activation studies have involved either straight-chain or partially branched alkanes. A few recent studies, however, have involved the trapping-mediated activation of cycloalkanes under UHV conditions. A study of the trapping-mediated activation of cyclopropane on Ir(111) via initial C−H bond cleavage (dominant at low temperature, i.e., $T < \sim 400$ K) and C−C bond cleavage (dominant at high temperature, i.e., $T > \sim 600$ K) reactions has very recently been completed in our laboratory.[4] Trapping-mediated activation studies of cyclopropane on Ru(001)[5] and

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10.1021/ja002459z CCC: $20.00

Table 1. Comparison of Strain Energies and Activation Barriers for C−C Bond Cleavage for Perhydrido Cyclopropane[5] and Cyclobutane[7] on Ru(001)[a]

reactant	total strain (cal/mol)	C−C activation barrier (cal/mol)
cyclopropane	28 300	9 470
cyclobutane	27 400	10 090

[a] The activation barrier for C−C bond cleavage of unstrained *n*-butane on Ru(001) is approximately 19 000 cal/mol.[52]

Table 2. Ring-Strain Energies for Selected Cycloalkanes[a]

reactant	total strain (kcal/mol)	strain per $-CH_2-$ group (kcal/mol)
cyclopropane	28.3	9.4
cyclobutane	27.4	6.9
cyclopentane	7.3	1.5
cyclohexane	1.4	0.2
cycloheptane	7.8	1.1
cyclooctane	11.5	1.4

[a] The calculated strain energies are based on enthalpies of formation for a hypothetical, strainless $-CH_2-$ unit of −5.15 kcal/mol and on the experimentally determined heats of formation for each gas-phase cycloalkane molecule.

Ir(110),[6] and cyclobutane on Ru(001),[7] which have been performed recently in our laboratory as well, reveal that activation of these cycloalkane molecules on these two surfaces occurs via initial C−C bond cleavage with surprisingly low activation barriers compared to their linear alkane analogues. The measured activation energies describing the activation of cyclopropane and cyclobutane C−C bonds on Ru(001), along with the ring-strain values for these two cycloalkanes, are displayed in Table 1; the ring-strain energies for the entire series of C_3-C_8 cycloalkanes are listed in Table 2. The cyclopropane and cyclobutane activation data displayed in Table 1 appear to indicate that relief of the ring-strain energy of the molecule via ring-opening C−C bond cleavage effectively reduces the activation barriers for C−C bond cleavage. Understanding the influence of ring strain on cycloalkane reactivity is the primary motivation behind the present study involving the activation of a number of cycloalkanes on the geometrically similar hexagonally close-packed (hcp) Ru(001) and Ir(111) surfaces. As a point of clarification, the definition of the term “ring strain” used in this article will include all components of ring strain: bond angle strain (Baeyer strain), torsional strain (Pitzer strain), and rehybridization effects (e.g., C−H bond strengthening), to name a few. The general definitions, concepts, and the particular contributions to ring strain are comprehensively reviewed by Liebman and Greenberg.[8]

These cycloalkane activation reactions are extremely interesting due to the possible influence of ring-strain on reactivity; however, they are of practical interest in hydrocarbon conversion as well. For example, the conversion of cycloalkanes to aromatic and straight-chain hydrocarbons, via C−H and C−C bond cleavage reactions, is an important process in the catalytic reforming of petroleum naphtha feedstocks.[1,9] Therefore, it is hoped that the experimental results presented here will not only illuminate the fundamental issues regarding reactivity and ring-strain but also provide valuable mechanistic and kinetic information regarding industrially important heterogeneously catalyzed reactions involving strained hydrocarbons.

The high reactivity of cyclopropane toward ring-opening C−C bond cleavage has been previously attributed in organic synthesis studies to the thermodynamic driving force provided by the release of the ring-strain energy.[10,11] Some other perspectives and additional information can be found in several recent theoretical computational studies involving cycloalkane ring-strain, including ring-strain energy calculations,[12−14] computations involving carbon[15] and hydrogen[16] bond acidity in ring-strained molecules, and reactions involving ring-strained hydrocarbons.[17,18] Particularly relevant to the experimental results reported here for the activation of cycloalkanes by transition metal surfaces are the computations by Siegbahn and Blomberg[17] involving the activation of C−C bonds in ethane, cyclopropane, and cyclobutane by transition metal atoms. These authors concluded that when there is strain involved in the C−C bonds, the activation barriers for breaking these bonds are, as expected, much lower. However, the reaction energy for the C−C bond-breaking reaction is not as much larger for the strained compared to the unstrained case as the difference in C−C bond strength would indicate. The reason for this is that there is strain involved also in the metallacycles that are formed after the strained C−C bonds have been broken.[17] The experimental data that are presented here concerning the activation of cycloalkanes on transition metal surfaces will be used to examine this principle for both C−C and C−H bond cleavage reactions of these strained cycloalkanes. To the best of our knowledge, no experimental study of the initial dissociative chemisorption of a series of unsubstituted cycloalkanes on a transition metal surface has been performed to date. We believe that data of this type (presented here) will make a valuable experimental contribution toward understanding the relationship between the ring-strain energies of these model cycloalkane molecules and their reactivity.

II. Experimental Methodologies

The experiments were carried out in a stainless steel UHV chamber (base pressure of 7×10^{-11} Torr) equipped with high-resolution electron energy loss spectroscopy (HREELS), Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), a twice differentially pumped radical beam source, and a differentially pumped quadrupole mass spectrometer for temperature-programmed desorption (TPD) measurements.[19−21] The Ru(001) and Ir(111) single-crystalline samples were mounted on a home-built cryostat that can cool the sample to 90 K using liquid nitrogen. The sample temperature could be varied from 90 to 1700 K by resistive heating and was monitored using a type-C thermocouple spot-welded to the back of the crystal. Standard methods of Ar^+ sputtering as well as annealing to 1550 K in a background of oxygen were used to clean the Ru(001) surface; the Ru(001) sample was heated to 1650 K in order

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to remove all chemisorbed oxygen. The Ir(111) surface was cleaned using standard methods of Ar^+ sputtering as well as annealing to 1100 K in a background of oxygen, followed by heating to 1450 K in order to remove all chemisorbed oxygen.[22] Surface cleanliness of both samples was verified by HREELS, LEED, carbon monoxide TPD, and AES.

The perhydrido cyclopentane (c-C_5H_{10}), cyclohexane (c-C_6H_{12}), and cyclooctane (c-C_8H_{16}) isotopomers were obtained from Sigma-Aldrich (Milwaukee, WI). The purities of these reagents as received from Sigma-Aldrich were 99+%, 99.5%, and 99+%, respectively, for c-CsHo0, c-C_6H_{12}, and c-C_8H_{16}. The perdeutero cyclopentane (c-C_5D_{10}), cyclohexane (c-C_6D_{12}), and cyclooctane (c-C_8D_{16}) isotopomers were obtained from C/D/N Isotopes (Pointe-Claire, Quebec, Canada). As received, the purities of these reagents were 99.6% (99.5% d_{10}), 99.9% (99.6% d_{12}), and 99.1% (98.6% d_{16}), respectively, for c-C_5D_{10}, c-C_6D_{12}, and c-C_8D_{16}. These cycloalkane reagents were purified further in our gas-handling manifold by performing multiple freeze−pump−thaw purification cycles on each reagent. After these purification cycles, the purity of each reagent was checked using mass spectrometry; no contaminant species were detected in the background mass spectrum collected from each of the six cycloalkane reagents. Perhydrido (c-C_4H_8) and perdeutero (c-C_4D_8) cyclobutane isotopomers were synthesized via Wurtz coupling reactions described elsewhere.[7] The cyclobutane was purified to greater than 99% purity (as verified by mass spectrometry) by performing multiple freeze−pump−thaw cycles in our gas-handling manifold.

The initial probabilities of trapping-mediated dissociative chemisorption of cyclopentane, cyclohexane, and cyclooctane on Ru(001) were measured by continuously flowing each cycloalkane into the chamber at a constant pressure between 1×10^{-7} and 1×10^{-6} Torr while holding the crystal at a constant temperature between 300 and 1000 K. For the Ir(111) surface, the initial probabilities of trapping-mediated dissociative chemisorption of cyclobutane, cyclopentane, and cyclohexane were measured by continuously flowing each cycloalkane into the chamber at a constant pressure between 1×10^{-8} and 1×10^{-7} Torr while holding the crystal at a constant temperature between 250 and 1100 K. The exposures were selected such that the coverage of carbon adatoms left on each surface following the dissociation of the cycloalkanes was between 4 and 10%. The lower limit was chosen to guarantee that activation at surface defect sites did not dominate the overall reaction probability, while the upper limit was selected in order to approximate a measurement of the *initial* probability of dissociative chemisorption. Immediately following each cycloalkane exposure, the sample was flashed to 800 K to fully decompose the hydrocarbon fragments produced by the dissociative chemisorption of the cycloalkanes. During decomposition, the hydrogen adatoms recombine and desorb as H2, while the carbon adatoms remain on the surface. The sample was then cooled to 90 K. For the experiments on Ru(001), the surface was then exposed to 100 L of molecular oxygen (Matheson, 99.9999%), and a TPD experiment was performed. This resulted in desorption of reaction-limited CO which was formed by the reaction of oxygen and carbon adatoms. Using this method,[5,23] the ratio of CO to CO_2 production was ∼100. The surface coverage of carbon adatoms, θ_C (number of carbon atoms per surface metal atom), deposited by dissociation of the cycloalkane, was calculated by comparing the time-integrated area of the reaction-limited CO desorption in each experiment to the desorption of a saturation coverage of CO on Ru(001), $\theta_{CO,sat} = 0.67$.[24,25] For the experiments on Ir(111), the surface was exposed to 10 L of molecular oxygen, after which a TPD experiment was performed in the presence of a background oxygen pressure of 1×10^{-7} Torr. This procedure also resulted in desorption of reaction-limited CO which was formed by the reaction of oxygen and carbon adatoms. Using this method, no CO_2 production was detected. The surface coverage of carbon adatoms, θ_C, deposited by the dissociation of the cycloalkane on Ir(111), was calculated by comparing the time-integrated area of the reaction-limited CO desorption in each experiment to the desorption of a saturation coverage of CO on Ir(111), $\theta_{CO,sat} = 0.71$.[26] Auger measurements performed immediately after the oxygen titration experiment was performed on both surfaces showed that no carbon remained on the surface.

Since the reaction probability of each cycloalkane is proportional to the surface coverage of carbon adatoms deposited on the surface for a constant exposure, we may calculate the probability of reaction, P_r, at a given surface temperature, T_s, as

$$P_r = \frac{\theta_C N_s}{N_c F \tau} \tag{1}$$

where N_s is the number of transition metal surface atoms per unit area (Ru(001) = 1.58×10^{15} atoms/cm^2, Ir(111) = 1.57×10^{15} atoms/cm^2),[27] N_c is the number of carbon atoms in the cycloalkane molecule, F is the impingement flux of cycloalkane molecules onto the surface, and τ is the exposure time. The initial probabilities of dissociative chemisorption, determined experimentally using eq 1 at various surface temperatures, were used to construct an Arrhenius plot for each cycloalkane/surface combination studied. The model presented next will be used as a tool with which to extract the relevant kinetic parameters which describe the rate-limiting steps in the dissociative chemisorption of these cycloalkanes on Ru(001) and Ir(111).

III. Trapping-Mediated Dissociative Chemisorption Model

The experimental conditions of this study, namely, low pressure and low incident kinetic energy of the cycloalkanes, which is characterized by a Maxwell−Boltzman distribution at 300 K, enable quantification of the probability of trapping-mediated dissociative chemisorption.[28] Under these experimental conditions, the contribution to the overall reaction probability by a direct dissociative chemisorption channel has been shown to be negligible.[28,29] Since the initial rate-limiting step in the trapping-mediated dissociative chemisorption of a cycloalkane molecule involves either C−C or C−H bond cleavage, the individual reaction steps describing cycloalkane dissociation may be written as[30]

$$\text{c-}C_nH_{2n}(g) \underset{k_d}{\overset{\xi R}{\rightleftarrows}} \text{c-}C_nH_{2n}(p) \tag{2}$$

$$\text{c-}C_nH_{2n}(p) \xrightarrow{k_{r,CC}} C_nH_{2n}(c) \tag{3}$$

$$\text{c-}C_nH_{2n}(p) \xrightarrow{k_{r,CH}} \text{c-}C_nH_{2n-1}(c) + H(c) \tag{4}$$

where the molecular cycloalkane impinging from the gas phase with impingement rate R traps with probability ξ into the physically adsorbed state (p), and then either desorbs with rate coefficient k_d, reacts irreversibly via C−C bond cleavage with rate coefficient $k_{r,CC}$ to a dissociatively chemisorbed product (c), or reacts irreversibly via C−H bond cleavage with rate coefficient $k_{r,CH}$ to a dissociatively chemisorbed product. The time rate of change of the fractional surface coverage of physically adsorbed cycloalkane can be expressed as

$$\frac{d\theta_{c-C_nH_{2n}(p)}}{dt} = \xi R - k_{r,CC}\theta_{c-C_nH_{2n}(p)} - k_{r,CH}\theta_{c-C_nH_{2n}(p)} - k_d\theta_{c-C_nH_{2n}(p)} \tag{5}$$

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Since the fractional coverage of physically adsorbed cycloalkane under our experimental conditions is always less than 10^{-4}, a pseudo-steady-state assumption may be used (to set the left side of eq 5 equal to zero) to determine a relationship for the fractional coverage of physically adsorbed cycloalkane. The fractional coverage of physically adsorbed cycloalkane may now be expressed as

$$\theta_{\mathrm{c-C}_n\mathrm{H}_{2n}(\mathrm{p})} = \frac{\xi R}{k_{\mathrm{r,CC}} + k_{\mathrm{r,CH}} + k_{\mathrm{d}}} \tag{6}$$

The reaction probability of a cycloalkane for a specific initial reaction channel is defined as the rate of reaction for the specific activation channel, i.e., $R_{\mathrm{r,CC}}$ for C−C bond cleavage, divided by the gas-phase impingement rate, R. Therefore, the initial probability of trapping-mediated dissociative chemisorption via initial C−C bond cleavage is given by

$$P_{\mathrm{r,CC}} = \frac{R_{\mathrm{r,CC}}}{R} = \frac{k_{\mathrm{r,CC}}\theta_{\mathrm{c-C}_n\mathrm{H}_{2n}(\mathrm{p})}}{R} \tag{7a}$$

and the initial probability of trapping-mediated dissociative chemisorption via initial C−H bond cleavage is given by

$$P_{\mathrm{r,CH}} = \frac{R_{\mathrm{r,CH}}}{R} = \frac{k_{\mathrm{r,CH}}\theta_{\mathrm{c-C}_n\mathrm{H}_{2n}(\mathrm{p})}}{R} \tag{7b}$$

Substitution of the expression for the fractional coverage of physically adsorbed cycloalkane from eq 6 into eq 7 yields the following expressions for the initial probability of dissociative chemisorption of a cycloalkane via either initial C−C or C−H bond cleavage:

$$P_{\mathrm{r,CC}} = \frac{\xi k_{\mathrm{r,CC}}}{k_{\mathrm{r,CC}} + k_{\mathrm{r,CH}} + k_{\mathrm{d}}} \tag{8a}$$

$$P_{\mathrm{r,CH}} = \frac{\xi k_{\mathrm{r,CH}}}{k_{\mathrm{r,CC}} + k_{\mathrm{r,CH}} + k_{\mathrm{d}}} \tag{8b}$$

The reaction probability expressions displayed in eq 8 must be used to fit the experimental data in order to extract the kinetic parameters for trapping-mediated dissociative chemisorption.

Using the Polanyi−Wigner form for each elementary rate coefficient, k_{i},

$$k_{\mathrm{i}} = k_{\mathrm{i}}^{(0)} \exp\left[\frac{-E_{\mathrm{i}}}{k_{\mathrm{B}}T_{\mathrm{s}}}\right] \tag{9}$$

yields the following expressions for the reaction probabilities for C−C and C−H bond cleavage when substituted into eq 8:

$$P_{\mathrm{r,CC}} = \frac{\xi(k_{\mathrm{r,CC}}^{(0)}) \exp(-E_{\mathrm{r,CC}}/k_{\mathrm{B}}T_{\mathrm{s}})}{(k_{\mathrm{r,CC}}^{(0)}) \exp(-E_{\mathrm{r,CC}}/k_{\mathrm{B}}T_{\mathrm{s}}) + (k_{\mathrm{r,CH}}^{(0)}) \exp(-E_{\mathrm{r,CH}}/k_{\mathrm{B}}T_{\mathrm{s}}) + (k_{\mathrm{d}}^{(0)}) \exp(-E_{\mathrm{d}}/k_{\mathrm{B}}T_{\mathrm{s}})} \tag{10a}$$

$$P_{\mathrm{r,CH}} = \frac{\xi(k_{\mathrm{r,CH}}^{(0)}) \exp(-E_{\mathrm{r,CH}}/k_{\mathrm{B}}T_{\mathrm{s}})}{(k_{\mathrm{r,CC}}^{(0)}) \exp(-E_{\mathrm{r,CC}}/k_{\mathrm{B}}T_{\mathrm{s}}) + (k_{\mathrm{r,CH}}^{(0)}) \exp(-E_{\mathrm{r,CH}}/k_{\mathrm{B}}T_{\mathrm{s}}) + (k_{\mathrm{d}}^{(0)}) \exp(-E_{\mathrm{d}}/k_{\mathrm{B}}T_{\mathrm{s}})} \tag{10b}$$

We can reasonably assume a value of unity for ξ for the gas translational energies employed in this study. This assumption is based on molecular beam studies which have quantified the trapping probability of various alkanes,[31−35] including cyclopropane,[6] on transition metal surfaces, and on recent work involving the trapping-mediated dissociative chemisorption of cyclopropane on Ru(001).[5] The expressions given in eq 10 for the initial probabilities of dissociative chemisorption for initial C−C and C−H bond cleavage will be referred to later when the determination of kinetic parameters and identification of reaction mechanisms are discussed in detail.

Table 3. Thermal Desorption Results for Submonolayer Cycloalkane Coverages on Ru(001) and Ir(111)[a]

	Ru(001)		Ir(111)	
reactant	T_{d} (K)	E_{d} (cal/mol)	T_{d} (K)	E_{d} (cal/mol)
cyclobutane			178	10 250
cyclopentane	185	10 590	184	10 610
cyclohexane	196	11 280	203	11 740
cyclooctane	244	14 140		

[a] The TPD data were collected using heating rates of 16 and 18 K/s, respectively, for the Ir(111) and Ru(001) surfaces. The activation energies were computed using the Redhead method and assuming a preexponential factor for desorption of 1 × 10^{13} s^{-1}. The uncertainty for each reported E_{d} value of ±50 cal/mol represents one standard deviation in the measured value.

IV. Results

Thermal desorption measurements of a submonolayer coverage of each physically adsorbed cycloalkane isotopomer were used to determine the kinetic parameters associated with desorption.[36] The peak desorption temperatures measured for each physically adsorbed cycloalkane isotopomer pair were identical; these temperatures are displayed in Table 3. Using these values and assuming a preexponential factor for desorption, $k_{\mathrm{d}}^{(0)} = 1 \times 10^{13}\ \mathrm{s}^{-1}$,[5,7,30,36] E_{d} values were calculated for each of the cycloalkane/surface combinations using the well-known Redhead[36] method. The calculated E_{d} values, listed in Table 3, will be used below in the quantification of the kinetic parameters associated with trapping-mediated dissociative chemisorption by fitting eq 10 to the experimental data.

A. Cycloalkane Activation on Ru(001). The Arrhenius constructions of the experimentally determined initial probabilities of dissociative chemisorption of cyclopentane, cyclohexane, and cyclooctane on Ru(001) as a function of reciprocal surface temperature are displayed in Figures 1−3, respectively. For each of these cycloalkanes, the reaction probability increases substantially with increasing surface temperature, indicative of an activation barrier for reaction that is much higher than the activation barrier for desorption. The linear Arrhenius constructions of the data for each cycloalkane provide compelling evidence for the existence of only one controlling reaction mechanism[37] over the entire range of temperatures studied here. Therefore, since one dissociation mechanism appears to dominate over the entire temperature range studied on this surface, the rate of the other mechanism may be neglected in the denominator of eq 10, to yield the following pair of expressions

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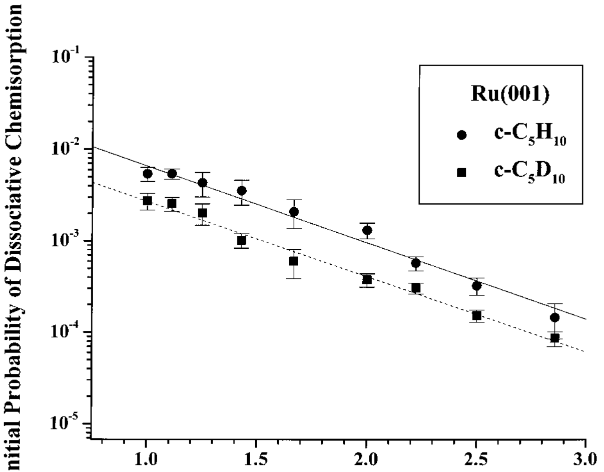

Figure 1. Initial probabilities of trapping-mediated dissociative chemisorption of perhydrido and perdeutero cyclopentane as a function of reciprocal surface temperature on Ru(001). The error bars represent one standard deviation in the measured reaction probability at each temperature.

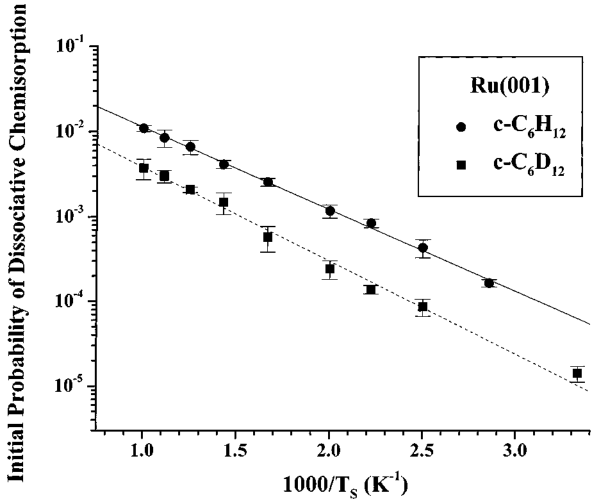

Figure 2. Initial probabilities of trapping-mediated dissociative chemisorption of perhydrido and perdeutero cyclohexane as a function of reciprocal surface temperature on Ru(001). The error bars represent one standard deviation in the measured reaction probability at each temperature.

for the probabilities of trapping-mediated dissociative chemisorption via C−C and C−H bond cleavage:

$$P_{\mathrm{r,CC}} = \frac{\xi(k^{(0)}_{\mathrm{r,CC}})\exp(-E_{\mathrm{r,CC}}/k_{\mathrm{B}}T_{\mathrm{s}})}{(k^{(0)}_{\mathrm{r,CC}})\exp(-E_{\mathrm{r,CC}}/k_{\mathrm{B}}T_{\mathrm{s}}) + (k^{(0)}_{\mathrm{d}})\exp(-E_{\mathrm{d}}/k_{\mathrm{B}}T_{\mathrm{s}})} \tag{11a}$$

$$P_{\mathrm{r,CH}} = \frac{\xi(k^{(0)}_{\mathrm{r,CH}})\exp(-E_{\mathrm{r,CH}}/k_{\mathrm{B}}T_{\mathrm{s}})}{(k^{(0)}_{\mathrm{r,CH}})\exp(-E_{\mathrm{r,CH}}/k_{\mathrm{B}}T_{\mathrm{s}}) + (k^{(0)}_{\mathrm{d}})\exp(-E_{\mathrm{d}}/k_{\mathrm{B}}T_{\mathrm{s}})} \tag{11b}$$

The Ru(001) activation data were fit (using a nonlinear curve-fitting algorithm) using the reaction probability expressions given in eq 11. Only two parameters are unknown in each of these equations since the kinetic parameters for desorption were determined independently. Since the forms of these two equations for C−C and C−H bond cleavage are identical, the activation data were fit with an equation of this general form, and identification of the dominant reaction mechanism as either initial C−C or C−H bond cleavage was determined afterward. The kinetic parameters (preexponential factor and activation energy for either C−C or C−H bond cleavage) yielding the best fit to the experimental data are displayed in Table 4. The reaction mechanism assignment as either initial C−C or C−H bond cleavage for each cycloalkane on Ru(001) will now be discussed.

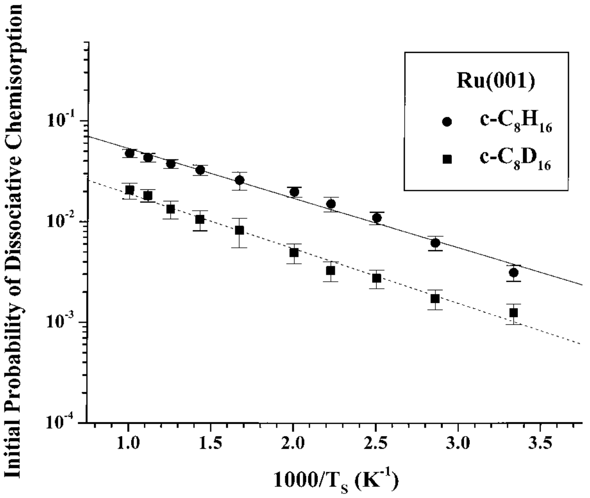

Figure 3. Initial probabilities of trapping-mediated dissociative chemisorption of perhydrido and perdeutero cyclooctane as a function of reciprocal surface temperature on Ru(001). The error bars represent one standard deviation in the measured reaction probability at each temperature.

The assignment of the initial trapping-mediated dissociation mechanism as either C−H or C−C bond cleavage for these cycloalkanes on Ru(001) was made possible by examination of the kinetic isotope effect between perdeutero and perhydrido cycloalkane isotopomer pairs.[38] If the reaction mechanism proceeds via initial C−H bond cleavage, a relatively large primary kinetic isotope effect should be observed due to ground-state zero-point energy differences between the perhydrido and perdeutero isotopomers. The relevant mode for alkane activation via C−H bond cleavage has been shown to be the asymmetric C−H (or C−D) stretching mode.[39] The ground-state zero-point energy difference between C−H and C−D bonds is approximately $3000 - 2250 = 750\ \mathrm{cm}^{-1} \approx 1100$ cal/mol.[23,38,39] This value is the expected apparent activation barrier difference for initial C−H bond cleavage between perhydrido and perdeutero isotopomer pairs if no vibrational motion is retained along the reaction coordinate; otherwise, a value slightly lower than this would be expected. On the other hand, if the reaction mechanism proceeds via initial C−C bond cleavage, only a slight kinetic isotope effect should be observed between isotopomer pairs since secondary kinetic isotope effects are generally small.[38]

Examination of the activation barrier differences measured here (and displayed in Table 4) for each cycloalkane isotopomer pair enables determination of the initial rate-limiting reaction step for dissociative chemisorption of each cycloalkane on Ru(001). For cyclopentane, the measured activation barriers for c-C_5H_{10} and c-C_5D_{10} of 14 420 and 14 360 cal/mol, respectively, are nearly identical. The lack of a significant kinetic isotope effect between these cyclopentane isotopomers implies that the

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(38) Laidler, K. J. *Chemical Kinetics*; HarperCollins: New York, 1987.

(39) Verhoef, R. W.; Kelly, D.; Mullins, C. B.; Weinberg, W. H. *Surf. Sci.* **1994**, *311*, 196.

Table 4. Kinetic Rate Parameters Describing the Trapping-Mediated Dissociative Chemisorption of Cycloalkanes on Ru(001)[a]

reactant	$E_{r,CH}$ (cal/mol)	$(k_{r,CH}^{(0)})/k_d^{(0)}))$	$E_{r,cc}$ (cal/mol)	$(k_{r,CC}^{(0)}/k_d^{(0)})$
c-C_3H_6	n.o.	n.o.	9 470 ± 120[b]	0.01[b]
c-C_3D_6	n.o.	n.o.	9 470 ± 120[b]	0.01[b]
c-C_4H_8	n.o.	n.o.	10 090 ± 180[c]	0.048 ± 0.005[c]
c-C_4D_8	n.o.	n.o.	10 180 ± 190[c]	0.021 ± 0.002[c]
c-C_5H_{10}	n.o.	n.o.	14 420 ± 260	0.045 ± 0.010
c-C_5D_{10}	n.o.	n.o.	14 360 ± 200	0.018 ± 0.003
c-C_6H_{12}	15 700 ± 130	0.10 ± 0.01	n.o.	n.o.
c-C_6D_{12}	16 320 ± 220	0.048 ± 0.008	n.o.	n.o.
c-C_8H_{16}[c]	16 390 ± 150	0.16 ± 0.02	n.o.	n.o.
c-C_8D_{16}[c]	16 630 ± 160	0.066 ± 0.007	n.o.	n.o.

[a] The reported activation barriers for C−C and C−H bond cleavage are referenced to the proper reference energy, the bottom of the physically adsorbed well. The preexponential factor for desorption, $k_d^{(0)}$, has been assumed to be equal to 10^{13} s^{-1} for all of the cycloalkanes. n.o.: reaction channel not observed. [b] References 5, 7. [c] Reference 7. [d] Tentative assignment as C−H bond cleavage. See text for details.

trapping-mediated dissociative chemisorption of cyclopentane on Ru(001) occurs via ring-opening C−C bond cleavage over the entire temperature range studied. It should be mentioned here that Hoffmann et al.[40] reported that cyclopentane adsorption at low temperature on Ru(001), followed by a subsequent slow anneal (0.1 K/s) in a TPD experiment, resulted in C−H bond cleavage to form cyclopentene below 200 K. Although this appears inconsistent with our results, the observation of a different reaction mechanism by Hoffmann et al. could be attributed to reaction of a small coverage of cyclopentane via C−H bond cleavage at highly reactive defect sites,[41] or the existence of a C−H bond cleavage reaction pathway in the presence of adsorbate−adsorbate interactions in the condensed layer at low temperature.[42] Finally, even if this C−H bond cleavage reaction does occur to an appreciable extent in the low coverage limit, a C−H bond cleavage mechanism with a combination of a relatively small activation barrier and a small preexponential factor may not appear in the Arrhenius plot of Figure 3 as the dominant reaction pathway until very low temperatures (below the 350 K lower limit measured here). Therefore, the explanation that C−C bond cleavage dominates over the temperature range studied here would still be valid.

Comparison of the measured cyclohexane activation barriers of 15 700 cal/mol for c-C_6H_{12} and 16 320 cal/mol for c-C_6D_{12} results in a significant difference in activation barriers of 620 cal/mol. On the basis of the relatively large kinetic isotope effect measured here between cyclohexane isotopomers, dissociative chemisorption of cyclohexane on Ru(001) is judged to proceed via initial C−H bond cleavage. The magnitude of the difference in activation barriers measured here for cyclohexane C−H bond cleavage on Ru(001) (620 cal/mol) is similar to previously reported C−H bond cleavage activation barrier differences for ethane[23] (590 cal/mol) and propane[23] (480 cal/mol) on Ru(001), and for propane[30] (600 cal/mol) and isobutane[30] (700 cal/mol) on Ir(111).

For cyclooctane, the determination of the dissociation pathway is not so obvious. Comparison of the measured activation barriers for c-C_8H_{16} and c-C_8D_{16} of 16 390 and 16 630 cal/mol, respectively, results in a moderate difference of 240 cal/mol. Because this value lies between the previously reported differences of ∼600 cal/mol for C−H bond cleavage and ∼0 cal/mol for C−C bond cleavage,[5,7] judgment of an initial dissociation pathway is not straightforward. Since the data in Figure 3 are linear within experimental error, it seems likely that one reaction mechanism dominates over the entire temperature range. If it is assumed that C−H bond cleavage will lead to a difference of 600 cal/mol, and C−C bond cleavage will lead to no activation barrier difference, then, on the basis of the calculated error associated with the measured cyclooctane activation barriers, C−C bond activation is the slightly more probable reaction mechanism. This is based on the fact that, within the quoted uncertainties, it is possible for the perhydrido and perdeutero cyclooctane activation barriers to have the same value (or no activation barrier difference), while it is not possible for the activation barriers to have a difference of 600 cal/mol. However, reaction mechanism arguments concerning the strain energy differences between the initial states and transition states for the reaction of cyclooctane on Ru(001) via initial C−C bond cleavage point to the conclusion that cyclooctane activation occurs via initial C−H bond cleavage. This point will be discussed in detail in the Discussion section below. Therefore, trapping-mediated dissociative chemisorption of cyclooctane on Ru(001) is tentatively judged to occur via initial C−H bond cleavage, on the basis of arguments concerning reaction energetics. We should point out, however, that it is possible that the activation barriers and preexponential factors for both C−C and C−H bond cleavage are of the proper magnitudes so that the sum of $P_{r,CC}$ and $P_{r,CH}$ (eq 10) appears to be linear in the Arrhenius plot of Figure 3. However, for this to occur, the activation barriers for both C−C and C−H bond cleavage must be rather close in magnitude to the measured "apparent" activation barrier; otherwise, a linear Arrhenius plot would not be observed over the large range of temperatures studied here. If the C−H and C−C bond activation barrier values are nearly identical, the reported activation barrier in Table 4 for cyclooctane C−H bond cleavage on Ru(001) would be a rather accurate value representing both initial C−C and C−H bond cleavage reactions.

B. Cycloalkane Activation on Ir(111). Displayed in Figures 4−6 are the Arrhenius constructions of the experimentally determined initial probabilities of dissociative chemisorption of cyclobutane, cyclopentane, and cyclohexane on Ir(111) as a function of reciprocal surface temperature. Unlike the activation data for cycloalkanes on the Ru(001) surface, the Arrhenius constructions of the data for Ir(111) are nonlinear, indicating a shift in the rate-limiting reaction mechanism with changing temperature.[37] Since only two initial rate-limiting reaction channels are possible for cycloalkanes, either initial C−H or C−C bond cleavage, clearly both initial C−H and C−C bond cleavage reaction mechanisms are active over the temperature range studied for each molecule. Extracting kinetic parameters from these activation data for Ir(111) is not as straightforward as for the Ru(001) data, however, since both initial bond cleavage mechanisms must be considered in the extraction of

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(40) Hoffmann, F. M.; O'Brien, E. V.; Hrbek, J.; De Paola, R. A. *J. Electon Spectrosc. Relat. Phenom.* **1983**, *29*, 301.

(41) Johnson, D. F.; Weinberg, W. H. *J. Chem. Phys.* **1994**, *101*, 6289.

(42) Fichthorn, K. A.; Weinberg, W. H. *Langmuir* **1991**, *7*, 2539.

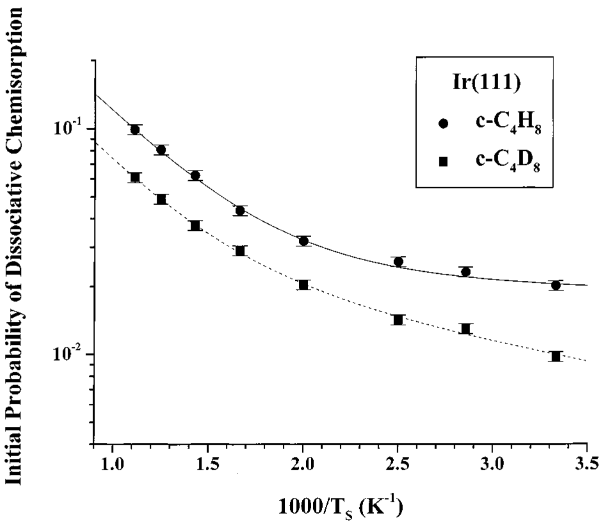

Figure 4. Initial probabilities of trapping-mediated dissociative chemisorption of perhydrido and perdeutero cyclobutane as a function of reciprocal surface temperature on Ir(111). The error bars represent one standard deviation in the measured reaction probability at each temperature.

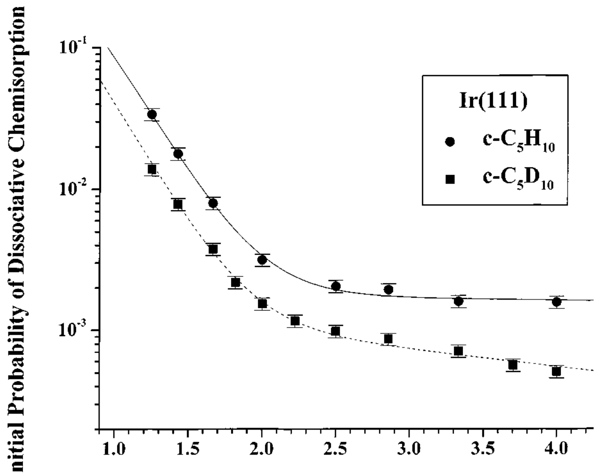

Figure 5. Initial probabilities of trapping-mediated dissociative chemisorption of perhydrido and perdeutero cyclopentane as a function of reciprocal surface temperature on Ir(111). The error bars represent one standard deviation in the measured reaction probability at each temperature.

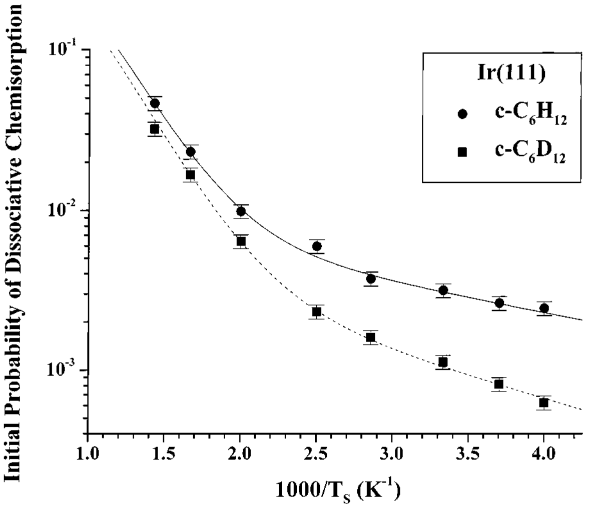

Figure 6. Initial probabilities of trapping-mediated dissociative chemisorption of perhydrido and perdeutero cyclohexane as a function of reciprocal surface temperature on Ir(111). The error bars represent one standard deviation in the measured reaction probability at each temperature.

the kinetic parameters. Because the reaction probabilities for both C—H and C—C initial bond cleavage displayed in eq 10 are separable by definition, their sum is equal to the total measured experimental reaction probability, P_r, where

$$P_r = P_{r,CC} + P_{r,CH} \tag{12}$$

$$P_r = \frac{\xi[(k^{(0)}_{r,CC})\exp(-E_{r,CC}/k_BT_s) + (k^{(0)}_{r,CH})\exp(-E_{r,CH}/k_BT_s)]}{[(k^{(0)}_{r,CC})\exp(-E_{r,CC}/k_BT_s) + (k^{(0)}_{r,CH})\exp(-E_{r,CH}/k_BT_s) + (k^{(0)}_d)\exp(-E_d/k_BT_s)]} \tag{13}$$

The eq 13 expression for P_r was fit to the measured Ir(111) cycloalkane activation data using a nonlinear curve-fitting algorithm. Since we can reasonably assume a value of unity for ξ for the gas translational energies employed in this study, and since the activation barrier, E_d, and the preexponential factor, $k_d^{(0)}$, for desorption have been independently measured, only four kinetic parameters were needed to fit eq 13 to the experimentally measured initial probabilities of dissociative chemisorption for each cycloalkane. These four kinetic parameters are the activation barriers for initial C—C and C—H bond cleavage, $E_{r,CC}$ and $E_{r,CH}$, and the preexponential factors for initial C—C and C—H bond cleavage, $k^{(0)}_{r,CC}$ and $k^{(0)}_{r,CH}$. The parameters yielding the best fit to the Ir(111) experimental data for each cycloalkane isotopomer are listed in Table 5. The lines plotted in Figures 4—6 represent the total reaction probabilities that were calculated using eq 13 and the best-fit kinetic parameters. The excellent fit of the initial probabilities of trapping-mediated dissociative chemisorption of cyclobutane, cyclopentane, and cyclohexane on Ir(111) with the reaction probability expression shown in eq 13 allows us to conclude with confidence that both initial C—H and C—C bond dissociation channels contribute to the overall reaction probability. The nonlinear curve-fitting algorithm yielded two sets of kinetic parameters for each cycloalkane isotopomer: one with a relatively low activation energy (which dominates at low temperature) and one with a relatively large activation energy (which dominates at high temperature). The assignment of the dissociation channel with the low activation barrier to initial C—H bond cleavage and the dissociation channel with the high activation barrier to initial C—C bond cleavage is discussed next.

Making the assignment of which mechanism dominates at each temperature extreme was relatively straightforward since we were able to use kinetic isotope effects and past activation results on Ir(111) to make this judgment. Examination of the Ir(111) activation data in Table 5 for cyclobutane, cyclopentane, and cyclohexane shows the presence of an isotope effect in the activation energies for the dissociation pathway that dominates at low temperature. For this reaction pathway, the activation barrier for the perdeutero isotopomer of each cycloalkane is consistently higher than that for the perhydrido isotopomer, thereby allowing us to conclude that C—H bond cleavage dominates at low temperature for each cycloalkane on Ir(111). Initial C—C bond cleavage is thus implicated as the dominant dissociation pathway at high temperatures. Further confirmation of these assignments is possible by comparing the measured activation barriers here with previously reported straight-chain alkane activation barriers on Ir(111). For instance, the measured

Table 5. Kinetic Rate Parameters Describing the Trapping-Mediated Dissociative Chemisorption of Cycloalkanes on Ir(111)[a]

reactant	$E_{r,CH}$ (cal/mol)	($k^{(0)}_{r,CH}/k^{(0)}_{d}$)	$E_{r,CC}$ (cal/mol)	($k^{(0)}_{r,CC}/k^{(0)}_{d}$)
c-C_3H_6	8 620 ± 280[b]	0.0012 ± 0.0005[b]	14 310 ± 350[b]	0.60 ± 0.05[b]
c-C_3D_6	9 140 ± 350[b]	0.006 ± 0.004[b]	13 930 ± 450[b]	0.31 ± 0.12[b]
c-C_4H_8	10 370 ± 250	0.025 ± 0.001	14 850 ± 550	1.1 ± 0.1
c-C_4D_8	11 020 ± 280	0.036 ± 0.005	15 250 ± 500	0.7 ± 0.1
c-CsH_{10}	10 680 ± 160	0.0019 ± 0.0006	18 550 ± 520	4.9 ± 0.4
c-C_5D_{10}	11 170 ± 180	0.0017 ± 0.0002	18 880 ± 540	2.6 ± 0.1
c-C_6H_{12}	12 600 ± 350	0.013 ± 0.006	19 180 ± 550	8.8 ± 2.5
c-C_6D_{12}	13 030 ± 200	0.009 ± 0.001	19 260 ± 530	7.7 ± 1.5

[a] The reported activation barriers for C−C and C−H bond cleavage are referenced to the proper reference energy, the bottom of the physically adsorbed well. The preexponential factor for desorption, $k^{(0)}_{d}$, has been assumed to be equal to 10^{13} s^{-1} for all of the cycloalkanes. [b] Reference 4.

activation barriers for initial C−H bond cleavage for propane and *n*-butane on Ir(111) were 11 300 and 11 400 cal/mol, respectively.[30] These values compare well with the value measured here for C−H bond cleavage of a relatively unstrained cyclohexane molecule of 12 600 cal/mol. Comparison of the C−C bond cleavage activation barriers for *n*-butane[43] and relatively unstrained cyclohexane on Ir(111) of 17 700 and 19 180 cal/mol, respectively, allows us to conclude that the larger activation barrier values can be assigned with confidence to C−C bond cleavage on Ir(111). These comparisons with previously measured activation barriers for C−H and C−C bond cleavage on Ir(111) provide further confirmation of the accuracy of the reaction mechanism assignments displayed in Table 5.

V. Discussion

A. Ir(111). 1. C−C Bond Activation. The kinetic parameters displayed in Table 5 for the activation of cycloalkanes on Ir(111) demonstrate that the activation energies for C−C bond cleavage follow the expected trend, i.e., the smaller, more strained rings are more readily opened by the surface. For example, the relatively small 900 cal/mol difference in ring-strain energies between cyclopropane and cyclobutane corresponds to a C−C activation barrier difference of 540 cal/mol, while the relatively large ring-strain energy difference of 26 900 cal/mol between cyclopropane and cyclohexane corresponds to a C−C activation barrier difference of 4870 cal/mol.

In addition to the comparisons that can be made within the series of cycloalkanes, we also may make comparisons to other compounds using data previously reported for the activation of unstrained alkanes on Ir(111). Recent work by Johnson and Weinberg[43] involving the activation of short-chain alkanes on Ir(111) reports activation barriers for C−C bond cleavage in propane (18 200 cal/mol), isobutane (17 600 cal/mol), *n*-butane (17 700 cal/mol), and neopentane (15 900 cal/mol). The most relevant unstrained alkane to use in comparison with the cycloalkanes is *n*-butane since the barriers for C−C bond cleavage seem to be strongly related to the number of carbon atoms bound to the carbon atoms being split during the bond cleavage reaction. Analysis of the Ir(111) data above allows us to conclude that the C−C bonds in neopentane are significantly easier to cleave than those in the linear alkanes. The ease of C−C bond cleavage in neopentane would follow from the well-known stability trend of alkanes; i.e., a tertiary radical is more stable than a secondary radical, which in turn is more stable than a primary radical.[44] Since C−C bond cleavage in cycloalkanes involves the separation of carbon atoms that are initially bound to two carbon atoms, a good comparison would be the cleavage of the *n*-butane central C−C bond. Admittedly, the activation barrier reported in this previous work represents an apparent activation barrier for both types of *n*-butane C−C bonds; however, we feel that this is the best standard at our disposal for use in making comparisons to the cycloalkane activation barriers on Ir(111).

Comparison of the C−C bond activation barriers for cyclopropane (14 310 cal/mol) and cyclobutane (14 850 cal/mol) with those for *n*-butane (17 700 ± 600 cal/mol) allows us to conclude that C−C bond cleavage of these two highly strained cycloalkanes is much easier than C−C bond cleavage of unstrained *n*-butane. The activation of cyclopentane (18 550 cal/mol) C−C bonds occurs with almost the same ease as for *n*-butane since the measured activation barriers are almost the same (the activation barrier difference is within the experimental error). Moreover, the cleavage of C−C bonds in relatively unstrained cyclohexane (19 180 cal/mol) is slightly more difficult than for *n*-butane. We believe that the ring-strain energy initially present in the molecule is, indeed, important in determining the C−C bond cleavage activation barrier; however, we also believe that the ring-strain energy present in the transition state for ring-opening C−C bond cleavage is crucial as well. The basic premise of our hypothesis is that it is not the absolute value of ring-strain energy present initially in the cycloalkane reactant molecule that determines the activation barrier for cycloalkane C−C bond cleavage, but rather the *ring-strain energy difference* between the initial state and the transition state for ring-opening C−C bond cleavage.

For example, initial C−C bond cleavage of cyclobutane on Ir(111) occurs with a much lower activation barrier than for the unstrained *n*-butane standard (14 850 versus 17 700 cal/mol). In this case, the ring-strain energy of the initial state of molecular cyclobutane is relatively high, while the ring-strain energy of the transition state for C−C bond cleavage is expected to be lower since it involves opening of the ring to break the C−C bond and subsequently form two Ir−C bonds. We must point out that we are not making any claims here regarding the exact nature of the metallacycle formed in this reaction (e.g., whether the metallacycle includes a single surface metal atom or multiple atoms); we are simply stating that in the process of cleaving a C−C bond to open the ring, the cyclobutane ring must be opened to some degree. This transition state ring-opening mechanism most likely results in the relief of some ring-strain energy compared to the initial state. Therefore, since the activation barrier is the difference between the initial state and transition state energies, and this *difference* is lowered (compared to that of an unstrained *n*-butane molecule) by the release of ring-strain in the transition state, we would expect the activation barrier for cyclobutane C−C bond cleavage to be lower than that for *n*-butane. Clearly, this proposed explanation is consistent with experimental observations for cyclobutane and *n*-butane activation on Ir(111).

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(43) Johnson, D. F.; Weinberg, W. H. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 3695.

(44) Wade, L. G., Jr. *Organic Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1991.

For this explanation to be correct, it must also be capable of explaining the higher C−C bond cleavage activation barrier measured for cyclohexane compared to that for *n*-butane (19 180 versus 17 700 cal/mol). For the case of C−C bond cleavage of cyclohexane, the initial state contains very little ring-strain energy since the six-membered cyclohexane ring contains the lowest strain energy of the C_3−C_8 cycloalkanes. The transition state for C−C bond cleavage of cyclohexane likely involves some ring-strain since this reaction would require that the cyclohexane ring open to form a metallacycle containing at least seven atoms. Opening the ring toward a "cycloheptane-like" carbon backbone structure would cause the ring-strain energy to increase compared to that of the initial state. Therefore, since the transition state contains more ring-strain energy than the initial state, we would expect the activation barrier for cyclohexane C−C bond cleavage to be higher than that for the unstrained *n*-butane standard. This reasoning is again consistent with the experimental data. Similar discussions for cyclopropane and cyclopentane activation on Ir(111) also lead to the conclusion that this argument is consistent with the measured activation barriers for these molecules. This topic will be discussed again below for the C−C bond activation of cycloalkanes on Ru(001).

Clearly, the arguments involving ring-strain energy differences between the initial and transition states presented above provide a firm explanation for the observed trends in the cycloalkane C−C bond activation barriers on Ir(111). However, we feel that it is necessary to mention two additional potential contributions to the trend of decreasing C−C bond cleavage activation barrier with decreasing ring size. First, it is possible that electronic considerations play a role in reducing the activation barrier for C−C bond cleavage as well. For instance, since the electron density maxima of the C−C σ bonds in strained cyclobutane lie outside of the C−C internuclear axis,[45] interaction of the C−C bond orbitals with the iridium orbitals in the transition state for C−C bond cleavage is sterically more favorable than for an unstrained alkane. On the basis of results by Cremer and Gauss[13] for cyclopropane and cyclobutane, it is expected that as the cycloalkane C−C−C bond angles become more acute, C−C bond orbitals will extend further outside of the lines joining the carbon atoms. This means that the magnitude of the C−C bond orbital extension outside of the C−C internuclear axis increases with decreasing C−C−C bond angle (and thus decreasing ring size). Therefore, we conclude that the interaction of the C−C bond orbitals with the iridium metal orbitals becomes more sterically favorable with decreasing cycloalkane ring size. Qualitatively, this explanation is consistent with the observed trend of decreasing activation barrier with decreasing cycloalkane ring size.

A second potential contribution to the C−C bond activation barrier trend is also related to steric arguments. This explanation is slightly different than that mentioned above since it involves the energies related to distortion of the shape of the ring in the transition state for C−C bond cleavage. For instance, distortion of the two methyl groups contained in ethane is necessary during C−C bond cleavage since the methyl carbons can only start to efficiently bind toward the metal when the methyl group is tilted toward the metal.[17] If we carry this analogy forward to the case of cycloalkanes, each of the pair of carbon atoms undergoing C−C bond cleavage is bonded to another carbon atom of the cycloalkane ring. Therefore, when each of the pair of carbon atoms tilts toward the metal in the transition state for C−C bond cleavage, it affects the conformation of the entire cycloalkane ring. It can be argued for the smaller cycloalkanes, such as cyclopropane, that this distortion results in only a slight increase in energy of the transition state since fewer carbon atoms (for cyclopropane, only one, the bridge carbon atom connecting the two carbon atoms being cleaved) are being perturbed by this distortion. For the case of the larger cycloalkanes, such as cyclohexane, this distortion likely results in a rather large increase in energy of the transition state since the four remaining cyclohexane carbon atoms are perturbed (and hence must adopt a new conformation) by this distortion. While we do not feel that these two steric explanations have a greater influence on the activation barrier trend than the ring-strain energy arguments presented above, we do feel that these explanations could contribute to the observed trend in C−C bond activation barriers.

Table 6. C-H Bond Strengths for Selected Cycloalkanes and Unstrained Linear Alkanes

hydrocarbon molecule	C−H bond strength (kcal/mol)
cyclopropane	106.3
cyclobutane	96.5
cyclopentane	94.5
cyclohexane	95.5
cycloheptane	92.5
methane	104.8
ethane	100.3
propane (primary)	99.7
propane (secondary)	95.9
n-butane (primary)	96.4
n-butane (secondary)	93.3
neopentane	100.0

We should mention here that we do not wish to speculate about trends in any of the preexponential ratios reported in this paper due to the complexity of these cycloalkane reactions. It is not obvious how one should expect the preexponential factors to vary with the ring-strain energy difference between initial and transition states and the geometry of the cycloalkane, since very few kinetic parameters have been reported in the literature for the reaction of cycloalkanes with transition metal surfaces under similar experimental conditions. Also, the influence of the well-known compensation effect, in which the preexponential factor varies commensurately with the activation barrier for a given kinetic process,[46] makes such conclusions difficult since a wide range of activation barriers are reported in this study, resulting in rather large expected compensation effects.

2. C−H Bond Activation. In previous work by Johnson and Weinberg involving alkane activation on Ir(111),[30] it was reported that for activation of methane, ethane, primary propane, and secondary propane, C−H bonds were cleaved with activation barriers of 12 600, 10 400, 11 600, and 11 300 cal/mol, respectively. Comparison of these activation barriers with the corresponding C−H bond strength energies displayed in Table 6[27] allows us to conclude, at least for these four different C−H bonds in unstrained alkanes, that the activation barriers for cleavage of these bonds do not correlate very closely with the C−H bond strengths (except possibly for methane, where the activation barrier and C−H bond strength values are relatively large). For C−H bond cleavage of cycloalkanes on Ir(111), comparison of the activation barriers in Table 5 with the corresponding C−H bond strengths in Table 6 allows us to conclude that the activation barriers decrease with increasing C−H bond strength. This result is superficially surprising since the C−H bond strength in cyclopropane is about 10 cal/mol

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[45] Stein, A.; Lehmann, C. W.; Luger, P. *J. Am. Chem. Soc*. **1992**, *114*, 7684.

[46] Christmann, K. *Surface Physical Chemistry*; Steinkopff, Darmstadt, Germany, 1991.

larger than for those of other cycloalkanes. On the basis of initial bond strength considerations alone, we would have expected cyclopropane to possess the largest barrier to C−H bond cleavage rather than the smallest. Since this clearly is not the case, discussion of possible explanations for this observation are necessary.

We propose that this observation can be partially explained by steric arguments concerning the transition state for C−H bond cleavage. These arguments can be separated into two contributions (although they are not independent of one another): steric issues associated with the carbon atom containing the C−H bond that is to be cleaved, and steric issues associated with the carbon atoms adjacent to the carbon atom containing the C−H bond that is to be cleaved. The former of these two potential steric contributions involves the interaction of the metal electron orbitals with the C−H bond electron orbitals, which is necessary to facilitate C−H bond cleavage. Very recent density functional calculations by Ciobici et al.[47] indicate that the energetically favored transition state for the dissociation of methane on the Ru(001) surface involves a methane configuration with two of the H atoms pointing toward the surface. The distortion of the bonds surrounding the tetrahedrally coordinated carbon atom during this process (similar in principle to the distortion of the methyl groups during the C−C bond cleavage of ethane described above) costs a significant amount of energy. This energy cost gives rise to a relatively large activation barrier for dissociative chemisorption. On the basis of these results, and on the basis of steric arguments concerning cycloalkane geometries, a plausible transition state for cycloalkane C−H bond cleavage on a transition metal surface involves the cycloalkane molecule oriented with the plane of the ring perpendicular to the surface, with both H atoms of the CH_2 group (containing the C−H bond that is to be cleaved) pointing toward the surface. Assuming that this transition state configuration is correct for cycloalkane C−H bond cleavage, the ease of C−H bond cleavage in the small cycloalkanes (C_3−C_5) may be due to a greater overlap between the C−H bond and metal electron orbitals afforded by the already compressed C−C−C bond angles. For instance, the molecular structure of cyclopropane,[48] which possesses C−C−C bond angles of 60°, would allow relatively easy overlap of the metal orbitals with the C−H bond orbitals. Moreover, since relatively little distortion of the bonds surrounding the tetrahedrally coordinated carbon atom would be required to facilitate C−H bond and metal orbital overlap, little energy is required to distort the cyclopropane molecule into the transition state configuration for C−H bond cleavage. As this angle is increased with increasing ring size, the accessibility of the C−H bonds by the metal orbitals becomes increasingly difficult due to the increasingly tetrahedral geometry of the carbon atoms. In order for the larger cycloalkanes, such as cyclohexane, to achieve the proper transition state for C−H bond cleavage, significant distortion of the bonds surrounding the tetrahedrally coordinated carbon atom is required. This significant distortion required at the transition state most likely results in a relatively high transition state energy, thereby resulting in a higher activation barrier for C−H bond cleavage. Therefore, these arguments are consistent with the observed trend of decreasing C−H bond cleavage activation barrier with decreasing ring size. This discussion will be continued below for the case of cyclohexane and cyclooctane C−H bond activation on Ru(001).

The steric issues associated with the carbon atoms adjacent to the carbon atom containing the C−H bond that is to be cleaved are quite straightforward. Since, in the transition state for C−H bond cleavage, the adjacent carbon atoms in the larger cycloalkanes are much closer to the surface than in the smaller cycloalkanes simply due to the cycloalkane geometries, steric hindrance between the adjacent carbon atoms (more appropriately, the adjacent CH_2 groups) is much greater for the larger cycloalkanes than for the smaller cycloalkanes. Therefore, it is more difficult for the C−H bond and metal electron orbitals to achieve the overlap necessary for C−H bond cleavage in the larger cycloalkanes than in the small ones. This steric argument is also consistent with the observed C−H bond activation barrier trend.

Another explanation for the observed decrease of C−H bond cleavage activation barriers with decreasing cycloalkane ring size is based on thermodynamic arguments. It is thought that a principal constraint on the activation of C−H bonds is thermodynamic, reflecting the relative weakness of product M(metal)−C bonds compared with reactant C−H bonds.[49] On the basis of this idea, the C−H bond cleavage transition state energy should be relatively low when strong M−C bonds are being formed rather than weak M−C bonds.

Therefore, cycloalkyl groups that form the strongest M−C bonds should, in theory, possess the smallest activation barrier for C−H bond cleavage. Comparison of recently computed M−C bond strengths for a number of unstrained alkanes[50] with the C−H bond strength data in Table 6 shows that there is a concomitant increase in M−C bond strength with increasing C−H bond strength. If we assume that the concomitant increase in M−C and C−H bond strength occurs for cycloalkyl−H and cycloalkyl−M bonds as well, then we would expect that the cycloalkanes containing the strongest C−H bonds would form very strong cycloalkyl−M bonds in the transition state for C−H bond cleavage. This would result in a lowering of the activation barrier for C−H bond cleavage; however, this activation barrier lowering would be offset by the increased strength of the C−H bonds to be broken. Therefore, it appears that there is a compensation between these two effects in their influence on the activation barrier for C−H bond cleavage. However, on the basis of the experimental results reported here, it would appear that the activation barrier is affected more by the influence of the cycloalkyl−M bond strength than by the initial C−H bond strength. The topic of M−C bond strengths will be addressed again below for the comparison of Ir(111) and Ru(001) activation results.

One final discussion concerning C−H bond cleavage on Ir(111) involves comparison of the activation barriers observed here for cycloalkanes with relative reaction rates observed for cycloalkane C−H bond cleavage in homogeneously catalyzed photolysis experiments by Janowicz and Bergman.[51] In this study, the photoinduced activation of cyclopropane, cyclopentane, cyclohexane, and cyclooctane C−H bonds by a (η^5-C_5Me_5)(PMe_3)IrH_2 catalyst was reported to occur with relative reaction rates of 2.65, 1.6, 1.0, and 0.09, respectively. The trend of increasing rate with decreasing cycloalkane size on this homogeneous iridium catalyst is consistent with our observation here of decreasing C−H bond activation barrier with decreasing cycloalkane size on Ir(111).

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Table 7. Comparison of the Activation Energies for C−C Bond Cleavage and the Ring-Strain Energies for the Perhydrido Cycloalkane Isotopomers

reactant	total strain (cal/mol)	C−C activation barrier on Ru(001) (cal/mol)	C−C activation barrier on Ir(111) (cal/mol)
cyclopropane	28 300	9 470	14 310
cyclobutane	27 400	10 090	14 850
cyclopentane	7 300	14 410	18 550
cyclohexane	1 400	> 16 160[a]	19 180

[a] Since the activation channel for perdeutero cyclohexane on Ru(001) was judged to be C−D bond cleavage, and only one reaction channel was observed for the temperature range studied here, the activation barrier for C−C bond cleavage in this relatively unstrained cycloalkane is most likely greater than 16 160 cal/mol.

B. Ru(001). 1. C−C Bond Activation. The kinetic parameters for initial C−C bond cleavage of cyclopropane, cyclobutane, and cyclopentane on Ru(001) are displayed in Table 7. The activation barriers for cyclopropane (9470 cal/mol), cyclobutane (10 090 cal/mol), and cyclopentane (14 420 cal/mol) also exhibit the expected trend of the smaller, more strained cycloalkanes being more easily opened by the Ru(001) surface. Comparison of these activation barriers with the recently measured C−C bond cleavage activation energy for *n*-butane on Ru(001) of 19 000 cal/mol[52] suggests that the data for cycloalkane activation on Ru(001) are consistent with the arguments presented earlier concerning steric effects and strain energy differences between the initial and transition states for C−C bond cleavage on Ir(111). Comparison of the C−C bond activation barriers for each C_3−C_5 cycloalkane on the two different surfaces shows that the activation barrier for C−C bond cleavage on Ru(001) is approximately 4−5 kcal/mol lower than that on Ir(111). It is interesting to point out that Ru(001) seems to be much better at cleaving cycloalkane C−C bonds than Ir(111), while Ir(111) seems to be better at cleaving unstrained alkane C−C bonds (e.g., propane, *n*-butane) than Ru(001).[23,43] These observations will be discussed in more detail in the Overview section below.

2. C−H Bond Activation. The activation of cyclohexane on the Ru(001) surface occurs via C−H bond cleavage with an activation barrier of 15 700 cal/mol. Relatively unstrained cyclohexane reacts via C−H bond cleavage rather than C−C bond cleavage since the transition state for C−C bond cleavage of cyclohexane is not lowered by the release of ring strain. In fact, as was discussed above for C−C bond cleavage of cyclohexane on Ir(111), it is likely that the transition state for ring-opening C−C bond cleavage of cyclohexane on Ru(001) contains more strain energy than the initial state. Moreover, the fact that cyclooctane appears to react via C−H bond cleavage, with an activation barrier of 16 390 cal/mol, is consistent with this argument as well, since we would expect that ring-opening C−C bond activation of cyclooctane would also be energetically disfavored since this transition state most likely possesses more ring-strain energy than the initial state.

Comparison of the activation barriers for C−H bond cleavage in these two molecules shows that the activation of C−H bonds in cyclooctane is slightly more difficult than that in cyclohexane. Since the activation barrier for C−H bond cleavage for cycloalkanes on Ir(111) increased with increasing cycloalkane ring size, this result is not surprising. The above discussion of C−H bond activation on Ir(111) presented possible steric explanations for this observed trend which we believe are valid for activation of cyclohexane and cyclooctane C−H bonds on Ru(001) as well. In particular, cyclooctane is a rather unwieldy cycloalkane;[53,54] therefore, we would expect a relatively large C−H bond cleavage activation barrier due to the necessary distortion of the bonds surrounding the tetrahedrally coordinated carbon atom (which contains the C−H bond that is to be cleaved) in the transition state for C−H bond cleavage. It should be kept in mind that such a distortion will cause the entire cyclooctane ring to strain, thus accounting for a large fraction of the transition state energy increase due to intramolecular steric interactions between C−H bonds. A similar explanation is also found in a recent report concerning photoinduced C−H bond activation of C_5−C_8 cycloalkanes with a homogeneous rhodium catalyst.[55] In this study, it was concluded that the remarkably slow reaction rates observed for cycloheptane and cyclooctane C−H bond activation might be due to transition states for formation of cycloheptyl and cyclooctyl Rh hydride species that are particularly conformationally demanding. This recent experimental observation is consistent with the activation results presented here.

In previous work by Jachimowski and Weinberg,[23] C−H bond cleavage reactions were implicated as the activation pathways in the reactions of ethane (9310 cal/mol) and propane (10 430 cal/mol) with the Ru(001) surface. These results for small, straight-chain alkanes on Ru(001) are much smaller (by about 6 kcal/mol) than those observed here for the activation of cyclohexane and cyclooctane C−H bonds. We believe that the large activation barrier differences between the small linear alkanes and these larger cycloalkanes on Ru(001) can be qualitatively explained by the steric arguments discussed above.

C. Overview. 1. C−H Bond Activation. The activation barriers for initial rate-limiting cleavage of a cycloalkane C−H bond on both the Ir(111) and Ru(001) surfaces exhibit a trend of decreasing activation barrier with decreasing cycloalkane ring size. We believe that this trend can be explained by steric hindrance effects associated with the changing geometries of the cycloalkanes with decreasing ring size. Specifically, distortion of the bonds surrounding the tetrahedrally coordinated carbon atom (on which the C−H bond being cleaved is connected) is necessary to achieve the overlap between C−H bond and metal electron orbitals which is necessary to promote C−H bond cleavage. This distortion leads to a higher energy for the transition state for C−H bond cleavage, which, in turn, leads to a higher activation barrier. As the size of the cycloalkane decreases, the amount of distortion required to achieve this necessary orbital overlap is thought to decrease due to the greater accessibility of the C−H bonds due to the decreasing C−C−C bond angles. Any distortions of the bonds surrounding the tetrahedrally coordinated carbon atom will also affect the overall conformation of the cycloalkane in the transition state. We feel that this effect will result in an increase in conformational energy with increasing ring size for the C_3 through C_8 cycloalkanes examined here due to the increased steric effects associated with altering the conformations for the larger cycloalkanes; this may or may not be the case for cycloalkanes larger than those studied here since intramolecular steric effects may begin to diminish at some point with increasing ring size. Also, it is thought that carbon atoms adjacent to the central carbon (on which the C−H bond being cleaved is connected) may introduce additional steric

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effects in the transition state for C−H bond cleavage due to the closer proximity of these adjacent carbon atoms to the surface in the larger cycloalkanes.

Comparison of the C−H activation barriers for the cycloalkanes on the two different surfaces studied here allows us to make the conclusion that Ir(111) is a more active catalyst for the cleavage of cycloalkane C−H bonds than is Ru(001). Specifically, the activation barrier for cyclohexane C−H bond cleavage on Ir(111) is 12 600 cal/mol, while on Ru(001) it is 15 700 cal/mol. As mentioned above, it is thought that a principal constraint on the activation of C−H bonds is thermodynamic, reflecting the relative weakness of product M−C bonds compared with reactant C−H bonds.[49] The average Ir−C and Ru−C σ bond strengths have been recently calculated to be 46.0 and 33.3 kcal/mol, respectively, on the basis of the adiabatic binding energy of CH_2CH_3.[50] Therefore, because these calculated values suggest that the cycloalkyl−Ir bonds may be expected to be much stronger than the cycloalkyl−Ru bonds, the transition state energy for C−H bond cleavage should be expected to be lower on Ir(111) than on Ru(001). This is indeed observed for the comparison of cyclohexane activation on both of these surfaces. Therefore, the approximately 3 kcal/mol difference between the activation barriers for cycloalkane C−H bond cleavage on Ir(111) and Ru(001) can be explained in the context of thermodynamic differences in the transition states for C−H bond cleavage.

2. C−C Bond Activation. The activation barriers for initial rate-limiting cleavage of a cycloalkane C−C bond on both the Ir(111) and Ru(001) surfaces exhibit a trend of decreasing activation barrier with decreasing cycloalkane ring size. The measured C−C bond cleavage activation barriers indicate that this trend on both surfaces can be attributed to the *ring-strain energy difference* between the initial state and transition state energies for ring-opening C−C bond cleavage. Other steric factors may also contribute to this trend, including larger distortions of the cycloalkane ring in the transition states for the larger cycloalkane molecules, and enhanced overlap between the extended (outside the internuclear axis between adjacent carbon atoms) C−C bond orbitals for the smaller cycloalkanes and the metal electron orbitals in the transition state for C−C bond cleavage. However, we believe the effect of these steric contributions will be small compared to the effect of the ring-strain energy differences on the activation barrier for C−C bond cleavage.

Comparison of the activation barriers for ring-opening C−C bond cleavage for C_3−C_5 cycloalkanes on the two surfaces results in lower activation barriers for C−C bond cleavage on Ru(001) compared to that on Ir(111) by about 4−5 kcal/mol. While the lower activation barrier for cycloalkane C−H bond cleavage on Ir(111) compared to that on Ru(001) of approximately 3 kcal/mol was qualitatively explained by thermodynamic differences between the Ir−C and Ru−C bonds in the transition state, the application of this reasoning to cycloalkane C−C bond cleavage (and subsequent formation of M−C bonds in the transition state) would be inconsistent with the observed data. Therefore, we speculate as to whether a stronger M−C bond is beneficial for the transition state for C−C bond cleavage. Obviously, the strength of the bond has to be higher than a critical value so that activation of the C−C bond and formation of the metallacycle product is thermodynamically possible. However, if the M−C bond is too strong, we speculate that this may result in an early transition state for the ring-opening C−C bond cleavage reaction. In other words, the cycloalkane ring may not open as much in the transition state for a transition metal surface with *extremely* strong M−C bonds as for a transition metal surface with *moderately* strong M−C bonds. If the ring does not open as far in the transition state for the case of *extremely* strong M−C bonds compared to the *moderately* strong M−C bonds, then the difference in ring-strain energies between the initial state and the transition state will not be as large for the *extremely* strong M−C bonds. This smaller difference in ring-strain energies for the surface with *extremely* strong M−C bonds would result in a higher activation barrier on that surface. This argument is consistent with our experimental observations.

VI. Conclusions

The results presented here demonstrate that the ring-strain energies present in smaller cycloalkanes effectively lowers the activation barrier for ring-opening dissociative chemisorption via C−C bond cleavage. However, the ring-strain energy present in the molecular cycloalkane precursor does not appear to be the only factor that influences the extent to which the activation barrier is lowered. The data presented here demonstrate that the difference in the ring-strain energies between the initial state and the transition state for the ring-opening C−C bond cleavage reaction is the factor that determines the extent to which the activation barrier for C−C bond cleavage is reduced or increased compared to that for unstrained alkanes. For activation of cycloalkane C−H bonds, the data demonstrate that the activation barrier decreases with decreasing cycloalkane ring size. These results are consistent with steric arguments that would predict a similar trend for the C−H bond cleavage activation barriers.

Analysis of the cycloalkane activation data on both the Ru(001) and Ir(111) surfaces allows us to conclude that Ir(111) is a selective catalyst for cycloalkane C−H bond cleavage at low temperatures ($T < 400$ K), while it is a selective C−C bond cleavage catalyst at high temperatures ($T > 600$ K). For the C_3−C_5 cycloalkanes, the Ru(001) catalyst is selective for C−C bond cleavage for the entire range of temperatures studied here. On the basis of the measured activation barrier differences for cycloalkane C−C and C−H bond cleavage on the two surfaces, Ru(001) is judged to be the more efficient catalyst for the cleavage of cycloalkane C−C bonds, while Ir(111) is judged to be the more efficient catalyst for cleavage of C−H bonds in these molecules.

Acknowledgment. This research was supported by the Department of Energy under Grant No. DE-FG03-89ER14048. C.J.H. and M.J.W. also received support from the NSF predoctoral fellowship program. The authors thank Pete Mikesell and Dan Little for synthesis of the cyclobutane isotopomers.

JA002459Z