

Trapping-Mediated and Multilayer-Induced Dissociative Chemisorption of Cyclobutane on Ru(001)

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Abstract: The dissociative chemisorption of cyclobutane on the Ru(001) surface has been studied using thermal desorption spectroscopy (TDS) and high-resolution electron energy loss spectroscopy (HREELS). Two distinct methodologies have been used to study this reaction. First, we investigated the trapping-mediated reaction by exposing the surface to cyclobutane at 180 K. Second, although an adsorbed monolayer of cyclobutane undergoes nearly complete desorption during subsequent heating, we find that the presence of the condensed multilayer induces significant reaction. Using HREELS we find that both reaction channels yield a common intermediate which we identify to be a C₄H₈ metallacycle. At moderate and high surface coverages, a small amount of butene from the isomerization of the metallacycle desorbs between 185 and 225 K. Following the desorption of butene, we observe a hydrocarbon fragment on the surface which is tentatively identified to be a C₄H₄ metallacycle.

Introduction

Metallacycles have been postulated to be intermediates in a variety of chemical reactions. Olefin metathesis,¹ thiophene hydrodesulfurization,² and acetylene tricyclization,³ as well as isomerization reactions of both alkanes and cycloalkanes,⁴ are just a few reactions in which metallacycles have been proposed to be intermediates. If we limit the discussion to metallacycles containing only saturated carbon, we find just a few examples of the identification of these species on single-crystalline surfaces under ultrahigh vacuum (UHV) conditions.⁵ In addition, the existing work is largely limited to C₃ species. Metallacyclobutanes have been isolated on Cu(110) and Cu(111) by Martel et al.⁶ through the electron bombardment of cyclopropane and on Al(100) by Bent et al.⁷ through the reaction of 1,3-diiodopropane. A C₄H₈ metallacycle was inferred by Bent et al.⁷ to be an intermediate in the formation of 1,3-butadiene and 1-butene from 1,4-diiodobutane on Al(100). A saturated C₆ metallacycle was inferred by Dubois et al.⁸ during the cyclization of 1,6-diiodohexane on Al(100).

If we concentrate on C₄ species and remove the restriction of saturated species, we find a number of reports of metalla-

cycles containing four carbons. Perhaps best characterized is the C₄H₄ intermediate formed from the decomposition of *cis*-3,4-dichlorocyclobutene on Pd(111).³ A C₄H₄ species has also been isolated following the decomposition of thiophene on Pt(111).²

In contrast to other small cycloalkanes, there are only a few investigations of the adsorption and reaction of cyclobutane on single-crystalline surfaces. The paucity of studies of cyclobutane is somewhat surprising in light of the theoretical interest in its decomposition (and formation).⁹ It is well-known that the thermally activated formation of cyclobutane from two ethylene molecules (as well as the reverse reaction) is forbidden (has a high barrier) on symmetry grounds. It has been shown, however, that the Woodward–Hoffmann rules, which forbid this reaction, no longer apply in the presence of a transition metal atom.^{9a} The symmetry-breaking role of the metal atom has been investigated theoretically for both homogeneous^{9a,d,e} and heterogeneous^{9b} systems.

Experimentally, Hoffmann and Upton¹⁰ studied the C–H stretching vibrations of cyclobutane as part of an investigation of “soft” C–H modes in adsorbed cycloalkanes on Ru(001). We have previously studied the coverage-dependent adsorption geometry of monolayer and submonolayer coverages of cyclobutane on Ru(001) using HREELS.¹¹ In a study of the trapping-mediated dissociative chemisorption of *c*-C₄H₈ and *c*-C₄D₈, we found barriers to reaction (with respect to the bottom of the physically adsorbed well) of 10 090 and 10 180 cal/mol, respectively.¹¹ On the basis of the absence of a primary isotope effect, the initial reaction step was inferred to be C–C bond cleavage. This inference was confirmed in a communication in

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which we spectroscopically identified a saturated C₄ metallacycle following the trapping-mediated dissociative chemisorption of cyclobutane at a surface temperature of 180 K.¹²

In addition, we have previously communicated a remarkable new phenomenon following the adsorption of cyclobutane multilayers on Ru(001). While a saturated monolayer of cyclobutane will desorb nearly completely when heated, we find that the presence of cyclobutane multilayers results in appreciable dissociative chemisorption.¹³ In the present work, we will show that the multilayer-induced reaction of cyclobutane proceeds by the same initial step as the trapping-mediated dissociative chemisorption, namely C–C bond cleavage to form a C₄H₈ metallacycle. We will also examine the thermal decomposition of this species.

Experimental Section

The experiments were carried out in a stainless steel ultrahigh vacuum chamber (base pressure of 7×10^{-11} Torr) equipped with 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.¹⁴ The HREEL spectra were acquired using a commercial LK-2000 HREEL spectrometer (LK Technologies) the resolution of which varied between 50 and 70 cm⁻¹ (full-width at half-maximum of the elastically scattered beam) while maintaining a counting rate of at least 5×10^4 Hz in the elastically scattered peak in the specular direction. Specular spectra were collected with a 60° angle of incidence with respect to the surface normal. Because both the monochromator and analyzer are fixed, off-specular spectra were collected by rotating the crystal by 7.5°. The angles of incidence and detection are then respectively 67.5° and 52.5° with respect to the surface normal. This geometry may produce off-specular spectra which do not show as strong of a decline in the intensity of dipolar active losses as is seen in the more traditional scattering arrangement.

The Ru(001) single-crystal sample was mounted on a home-built cryostat that can cool the sample to 80 K using liquid nitrogen. The temperature of the crystal could be varied from 80 to 1700 K by resistive heating; the sample temperature was monitored using a type-C thermocouple that was spot-welded to the back of the crystal. The surface was cleaned using standard methods of Ar⁺ sputtering as well as annealing to 1100 K in a background of oxygen. The crystal was heated to 1650 K to remove all chemisorbed oxygen, and surface cleanliness was verified by HREELS, LEED, temperature-programmed desorption of CO, and AES.¹⁵

We note that AES cannot be reliably used to estimate surface carbon coverages due to the near overlap of the C (273 eV) and Ru (272 eV) transitions.¹⁶ Instead, carbon coverages are measured through titration with oxygen. After annealing the crystal to 800 K, 20 L (1 L = 10⁻⁶ Torr s) of oxygen is adsorbed at 90 K. This annealing temperature is sufficient to completely dehydrogenate all surface hydrocarbon fragments without forming unreactive graphite. A TPD experiment is performed to measure the desorption of reaction-limited CO, which is formed by the reaction of oxygen and carbon adatoms. Using this method,¹⁷ the ratio of CO to CO₂ production is ~100. The background adsorption of CO onto the surface during the exposure of oxygen was found to be negligible. Previous work¹⁷ shows that there is no carbon loss into the bulk on Ru(001) under experimental conditions similar to those utilized in the present work. The surface coverage of carbon

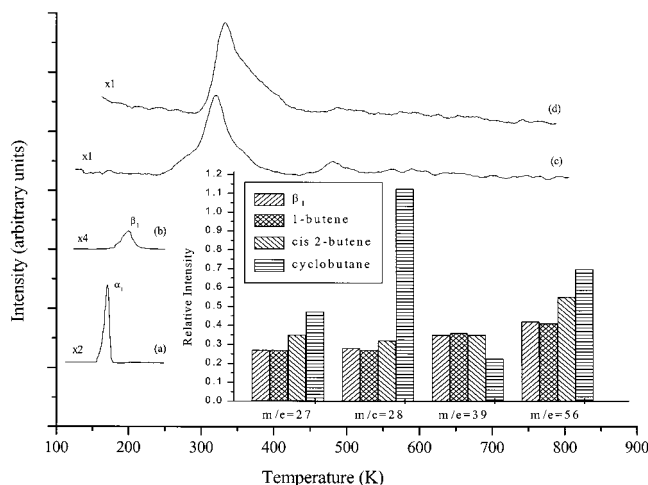


Figure 1. Thermal desorption spectra for (a) 1.8 L of cyclobutane adsorbed on Ru(001) at 90 K ($m/e = 56$), (b) 100 L exposure at 180 K ($m/e = 56$), (c) same as part b, but with $m/e = 2$, and (d) same as Figure 2g, but with $m/e = 2$. The heating rate is 5 K/s for all spectra. Inset: Comparison of the cracking patterns for cyclobutane, 1-butene, *cis*-2-butene, and the β_1 desorption product. The relative intensities are scaled so that the $m/e = 41$ intensity is unity for each compound. The pattern for *trans*-2-butene is not shown since it is indistinguishable from that of *cis*-2-butene.

adatoms, θ_C (number of carbon atoms per surface ruthenium atom), deposited by the dissociation of cyclobutane, 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), $\theta_{CO,sat} = 0.67$.¹⁸ Coverages determined using TPD (both hydrogen and carbon) are accurate to better than 0.005 of a monolayer. We note that for high initial carbon coverages, there is a small loss of carbon through the desorption of butene as the surface is heated between 185 and 225 K. A method for estimating this loss is given below.

Cyclobutane and cyclobutane-*d*₈ were synthesized via Wurtz coupling reactions which are described elsewhere.^{11,19} The cyclobutane product was then purified to greater than 99% purity (as verified by mass spectrometry) by performing several freeze–pump–thaw cycles on our gas-handling manifold. The isotopic purity of the *c*-C₄D₈ was estimated to be greater than 97% D. Cyclobutane was background dosed through a leak valve.

Results

Thermal desorption spectra are shown in Figure 1 following exposure of a clean Ru(001) surface to varying exposures of cyclobutane at 90 and 180 K. In Figure 1a, a 1.8 L exposure at 90 K results in the formation of a saturated monolayer of *c*-C₄H₈ and a single (α_1) peak in the desorption spectrum. Titration with oxygen following the desorption of the monolayer shows that only a small fraction of the monolayer has decomposed ($\theta_C \approx 0.005$). Figure 1b shows a TPD spectrum taken following a 100 L exposure at 180 K. This spectrum shows a single (β_1) peak between 185 and 225 K. The β_1 desorption product is tentatively identified to be 1-butene based on a comparison to the cracking patterns of selected reference compounds, cf., Figure 1, inset. Figure 1c shows the $m/e = 2$ TPD spectra corresponding to Figure 1b. The hydrogen coverage was found to be $\theta_H = 0.78$ by comparison to a surface saturated with molecular hydrogen ($\theta_H = 1$).²⁰ Following the TPD of Figures 1b and 1c, the surface was found to have a carbon coverage of $\theta_C = 0.38$.

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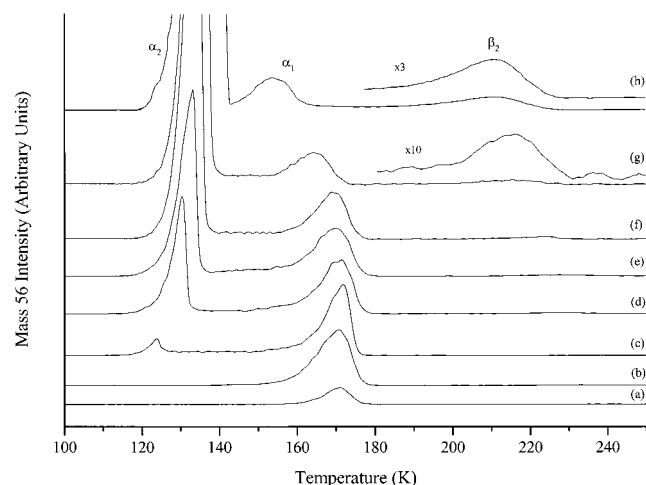


Figure 2. Thermal desorption spectra ($m/e = 56$) for: (a) 0.35, (b) 1.0, (c) 2.0, (d) 3.5, (e) 5, (f) 10, (g) 20, and (h) 100 L of cyclobutane adsorbed at 90 K on Ru(001). The heating rate is 5 K/s for all spectra. The residual carbon coverages following these experiments are (a) 0.003, (b) 0.003, (c) 0.005, (d) 0.02, (e) 0.03, (f) 0.06, (g) 0.11, and (h) 0.44.

Thermal desorption spectra showing the multilayer-induced decomposition of cyclobutane are shown in Figure 2. For submonolayer exposures, we see only a single desorption feature (α_1) which corresponds to desorption from a first adsorbed layer. As the exposure is increased beyond the 1.8 L needed to saturate the monolayer, a second (α_2) peak appears which does not saturate with increasing exposure and which represents desorption from a condensed multilayer. Concomitant with the rise of the α_2 peak, we observe a decrease in the intensity of the α_1 peak and an increase in the quantity of carbon left on the surface. Following a 20 L exposure (Figure 2g), the α_1 peak has shifted downward in temperature, its integrated intensity has decreased to 52% of that for a saturated monolayer, and the residual carbon has increased to $\theta_C = 0.11$. After a 100 L exposure at 90 K (Figure 2h), the α_1 peak has shifted further downward in temperature, and the residual carbon has increased to $\theta_C = 0.44$. Furthermore, starting at about 10 L, we see the appearance and growth of a third peak (β_2) in the $m/e = 56$ spectra. This peak is at approximately the same position as the β_1 (butene) peak seen following the trapping-mediated dissociative chemisorption of cyclobutane (Figure 1b). An analysis of the cracking patterns shows that the species giving rise to the β_1 and β_2 features are identical. A $m/e = 2$ TPD spectrum taken simultaneously with that of Figure 2g is shown in Figure 1d, and represents a surface hydrogen coverage of $\theta_H = 0.90$. The ratio of surface hydrogen to surface carbon following both the trapping-mediated dissociative chemisorption and the multilayer-induced reaction of cyclobutane is very close to 2:1. The slight excess of hydrogen in each case likely represents background adsorption of molecular hydrogen during the dosing of cyclobutane.

HREELS following the trapping-mediated dissociative chemisorption of 100 L of $c\text{-C}_4\text{H}_8$ and $c\text{-C}_4\text{D}_8$ at 180 K are shown in Figures 3 and 4, respectively. Reference HREEL spectra are also shown (Figure 5) for molecularly adsorbed $c\text{-C}_4\text{H}_8$ and $c\text{-C}_4\text{D}_8$. HREELS spectra are shown for the multilayer-induced decomposition of cyclobutane in Figure 6.

We have also studied the coadsorption of carbon monoxide, hydrogen, and oxygen with the species which we have previously identified to be a C_4H_8 metallacycle.¹² A metallacycle-covered surface was prepared through the trapping-mediated dissociative chemisorption of 20 L of cyclobutane at a surface temperature of 180 K. With no coadsorbates, this surface shows

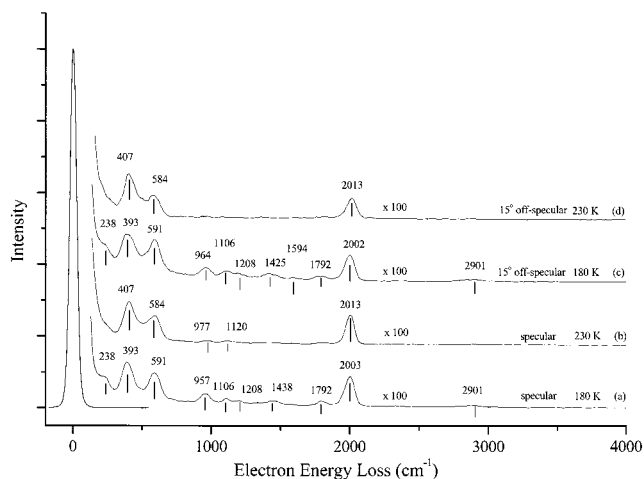


Figure 3. High-resolution electron energy loss spectra following a 100 L exposure of $c\text{-C}_4\text{H}_8$ at 180 K followed by a brief anneal to the indicated temperatures.

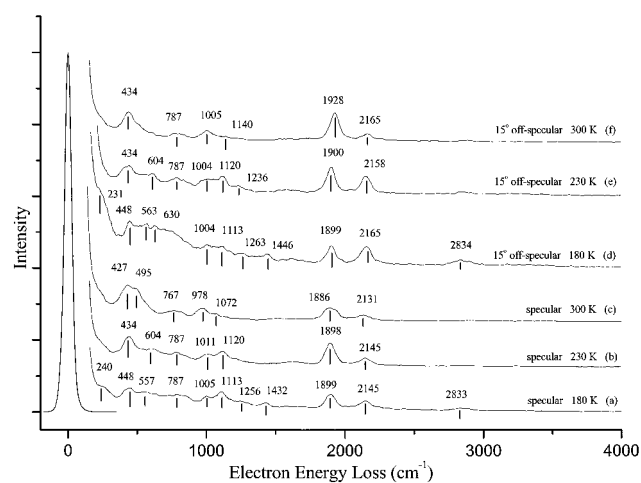


Figure 4. High-resolution electron energy loss spectra following a 100 L exposure of $c\text{-C}_4\text{D}_8$ at 180 K followed by a brief anneal to the indicated temperatures.

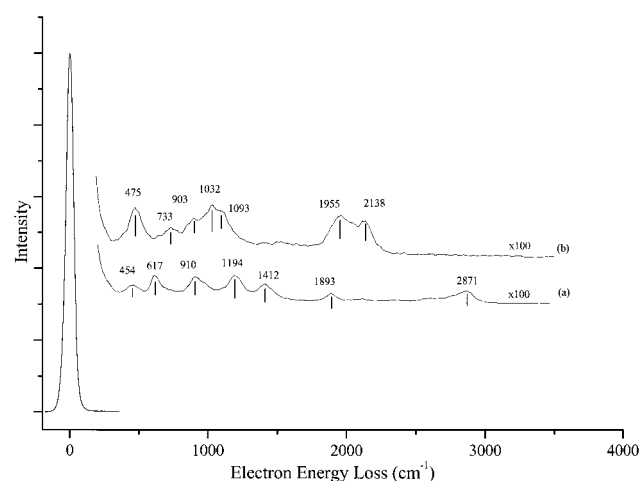


Figure 5. High-resolution electron energy loss spectra of (a) 1.8 L of $c\text{-C}_4\text{H}_8$ at 90 K and (b) 1.8 L of $c\text{-C}_4\text{D}_8$ at 90 K.

the butene desorption of Figure 7a, and a residual carbon coverage of 0.35. Thermal desorption results are shown for hydrogen and oxygen post-adsorption in Figures 7b and 7c, respectively. The post-adsorption of 100 L of hydrogen and 20 L of oxygen results in the adsorption of $\theta_H \approx 0.12$ and $\theta_O \approx 0.1$ and increases the butene desorption by factors of 1.7 and

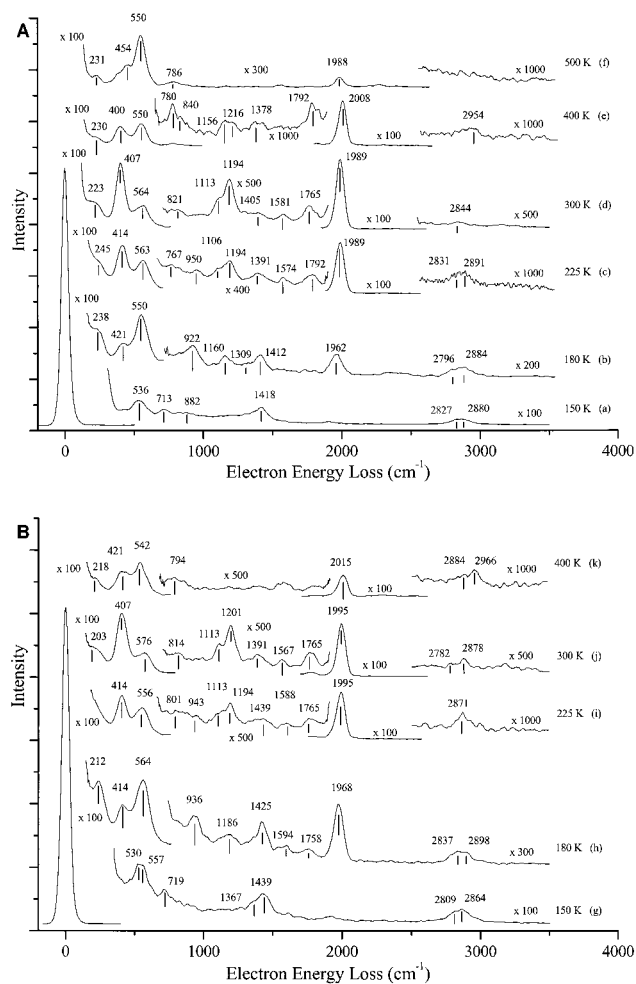


Figure 6. High-resolution electron energy loss spectra following a 100 L exposure of $c\text{-C}_4\text{H}_8$ at 90 K followed by a 5 K/s ramp to the indicated temperatures. Parts a–f were taken in the specular direction. Parts g–k were taken 15° off-specular.

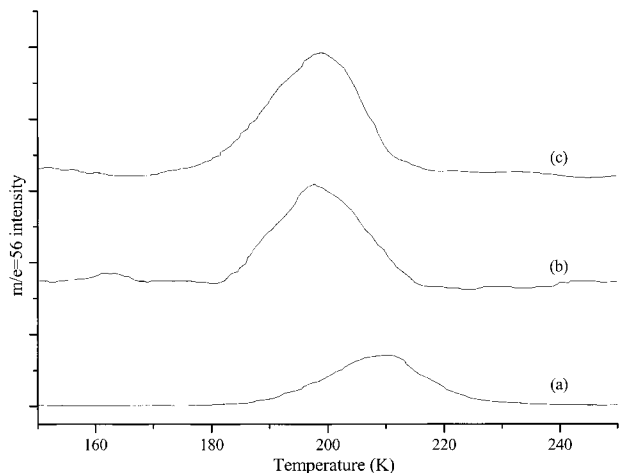


Figure 7. Thermal desorption spectra ($m/e = 56$) following the adsorption of (a) 20 L of $c\text{-C}_4\text{H}_8$ at 180 K, (b) same as part a, but with 100 L of H_2 post-adsorbed at 90 K, and (c) same as part a, but with 20 L of O_2 post-adsorbed at 90 K. The heating rate is 5 K/s for all spectra.

2.2, respectively. The post adsorption of 20 L of CO results in the adsorption of $\theta_{\text{CO}} \approx 0.12$ but does not produce any significant change in the butene desorption. If we examine the post-adsorption of H_2 , we observe no new desorption products but a decrease in the residual carbon coverage to $\theta_{\text{C}} = 0.315$. Since there are no new desorption products, we can assume

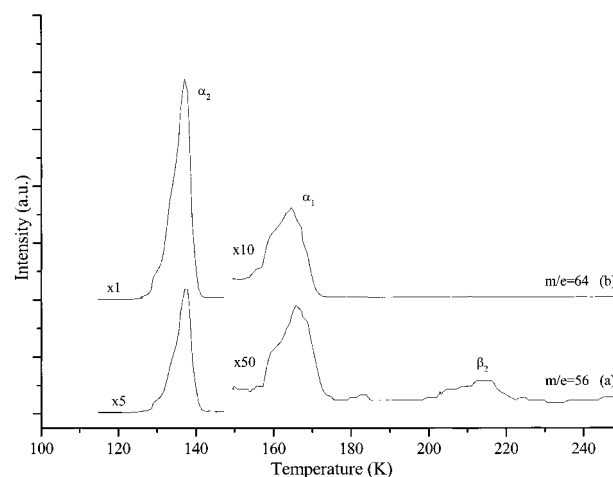


Figure 8. Thermal desorption spectra following the adsorption of 1.8 L of $c\text{-C}_4\text{H}_8$ at 90 K, annealing to 130 K, and adsorbing 18.2 L of $c\text{-C}_4\text{D}_8$ at 90 K: (a) $m/e = 56$ and (b) $m/e = 64$. The heating rate is 5 K/s for all spectra.

that the increase in the carbon lost to butene desorption corresponds to the decrease in residual carbon coverage. Using this carbon conservation principle, we are able to estimate the carbon lost to butene desorption to be $\theta_{\text{C}} = 0.05, 0.085,$ and 0.11 for Figures 7a, 7b, and 7c, respectively. This estimate should be considered to be approximate, due to the small coverages involved. To obtain absolute coverages of desorbing butene in terms of molecules per surface ruthenium atom, the previously listed numbers must be divided by four.

We also investigated the multilayer-induced decomposition phenomenon by adsorbing a monolayer (1.8 L) of $c\text{-C}_4\text{H}_8$ at 90 K, annealing to 130 K to remove any second layer $c\text{-C}_4\text{H}_8$, and adsorbing a multilayer of $c\text{-C}_4\text{D}_8$ (18.2 L) at 90 K. Note that the 130 K anneal results in a negligible amount of $c\text{-C}_4\text{H}_8$ decomposition. Thermal desorption spectra for this experiment are shown in Figure 8. The ratios of the integrated intensities of the α_1 and α_2 peaks are $\alpha_1(64):\alpha_1(56) = 9.5$ and $\alpha_2(64):\alpha_2(56) = 13.4$. Since there is no $m/e = 56$ cracking fragment for $c\text{-C}_4\text{D}_8$, this result indicates a mixing of layers prior to desorption of the multilayer. Thermal desorption spectra ($m/e = 2, 3,$ and 4) taken concurrently with those in Figure 8 show the desorption of $\theta_{\text{H}} = 0.16$ and $\theta_{\text{D}} = 0.08$ between 250 and 750 K. The isotopic composition of the desorbing hydrogen indicates that, despite the mixing, the first isotope deposited ($c\text{-C}_4\text{H}_8$) reacts preferentially. Note that a 20 L layer of $c\text{-C}_4\text{D}_8$ yields essentially all deuterium after decomposing. The residual carbon coverage following the experiment in Figure 8 is found to be $\theta_{\text{C}} = 0.11$ by titration with oxygen.

Discussion

We have studied two distinct methodologies to effect the dissociative chemisorption of cyclobutane on Ru(001). Whereas the trapping-mediated dissociative chemisorption of alkanes on transition metal surfaces is a well-studied phenomenon,²¹ we believe the cyclobutane/Ru(001) system to be the first for which a multilayer-induced reaction has been observed. In light of the novelty of the multilayer-induced decomposition, we will begin our discussion with the better understood trapping-mediated reaction.

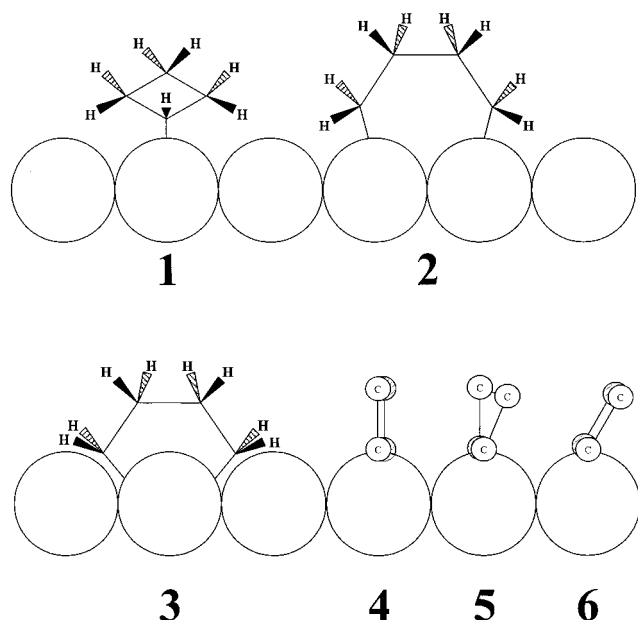
The initial step in the reaction of cyclobutane with the surface may be either C–C or C–H bond cleavage. The initial reaction

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Table 1. Literature Vibrational Spectra^a

bromocyclobutane ²⁴		tetrahydrofuran ²⁵		1,4-DBB ²²	thiophene ³⁶	Fe ₂ (CO) ₆ (C ₄ H ₄) ³⁷ (s.p.)
C–Br stretch	301	ring deformation	644	572	χ (CH) 714	844
ring deformation	486	ring deformation	932	969	(CH) 834	954
CH ₂ rock	701	ring deformation	1026	1117	γ (CH) 1081	1224
α C–H deformation	824	CH ₂ twist/wag	1176	1223	δ (CH) 1256	1247
ring stretch	1016	CH ₂ wag	1368	1445	ν (CC) 1409	1399
β CH ₂ wag	1262	β CH ₂ scissor	1464	2971	ν (CC) 1504	1543
C–H stretch	2856–2996	CH stretch	2852–2981		ν (CH) 3086, 3098, 3126	2990, 3060

^a s.p. = solid phase; 1,4-DBB = 1,4-dibromobutane.

Scheme 1

is therefore likely to yield one of three intermediates (Scheme 1): a cyclobutyl group (**1**), a metallacycle with the terminal carbons bound to different ruthenium atoms (**2**), or a true metallacyclopentane with both carbon atoms bound to the same surface atom (**3**). We have previously measured barriers of $10\,090 \pm 180$ and $10\,180 \pm 190$ cal/mol for the trapping-mediated dissociative chemisorption of *c*-C₄H₈ and *c*-C₄D₈, respectively.¹¹ The absence of a primary kinetic isotope effect strongly suggests that the cyclobutane reacts via cleavage of the strained C–C bond. As discussed in previous work, we would have expected an increase in the barrier on the order of 1100 cal/mol upon deuteration were the reaction to proceed via C–H bond cleavage.¹¹

A number of investigators have successfully utilized comparisons to vibrational spectra of 1,3-dihalopropanes to identify surface metallacyclobutanes. This is perhaps best seen in the work of Bent et al.⁷ where there is good agreement between the loss energies of a surface metallacyclobutane and an infrared spectrum of 1,3-diiodopropane. The similarities between HREEL spectra of the trapping-mediated reaction product (Figure 3a) and an infrared spectrum of 1,4-dibromobutane²² (Table 1) thus provide convincing evidence that the reaction product is indeed a metallacycle. The spectra are very similar, sharing losses at approximately 580, 970, 1110, 1210, and 1440 cm⁻¹.

Just as terminal dihalohydrocarbons are useful for the identification of surface metallacycles, halocycloalkanes are useful analogues for the identification of adsorbed cycloalkyl

groups. One example of the use of this analogy is seen in the work of McBreen et al.,²³ who utilized comparisons to the infrared spectrum of bromocyclopropane to identify a surface cyclopropyl on Cu(110) and Cu(111). Thus, we can also rule out a cyclobutyl species based on differences between the HREELS spectrum of Figure 3a and the infrared spectrum of bromocyclobutane (Table 1).²⁴ This is particularly evident in the absence of a C–H deformation mode at approximately 820 cm⁻¹ in Figure 3a.

The significant losses in Figure 3a include the mode at 591 cm⁻¹, which we assign to a ring deformation in analogy to the similar mode in tetrahydrofuran (Table 1).²⁵ We also observe a mode at 957 cm⁻¹ that is also likely a ring deformation. We assign the mode at 1438 cm⁻¹ to be a CH₂ scissor, and there is also a weak CH stretch at 2901 cm⁻¹. There is a loss at 238 cm⁻¹ that is likely a frustrated translation, as well as one at 1208 cm⁻¹, which is in the region where CH₂ wagging losses are typically observed. The loss at 1106 cm⁻¹ may involve a combination of a CH₂ wag and twist since there is a similar loss seen in the infrared spectrum of tetrahydrofuran²⁵ at 1176 cm⁻¹. The losses at 393 and 2003 cm⁻¹ correspond to the frustrated translation and C–O stretch of carbon monoxide that has adsorbed in an on-top site.²⁶ The loss at 1792 cm⁻¹ is likely due to the adsorption of CO in a site of increased coordination.²⁷ We estimate the CO coverage to be less than 5% of a monolayer based on thermal desorption measurements.

A HREEL spectrum following the trapping-mediated dissociative chemisorption of *c*-C₄D₈ shows the expected shifts in the losses (Figure 4a). While the frustrated translation loss energy remains relatively unchanged at 240 cm⁻¹, the low-frequency ring deformation has decreased slightly to 557 cm⁻¹. The vibrations at 787 and 1005 cm⁻¹ can likely be ascribed to the high-frequency ring deformation and CD₂ wag, respectively. The CD₂ scissor is now found at 1113 cm⁻¹, and the C–D stretch is seen at 2145 cm⁻¹. Although the *c*-C₄D₈ initially has an isotopic purity of greater than 97%, we find that there is some enrichment of the H content during reaction. While there is only a slight increase in activation barrier upon deuteration, from our previous work¹¹ we know that there is a higher effective probability of reaction for the *c*-C₄H₈ due to a higher rate of desorption for the *c*-C₄D₈.²⁸ TPD spectra indicate the isotopic surface composition to be about 10% H.

If we examine the thermal decomposition of the C₄H₈ metallacycle formed from the trapping-mediated dissociative

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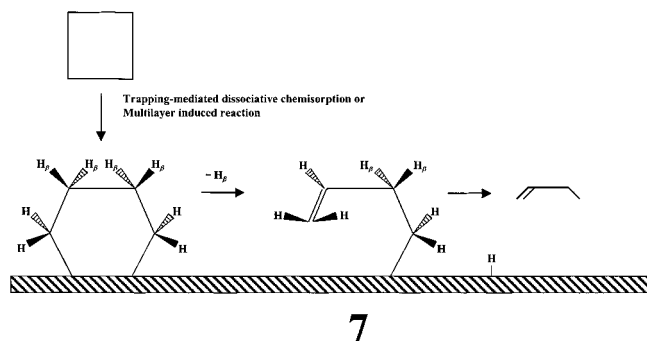
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Scheme 2



chemisorption at 180 K, we see a desorption feature (β_1) in the $m/e = 56$ TPD spectrum between 185 and 225 K (Figure 1b). The cracking pattern of this desorption product is compared to reference compounds (measured under the same conditions) in the inset of Figure 1. The β_1 product is tentatively identified as 1-butene, but due to the similar cracking fragments of the butene isomers it is possible that another isomer is responsible for this peak. No desorbing products with masses 54 or 58 are observed, thus precluding 1,3-butadiene or butane desorption.

To understand the decomposition reaction of our metallacycle, there are strong analogies that can be found in the organometallic and surface chemical literature. Several metallacyclopentane complexes have been found which decompose to yield 1-butene when heated.²⁹ This reaction is generally presumed to occur via β -hydrogen elimination to form a 3-butenyl species (7) followed by rehydrogenation to give 1-butene (Scheme 2). The mechanism depicted in Scheme 2 was also invoked by Bent *et al.*⁷ to account for the formation of 1-butene from 1,4-diiodobutane on Al(100). On Al(100), 1,3-butadiene was also formed, and this was believed to be due to the loss of a β -hydrogen from the butenyl intermediate. Given the small butene yield, it is apparent that complete dehydrogenation is favored over butene formation on Ru(001).

We now turn our attention to the multilayer-induced decomposition. In Figure 2, we see an unusual behavior in the sequence of TPD spectra. As the initial multilayer coverage is increased, we see a significant decrease in the intensity of the monolayer (α_1) peak which is accompanied by an increase in the residual surface carbon coverage. We interpret this result to mean that the presence of the multilayer increases the rate of dissociative chemisorption of first layer cyclobutane sufficiently for reaction to occur prior to the completion of the multilayer desorption. Larger initial coverages were found to increase the extent of reaction. This trend is a result of the thicker multilayer persisting for longer times and to higher surface temperatures during the TPD experiments. In any reaction, the total amount of product formed is, of course, equal to the product of the reaction rate and the time allowed for the reaction to take place. In the present experiment, the time allowed for multilayer-induced reaction is simply the length of time that the multilayer is present. A thicker initial multilayer takes more time to desorb during the TPD experiments and thus provides a longer time for the multilayer-induced reaction to occur.

While we cannot pinpoint the exact temperatures over which the multilayer-induced reaction occurs, an examination of Figure 6a shows that at least some reaction has occurred below 150

K. The spectrum of Figure 6a is significantly perturbed from that of molecularly adsorbed cyclobutane, and shows a loss at 536 cm^{-1} that is assigned to the ring deformation of the C_4H_8 metallacycle. The identification of the metallacycle at 150 K is discussed in more detail below. The presence of the metallacycle after heating to just 150 K clearly demonstrates a multilayer-induced increase in reaction rate since the trapping-mediated reaction will not occur to an appreciable extent at 150 K.

We should note that, in some systems, it is possible that a thick condensed multilayer may persist to high enough temperature to encourage reaction by inhibiting desorption from the monolayer at temperatures at which desorption would ordinarily occur. That this effect does not occur in the present investigation can be readily seen in Figure 2, where even at the highest multilayer coverages, the trailing edge of the multilayer desorption falls well short of the approximately 165 K leading edge of the monolayer desorption from the clean surface. We must note, however, that after a 100 L exposure, *cf.*, Figure 2h, the trailing edge of the multilayer desorption at about 145 K may have some overlap with the leading edge of the monolayer desorption peak, which has shifted downward in temperature due to the high surface metallacycle coverage. Even if there is a slight inhibition of the monolayer desorption in the experiment of Figure 2h, such an effect will not contribute to an increased trapping-mediated reaction because the monolayer cyclobutane has completely desorbed from the surface by about 165 K, still short of the temperatures required for appreciable trapping-mediated dissociative chemisorption.

One possible explanation for the observed increase in reaction rate is that the barrier to reaction is reduced in the presence of the multilayer. Elsewhere, we have conducted experiments varying the multilayer thickness and the TPD heating rate to further investigate the kinetics of the multilayer-induced reaction.³⁰ Using these data we estimated the activation energy for multilayer-induced dissociation to be approximately 7510 ± 500 cal/mol.³⁰ This value represents a substantial reduction from the $10\,090 \pm 180$ cal/mol barrier measured for the trapping-mediated reaction¹¹ and strongly supports the existence of a multilayer-induced reduction in activation energy.

Following the multilayer-induced decomposition of $c\text{-C}_4\text{H}_8$, we obtain HREEL spectra very similar to those obtained from the trapping-mediated dissociative chemisorption of this molecule. The similarities are best seen if we compare the spectrum of Figure 6b to the metallacycle of Figure 3a. Figure 6b depicts a spectrum taken after exposing the surface to 100 L of cyclobutane at 80 K and heating at 5 K/s to 180 K. After heating to 180 K, all of the unreacted cyclobutane has desorbed, and thus does not contribute to the HREEL spectrum. The losses in Figure 6b are sharper than and slightly shifted from those in Figure 6a (150 K) due to the desorption of unreacted cyclobutane and possibly also due to thermal ordering of the layer. It seems apparent that Figures 3a and 6b represent the same species. We can, therefore, conclude that both the multilayer-induced decomposition and the trapping-mediated dissociative chemisorption of cyclobutane proceed via the same path, namely cleavage of the strained C—C bond to form a surface metallacycle. In both cases the metallacycle decomposes to yield a butene desorption product and surface hydrocarbon fragments between 185 and 225 K.

While the HREEL spectra of Figures 3a and 6b are very similar, there are slight differences which are worthy of some comment. First, we note that the differences can likely be ascribed to a coverage-dependent adsorption geometry. The

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Table 2. HREELS Loss Assignments for the Saturated C₄ Metallacycle on Ru(001)^a

vibrational mode approximate description	20 L c-C ₄ H ₈ 180 K/Ru(001) ^{t,12}	100 L c-C ₄ H ₈ 180 K/Ru(001) ^t	100 L C-C ₄ H ₈ 80 K/Ru(001) ^m	100 L c-C ₄ D ₈ 180 K/Ru(001) ^t
frustrated translation	239	238	238	240
ring deformation	598	591	550	557
ring deformation	974	957	922	787
CH ₂ wag/twist	1127	1106	1160	1005
CH ₂ wag	1201	1208	1309	
CH ₂ scissor	1444	1452	1412	1113
C-H stretch	2951	2891	2796, 2884	2145

^a t = trapping-mediated dissociative chemisorption; m = multilayer induced decomposition.

carbon coverages are estimated to be $\theta_C = 0.38$ and 0.44 for Figures 3a and 6b. We can add a third datum point to this series by examining a HREEL spectrum previously reported¹² following the trapping-mediated dissociative chemisorption of 20 L of c-C₄H₈ at 180 K for which a carbon coverage of $\theta_C = 0.35$ was measured (Table 2). As the surface coverage increases, we see that the low-frequency ring deformation shifts down from 598 to 591 to 550 cm⁻¹. Comparing Figures 3a and 6b, we also see an increase in intensity that is greater than linearly proportional to the coverage increase. The high-frequency ring deformation also shifts down, from 974 to 957 to 922 cm⁻¹ with increasing coverage. We see a significant "softening" of the C-H stretching modes from 2951 cm⁻¹ at the lowest coverage studied to 2796–2894 cm⁻¹ at the highest. The symmetric and asymmetric C-H losses have also increased in intensity for the high surface coverage generated following the multilayer-induced decomposition. A possible explanation for these observations is that as the coverage is increased, the metallacycle adopts a more vertical geometry. This argument is appealing in that we would expect a more crowded surface to favor configurations utilizing less effective surface area. This type of coverage-dependent adsorption geometry is known, for example, for the adsorption of thiophene on Cu(100).³¹ Thiophene adsorbs with its molecular plane parallel to the surface at low coverages on Cu(100), and shifts to an inclined geometry as the coverage is increased. It is difficult to reconcile a vertical geometry (4) with the mode-softening in the HREELS for the reasons discussed below. In a vertical geometry, the symmetric CH₂ stretches of the β -carbons would have their dynamic dipole moments within about 35° of the surface normal. The β -CH₂ groups would also be well separated from the surface, and thus not in a position to undergo mode-softening.³² Thus, for a species such as 4, we would have expected a moderately strong loss in the 2850–3000 cm⁻¹ range, which is not observed. In addition, dipolar active soft modes of the type seen in Figure 6b are often believed to involve a geometry in which the C-H bond points toward a surface metal atom, with the C-H...Me line nearly normal to the surface.³² We are thus inclined to believe that the metallacycle remains somewhat tilted even at the highest coverages.

Having presented a large body of evidence for the surface species to be a C₄H₈ metallacycle, we can consider some possible bonding geometries. Due to the diversity of compounds known, the organometallic literature does not, unfortunately, offer any clear guidance on this issue. One significant question is whether the terminal carbons are bonded to the same (3) or to different ruthenium atoms (2). A number of mononuclear metallacyclopentanes are, in fact, known.^{29,33–35} We are also

aware of two dinuclear compounds containing saturated four-carbon rings.³⁶ In these compounds, the terminal carbons are, in fact, bound to different metal atoms.

If the surface species is indeed a metallacyclopentane (3), there are further geometric issues which can be addressed. Collman et al.³³ have speculated that there is little energetic difference between several possible conformations of metallacyclopentane complexes. This speculation seems to be based on the identification of compounds with several different conformations. Metallacyclopentane complexes seem to favor the "puckered envelope" configuration, with four coplanar atoms and the fifth sitting out of this plane. In some complexes, it is the four carbon atoms which are coplanar (5).³⁴ In others, the metal atom resides in a plane with three carbons, and one of the β -carbons sits out of the plane (6).³⁵

We began our look at the multilayer-induced decomposition of cyclobutane by considering spectra taken after annealing to 180 K. This temperature is sufficiently high that all molecular cyclobutane has desorbed, thus simplifying the interpretation of the HREEL spectrum. If we examine the HREEL spectra taken after annealing a 100 L multilayer to just 150 K, we see that the metallacycle is indeed present at this temperature. This is evident by the presence of the low-frequency ring mode at 536 cm⁻¹ and the CH₂ scissoring mode at 1418 cm⁻¹. Note that this ring mode has shifted to even lower frequency, presumably as a result of lateral interactions with the cyclobutane which remains adsorbed at 150 K. The 1418 cm⁻¹ loss contains contributions from the CH₂ scissoring modes of the metallacycle and unreacted cyclobutane. The loss at 713 cm⁻¹ is likely a CH₂ rock of the unreacted cyclobutane which is shifted from its normal position due to the presence of the metallacycle.¹¹ The other modes of cyclobutane and the metallacycle overlap and are not individually resolved, instead forming a broad loss between 713 and 1418 cm⁻¹.

If we examine the thermal decomposition of the metallacycle spectroscopically, we see a significant change in the HREEL spectra as the surface is heated from 180 to 230 K. The species which is present (following the desorption of butene) at 230 K is stable to at least 300 K. We note that the spectra of Figures 6c and 6d are nearly identical to a HREEL spectrum obtained by Stöhr et al.² following the decomposition of thiophene on Pt(111). Although Stöhr et al. truncated their HREEL spectrum at 2000 cm⁻¹, there is excellent agreement in both the loss energies and intensities between Figure 6d and the Pt(111) species, cf., Table 3. The only difference between the two spectra is the presence of a strong mode at 500 cm⁻¹ in Figure 6d, which is not present on Pt(111). It is possible that there is such a mode on Pt(111), and that it is weak or partially obscured by the frustrated translation of sulfur adatoms at 370 cm⁻¹. Stöhr et al.² report this species to be a C₄H₄ metallacycle in which

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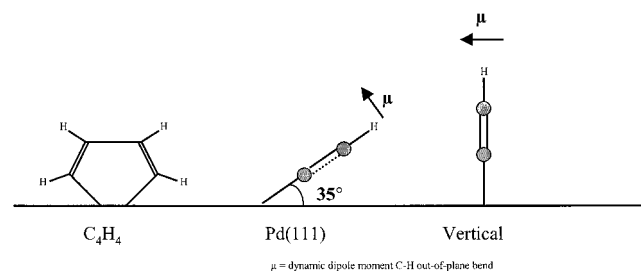
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Table 3. HREELS Loss Assignments for C₄H₄ Species^a

vibrational mode approximate description	100 L c-C ₄ H ₈ 80 K→300 K Ru(001)	C ₄ H ₄ S 350 K Pt(111) ²	C ₄ H ₄ Cl ₂ 235 K Pd(111) ^{3a}
γ(CH)	563 s		610/630 s
δ(CH)	776 w	754 m	790 vs
δ(CH)	950 w-m	925 m	890 w
δ(CH)	1106 s	1090 vs	1100 w
δ(CH) or ν(CC)	1194 vs	1210 m,sh	1220 w
ν(C=C)	1391 m	1400 s	
ν(C=C)	1574 m	1620 w-m	
ν(CH)	2831 w		
ν(CH)	2891 w		2915 w

^a w = weak; m = medium; s = strong; vs = very strong; sh = shoulder.

Scheme 3

the sulfur atom of the thiophene is replaced by a surface platinum atom. The surface vibrational spectra do indeed show similarities to the infrared spectra of thiophene³⁷ and that of an Fe₂(CO)₆(C₄H₄) complex,³⁸ in which the terminal carbons of the C₄H₄ ligand are bound to the same iron atom. Using NEXAFS, the investigators claimed that this species was adsorbed nearly parallel to the surface, with the C₄H₄ molecular plane making an angle of less than 20° with the surface.² In the discussion that follows, we shall see that there is reason to question the assigned geometry.

After the work of Stöhr et al.,² a C₄H₄ species has been isolated on Pd(111) from the decomposition of *cis*-3,4-dichlorocyclobutene.³ A HREEL spectrum of the C₄H₄ species on Pd(111)³ (Table 3) differs significantly from the spectrum of the C₄H₄ species on Pt(111).² Specular HREEL spectra of the Pd(111) species show a very intense out-of-plane C–H bending loss at 790 cm⁻¹ which is present, but rather weak, in Figure 6d and in the work of Stöhr et al. NEXAFS seem to indicate a slightly tilted geometry for this species with the C₄H₄ plane estimated to make a 35° angle with the Pd(111) surface,³ cf., Scheme 3. HREEL spectra are consistent with the geometry determined using NEXAFS on Pd(111). At a 35° angle, significant rehybridization of the C–C double bonds is expected,³ thus accounting for the absence of losses above 1400 cm⁻¹. In addition, since the dynamic dipole moment of the C–H out-of-plane bend is perpendicular to the C₄H₄ ring, the inclined position is consistent with the C–H bend dominating the specular HREEL spectrum.

An examination of the HREEL spectrum suggests that the inclination angle determined for the C₄H₄ species on Pt(111) was incorrect.² The Pt(111) spectrum and that of Figure 6d both show losses at 1400 and 1620 cm⁻¹ which are absent from the Pd(111) species and which are indicative of C–C double bonds unrehybridized in an upright geometry.³ Even more convincing is the weak C–H out-of-plane mode both on Pt(111) and in

the present work. Thus, it seems likely that the Pt(111) species as well as the species present in Figures 6c and 6d are C₄H₄ species adsorbed in upright, and possibly nearly vertical orientations.

Annealing the surface to 400 K yields further dehydrogenation. Identifying the surface hydrocarbon fragments in this system is more difficult than in other systems such as the decomposition of ethylene,³⁹ where there are both fewer possibilities and more analogies on which to draw. Nonetheless, we note that the HREEL spectra taken after annealing above 400 K show features somewhat similar to those seen following the decomposition of *trans*-2-butene on Pt(111).⁴⁰ After annealing a *trans*-2-butene covered Pt(111) surface to 450 K, Avery and Sheppard⁴⁰ observed a species which they believe to be a CCHCHC metallacycle. This species shows a strong triplet of losses at 720, 790, and 840 cm⁻¹, as well as weaker losses at 1110, 1280, and 1410 cm⁻¹. Moderately intense losses at 260 and 420 cm⁻¹ likely correspond to frustrated translations, and there is also a fairly strong C–H stretching loss at 3070 cm⁻¹. In Figure 6e we assign the vibration at 780 cm⁻¹ to be a C–H bend, and the weak loss at 2954 cm⁻¹ to be a C–H stretch. Losses at 1167 and 1378 cm⁻¹ are possibly a C–H bend and a C–C stretch, respectively. The loss at 550 cm⁻¹ might correspond to a ring deformation. On Pd(111), C₄H₄ decomposes via C–C bond cleavage to form vinylidene. This does not seem to be the case on Ru(001), since the vibrational spectrum of Figure 6e does not correspond to any of the likely C₂ fragments, including vinylidene and acetylide.³⁹

A HREEL spectrum taken after annealing to 500 K shows definite similarities to methylidyne, but with some differences. Methylidyne formed from the decomposition of ethylene on Ru(001)³⁹ shows losses at 465, 550, and 810 cm⁻¹, which are also seen in Figure 6f. Figure 6f also shows a loss at 231 cm⁻¹ which was not seen for methylidyne, and also lacks the weak loss at 3010 cm⁻¹ which is observed for methylidyne. We consider it likely that Figure 6f represents a methylidyne-like hydrocarbon fragment with the slightly different vibrational spectrum possibly due to a higher carbon-to-hydrogen ratio in the present work.

A number of reactions of metallacyclopentanes have been observed in the organometallic literature. In particular, these compounds have reacted with protons to yield butane and with CO to yield cyclopentanone.^{29d} We have unsuccessfully attempted to observe analogous surface reactions by adsorbing oxygen, hydrogen, and carbon monoxide onto a metallacycle-covered surface. In the case of hydrogen and oxygen, the yield of butene is increased, and the residual surface carbon coverage is decreased. This is fortuitous in that it provides a method of estimating the butene yield (*vide supra*). Interestingly, Grubbs et al.^{29b} have also observed a change in products formed from the thermal decomposition of homogeneous metallacyclopentanes after oxidation. In one case, ethylene formation was suppressed in favor of cyclobutane following oxidation. In another, oxidation favored the formation of cyclobutane, in contrast to butene for the unoxidized complex. On the surface, we believe that hydrogen coadsorption increases the butene yield by providing additional reactant for the hydrogenation of a butenyl species. Oxygen coadsorption may favor butene formation by lowering the barrier to hydrogenation through a weakening of the Ru–H and/or Ru–C bonds. Coadsorbed CO is expected to have less influence on the Ru–H and Ru–C

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bonds, thus accounting for its failure to measurably influence this reaction.

To investigate further the multilayer-induced decomposition phenomenon, we studied the use of a mixed multilayer. Specifically, we deposited a monolayer of $c\text{-C}_4\text{H}_8$ followed by an 18.2 L dose of $c\text{-C}_4\text{D}_8$. This system represents an isotopically labeled analogue to the 20 L $c\text{-C}_4\text{H}_8$ system. If there were no mixing between the first and higher layers, this system would provide a rigorous test of our hypothesis that the mechanism of multilayer-induced decomposition involves the enhanced reactivity of the first layer in the presence of the multilayer. Unfortunately, as seen in Figure 8, there is substantial interlayer mixing below the onset multilayer desorption. The integrated intensity of $c\text{-C}_4\text{H}_8$ desorbing in the multilayer (α_2 peak) corresponds to approximately 63% of a saturated monolayer. The amount of $c\text{-C}_4\text{H}_8$ desorbing in the α_1 peak corresponds to about 5% of a saturated layer. Measurements of H_2 , HD, and D_2 during this thermal desorption experiment show the desorption of $\theta_{\text{H}} = 0.16$ and $\theta_{\text{D}} = 0.08$. In addition, we find that the surface has a carbon coverage of $\theta_{\text{C}} = 0.11$. While there is clearly some interlayer mixing, we can draw a few conclusions from this experiment. First, the interlayer mixing does not result in complete randomization, as seen by the preferential reaction of $c\text{-C}_4\text{H}_8$. Were there to be complete mixing, we would have expected to see a $\theta_{\text{D}}:\theta_{\text{H}}$ ratio of approximately 9:1.¹³ Second, we might say that in some sense the presence of the multilayer decreases the activation energy for desorption of the first layer. Without a multilayer, the monolayer remains on the surface to above 160 K. In the presence of the multilayer, we see the loss of some $c\text{-C}_4\text{H}_8$ even at 130 K. Thus, we might take this as an indication that the activation energy for "desorption" from the first layer into the condensed multilayer (i.e., exchange of $c\text{-C}_4\text{H}_8$ by $c\text{-C}_4\text{D}_8$ in the first layer) is lower than that for desorption directly from the first adsorbed layer into vacuum.

As a last point of discussion, we wish to examine the possibility that the multilayer-induced decomposition phenomenon might provide some insight into heterogeneous catalysis at the solid–liquid interface. While much is known on a macroscopic level about liquid phase heterogeneous catalysis, relatively little is known on the microscopic level. Thus, given the difficulties inherent in studying catalysis at the liquid–solid interface, it may be useful to probe model systems such as the one investigated in the present work. One obvious concern is the assumption that the condensed layer at cryogenic temperatures can be accurately equated to a liquid at room (or higher) temperature. The mobility present in the layer, as evidenced by the interlayer mixing, should certainly assuage some of these concerns. We also note that a similar issue has been addressed by a number of investigators who have successfully utilized condensed layers of water and electrolytes to "simulate" electrochemical interfaces under UHV conditions.⁴¹ Particularly impressive is the agreement between the coverage-dependent

work function changes measured in situ and under UHV conditions using condensed halogens and water on Ag(110).^{41c}

If one accepts this connection between multilayer-induced reaction and catalysis at the solid–liquid interface, some discussion of the multilayer-enhanced reactivity of cyclobutane is in order. There is certainly much industrial interest as to whether certain reactions occur more rapidly at the solid–liquid or the solid–vapor interfaces. Despite this interest, there have been only a handful of reactions at well-defined surfaces for which this question has been investigated. A theoretical investigation of a model isomerization reaction found essentially no difference in rate between the solid–vapor and solid–liquid vapor interfaces.⁴² A significant reduction in barrier was found, however, for the hydrogenation of ethylene in an electrochemical reaction compared to the same reaction at the Pt(111)–vapor interface.⁴³ There is also a report of an approximately order-of-magnitude reduction in the rate of cyclohexene hydrogenation when one goes from the Pt(223)–vapor interface to the polycrystalline Pt–liquid interface.⁴⁴ In this extremely limited data set, we see that some reactions seem to occur faster at the solid–vapor and others at the solid–liquid interface. A better understanding of the differences between the solid–vapor and solid–liquid interfaces will lead to better selection of the optimum operating conditions for heterogeneous catalytic processes. It is our belief that the study of multilayer-induced reactions under ultrahigh vacuum conditions can contribute to a better understanding of catalysis at the solid–liquid interface.

Conclusions

We have studied the trapping-mediated dissociative chemisorption and the multilayer-induced decomposition of cyclobutane on Ru(001). Both routes lead to a common intermediate which we have identified to be a surface C_4H_8 metallacycle. The metallacycle decomposes between 185 and 225 K to yield a butene desorption product and surface hydrocarbon fragments. We believe that, at high surface coverages, the C_4H_8 metallacycle decomposes to a C_4H_4 metallacycle between 185 and 230 K. Coadsorption of hydrogen or oxygen with the metallacycle does not result in reaction, but does increase the yield of the butene desorption product.

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