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Decomposition of Cyclobutane on Ru(001): Identification of a Surface Metallacycle

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Although metallacycles are of interest as intermediates in surface-catalyzed reactions, investigations of these species remain somewhat rare.[1−4] The study of saturated four-carbon metallacycles on surfaces is limited to the work of Bent et al.,[3] who postulated this species to be an intermediate in the formation of 1,3-butadiene and 1-butene from 1,4-diiodobutane on Al(100). In this paper we utilize the thermal decomposition of cyclobutane to produce what we believe to be the first spectroscopic identification of a saturated C_4 metallacycle on a transition metal surface.

Although there have been numerous investigations of the adsorption and decomposition of small (C_3−C_6) cycloalkanes on single-crystalline surfaces,[4−8] we are aware of only a few involving cyclobutane. In a study of "soft" C−H stretching vibrations of cycloalkanes, Hoffmann et al.[6] studied the molecular adsorption of a saturated monolayer of cyclobutane on Ru(001). Recently, we have investigated the trapping-mediated dissociative chemisorption of cyclobutane[7] as well as its dissociation reaction in the presence of a condensed multilayer on Ru(001).[8]

This study utilizes standard ultrahigh vacuum techniques for the preparation and characterization of the Ru(001) surface, methods which are described in more detail elsewhere.[9] Of note to the present work is the fact that our HREEL spectrometer shows below-average sensitivity[9] above 2500 cm^{-1}. Cyclobutane was synthesized from 1,4-dibromobutane (Aldrich, 99%) using a Wurtz coupling reaction, which is described elsewhere.[7,10]

As shown in Figure 1a, a saturated monolayer of cyclobutane desorbs between 160 and 180 K with an activation energy for desorption estimated to be 10 100 cal/mol.[11] Following the desorption of a saturated monolayer of cyclobutane, the surface carbon coverage is measured to be $\theta_C \approx 0.001$. This residual carbon is likely due to the dissociation of a small amount of cyclobutane at surface defect sites.

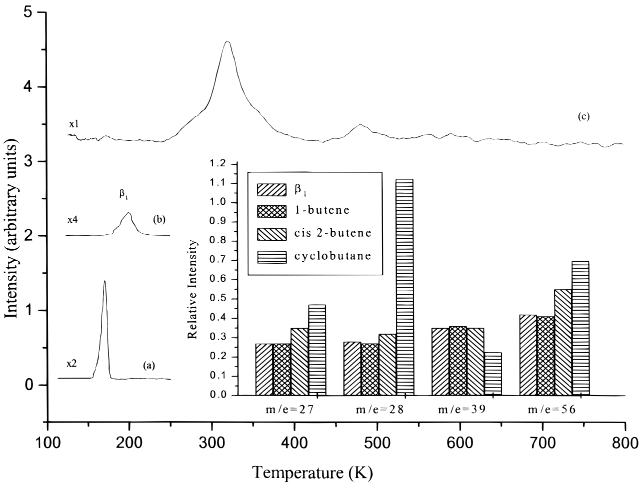

Figure 1. Thermal desorption spectra for: (a) 1.8 L of cyclobutane adsorbed on Ru(001) at 80 K (*m*/*e* = 56), (b) 20 L exposure at 180 K (*m*/*e* = 56), and (c) same as (b), but with *m*/*e* = 2. Inset: Comparison of the cracking patterns for cyclobutane, 1-butene, *cis*-2-butene, and the β_1 desorption 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.

Although a saturated monolayer of cyclobutane does not appreciably react with the surface upon heating, by holding the surface just above the desorption temperature and exposing it to c-C_4H_8, we can observe the dissociative chemisorption of cyclobutane. Exposing the surface to 20 L of cyclobutane at a surface temperature of 180 K results in significant dissociation, and TPD spectra taken following this procedure are shown in Figure 1b and c. Figure 1c shows hydrogen desorption from the hydrocarbon fragments on the surface. In Figure 1b, we see that the cyclobutane dissociation product yields a feature (β_1) in the *m*/*e* = 56 thermal desorption spectrum between 185 and 210 K. The cracking pattern of this desorption product is compared to those of reference compounds (measured under the same conditions) in the inset of Figure 1. The β_1 product is *tentatively* identified as 1-butene, but because of the similar cracking fragments of the butene isomers it is possible that another isomer is also responsible for this feature. No desorbing products with masses 54 or 58 are observed, thus precluding 1,3-butadiene or butane desorption. The amount of carbon present on the surface following the TPD experiment of Figure 1b was found to be $\theta_C = 0.35$, and the carbon lost to butene desorption was estimated to be $\theta_C = 0.03$.[7]

The first step in the reaction of cyclobutane with the surface may be either C−C or C−H bond cleavage. The initial reaction 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 atom (**3**). In our studies of the trapping-mediated dissociative chemisorption of cyclobutane and its fully deuterated isotopomer on Ru(001), we measured activation energies for dissociative chemisorption of 10 090 cal/mol for c-C_4H_8 and 10 180 cal/mol for c-C_4D_8 for surface temperatures between 190 and 1200 K.[7,12] The lack of a primary kinetic isotope effect suggests strongly that the initial step in the dissociative chemisorption of cyclobutane is cleavage of the strained C−C bond and formation of a metallacycle.

We can attempt to identify conclusively the surface intermediate responsible for the 1-butene desorption with vibrational spec-

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(12) The activation energies reported are for the low coverage limit (θ_C < 0.12). Butene desorption will not occur under these conditions.[7]

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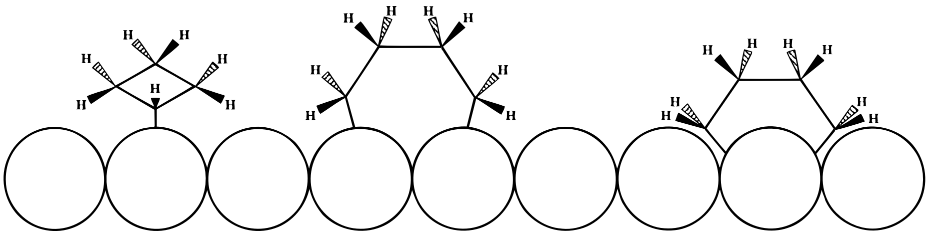
Scheme 1



1 **2** **3**

Table 1. HREELS Peak Assignments for the C_4 Metallacycle on Ru(001)

vib. mode approx. description	HREELS 20 L c-C_4H_8 180 K/Ru(001)	selected peaks from vapor phase IR spectra				
		BrC_4H_8Br[13]	vib. mode approx. description	bromocyclobutane[16]	vib. mode approx. descriptions	tetrahydrofuran[14]
frustrated translation	239		C−Br stretch	301	ring deformation	644
CCC deformation	598	572	ring deformation	486	$C_\alpha C_\beta$ + CH_2 rock	932
C−Ru−C deformation or	974	969	CH_2 rock	701	COC as stretch	1088
CC stretch + CH_2 rock			α CH deformation	824	CH_2 twist + CC stretch	1175
CC stretch + CH_2 wag/twist	1127	1117	ring stretch	1016	α CH_2 wag	1368
	1201	1223	β CH_2 wag	1262	β CH_2 scissor	1453
CH_2 scissor	1444	1445	C−H stretch	2856−2996	CH stretch	2871
					CH stretch	2983
C−H stretch	2931	2971				

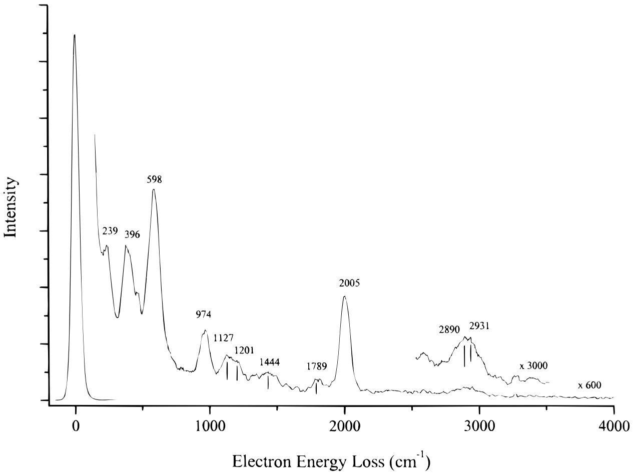


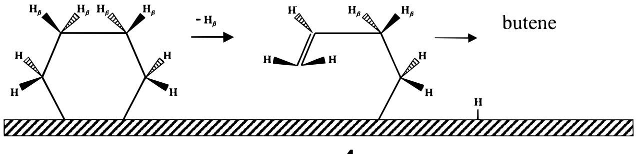
Figure 2. HREELS spectrum taken after dosing 20 L of cyclobutane at 180 K.

troscopy. A HREEL spectrum of a surface prepared using the aforementioned procedure is displayed in Figure 2. Mode assignments for the cyclobutane decomposition product are shown in Table 1.

The identification of metallacycles via HREELS has typically relied on comparisons to appropriately selected reference compounds as a result of the dearth of spectra of actual metallacylic species. In particular, dihalohydrocarbons have proven to be extremely useful references. Bent et al.[3] have found that the IR spectrum of liquid-phase 1,3-diiodopropane is quite similar to that of a metallacyclobutane on Al(100). The similarities between the HREEL spectrum in Figure 2 and an IR spectrum of 1,4-dibromobutane[13] (shown in Table 1) strongly support our identification of this surface species as a saturated C_4 metallacycle. Lending further support to this assignment are the similarities between the spectrum in Figure 2 and the IR spectrum of tetrahydrofuran, cf., Table 1.[14]

We also note that comparisons to bromocyclopropane have been successfully utilized in the identification of cyclopropyl species on Cu(110) and Cu(111).[4] The differences between the vibrational spectra of the surface species and bromocyclobutane show that a cyclobutyl species can safely be excluded. This is particularly evident in the absence of a CH deformation mode at approximately 820 cm^{-1}. While we can confidently assign the species of Figure 2 to be a metallacycle, the anticipated similarities between the vibrational spectra of **2** and **3** and the lack of suitable reference compounds make a definitive identification of the surface bonding configuration quite difficult.

Scheme 2



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To understand the decomposition reaction of our metallacycle, there are strong analogies that can be found in the organometallic literature. Several metallacyclopentane complexes have been found which decompose to yield 1-butene or 2-butene when heated.[15] (This fact is not intended as an endorsement of a surface metallacyclopentane bonding configuration.) The formation of 1-butene is generally presumed to occur via β-hydrogen elimination to form a 3-buteneyl species (**4**) followed by rehydrogenation-(Scheme 2). The mechanism depicted in Scheme 2 was also invoked by Bent et al.[3] to account for the formation of 1-butene from 1,4-diiodobutane on Al(100).

In conclusion, we have presented evidence for the formation of a C_4 metallacycle from the dissociative chemisorption of cyclobutane on Ru(001) at 180 K. Upon heating, this species decomposes to yield a 1-butene desorption product as well as surface carbon and hydrogen.

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