

Temperature programmed desorption study of C₆H₁₂/Zr(0001)

N. Stojilovic, J. C. Tokash, S. P. McGinnis, and R. D. Ramsier^{a)}

*Departments of Physics, Chemistry, and Chemical Engineering, The University of Akron,
Akron, Ohio 44325*

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Temperature programmed desorption (TPD) has been used to investigate the behavior of cyclohexane (C₆H₁₂) on Zr(0001) and the effects of 500 eV electron bombardment on its desorption characteristics. Following adsorption at 150 K, molecular desorption above 600 K suggests exceptionally strong interaction between C₆H₁₂ and Zr(0001). These high-temperature desorption features shift to higher temperatures with increasing exposure. Electron bombardment alters TPD profiles and results in small quantities of H₂ desorption from C₆H₁₂/Zr(0001) at about 310 K.
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I. INTRODUCTION

The technological use of zirconium and its alloys in the production of a wide variety of organic compounds is well known.¹ This class of structural materials offers advantages such as excellent corrosion resistance in organic media with respect to other engineering alloys. Understanding the interaction of the surface of these materials with organic species is therefore of applied interest. Our recent studies of the behavior of organic molecules on Zr(0001) indicate an unusually strong interaction between the adsorbed molecules and zirconium surfaces. Following adsorption at 150 K, methanol² desorbs near 600 K, whereas benzene^{3,4} desorbs above 700 K. Based on a recent detailed study of the benzene/Zr system, which included Auger electron spectroscopy (AES) and temperature programmed desorption (TPD),⁴ the following picture emerges: benzene dissociates at low exposures, forming a carbidic layer that initially involves the exchange of carbon with subsurface oxygen. This modified surface strongly adsorbs benzene, producing C₂H₂ and C₄H₄ in thermal desorption experiments. The amount of molecular benzene desorbing, relative to that of the dissociation by-products, increases with exposure as the surface becomes less aggressive with increasing coverage. Consistently, AES data indicate the presence of graphitic carbon at high coverages, and carbidic remnants after thermal desorption.

The present study builds on this previous work, and investigates the C₆H₁₂-Zr(0001) interaction. It is of fundamental interest to compare cyclohexane with benzene on Zr(0001), as each molecule exhibits the same hexagonal symmetry as the surface. In addition, the pi bonding of the aromatic six-member ring to the surface will differ from that of the cyclic alkane, and we are interested in determining how these differences manifest themselves during heating. We also report here on electron bombardment effects on adsorbed C₆H₁₂, and compare these to the benzene system as well. Our preliminary results on C₆H₁₂/Zr(0001)⁵ revealed

unusually high desorption temperatures and electron bombardment effects, making this comparison worth pursuing in more detail here.

Numerous studies of cyclohexane on various surfaces exist in the literature. In most of these studies molecular desorption occurs below room temperature. For example, cyclohexane desorption is observed from Pt(100) at temperatures as low as 180 K.⁶ In the same study dehydrogenation of cyclohexane to benzene is observed. From a ZnO(0001) surface, cyclohexane desorbs intact near 220 K, whereas with the introduction of Pt islands, only a fraction of the parent molecules desorb at 250 K and more than 60% dehydrogenate.⁷ In a study of cyclohexane on Ni(111), molecular desorption shifted from 185 to 192 K with increasing exposure but dehydrogenation was not observed.⁸ Madey and Yates reported monolayer cyclohexane desorption at 227 K from Ru(001), with multilayers desorbing at lower temperatures.⁹ Their electron stimulated desorption (ESD) studies with 100–200 eV electrons indicate that H⁺ is liberated from adsorbed C₆H₁₂ at coverages less than 1 ML. However, multilayers produce ESD ions in a distribution similar to what one would measure from gas phase cyclohexane using a mass spectrometer.

II. EXPERIMENTAL DETAILS

Experiments were conducted under ultrahigh vacuum conditions at a base pressure of approximately 2×10^{-10} Torr. Details of the ultrahigh vacuum chamber and its pumping system can be found elsewhere.¹⁰ Exposure to cyclohexane (B&J, purity >99.9%) was performed with the sample at 150 K in line of sight with respect to a molecular beam doser.⁴ During dosing the background pressure increases by a factor of ~10, as measured by an ion gauge. Zirconium is a reactive getter material, and requires several sputtering cycles before each experiment (Ar⁺, 2 keV, 2 μ A cm⁻²). The first sputtering cycle for each day's experiments was with the sample at room temperature. After cooling and then annealing, subsequent sputtering was performed with the sample near 150 K. The heating rate for TPD and

^{a)}Author to whom correspondence should be addressed; electronic mail: rex@uakron.edu

annealing was 1.8 K/s, and the annealing temperature was kept below 870 K to avoid possible sulfur diffusion to the surface.¹¹

After several 2 h sputtering/annealing cycles the cleanliness of the surface was monitored by retarding-field AES. For these measurements an electron beam with 3 keV energy and 15 $\mu\text{A cm}^{-2}$ current density were used. For collecting TPD spectra the sample was positioned in line of sight with respect to a quadrupole mass spectrometer. Reverse-view low-energy electron diffraction (LEED) is used to probe the ordering of the surfaces. For LEED experiments the electron beam energy was 67 eV, with a current density of 2 $\mu\text{A cm}^{-2}$.

The Zr(0001) single crystal is cylindrical, with radius and thickness 3 and 1 mm, respectively. The crystal is polished on one side down to 30 nm with uncertainty in orientation less than 1°. Two thermocouples (type E) and two tantalum wires are spot welded to the sample. The tantalum wires provide dc heating, whereas the thermocouples complete a temperature-controlled feedback loop. For cooling the sample, a copper braid, attached to a liquid-nitrogen cold finger, was used.

III. RESULTS AND DISCUSSION

Figure 1 shows TPD spectra of C₃H₅⁺ obtained following C₆H₁₂ adsorption at 150 K. The C₃H₅⁺ fragment has been chosen for presentation due to higher signal intensity than the parent molecular ion. For exposures below 3 $\times 10^{14}$ molecules/cm² only a small amount of desorption is observed below 600 K. On the other hand, exposures above 4 $\times 10^{14}$ molecules/cm² result in desorption peaks that contain high-temperature shoulders. The main peaks and shoulders most likely reflect tilted and flat-lying geometries of adsorbed molecules. The peak profile changes as a function of exposure and the desorption yield appears to saturate near 20 $\times 10^{14}$ molecules/cm². Note the small peak below 200 K, possibly from a physisorbed layer. However, since the temperature ramp is not linear below 200 K in our experiments, we make no attempt to determine the activation energy for desorption. It should be noted that only desorption of cyclohexane and its cracking fragments have been observed in our thermal desorption experiments.

Figure 2 shows TPD spectra of C₃H₅⁺ obtained following C₆H₁₂ adsorption at 150 K and 500 eV electron bombardment at the same temperature. In this series of experiments, the electron fluence was kept at approximately 9 $\times 10^{16}$ electrons/cm² for various cyclohexane exposures. Desorption peak positions shift to higher temperature with increasing exposure, similar to what is observed when no electron bombardment is applied. It is evident that electron bombardment affects desorption peak profiles in such a way that the high-temperature shoulder is now unresolved. However, there is an indication of a low-temperature shoulder at the highest exposures. These differences may indicate changes in molecular orientation (i.e., flat versus tilted adsorbates) due to electron bombardment. TPD yields are slightly

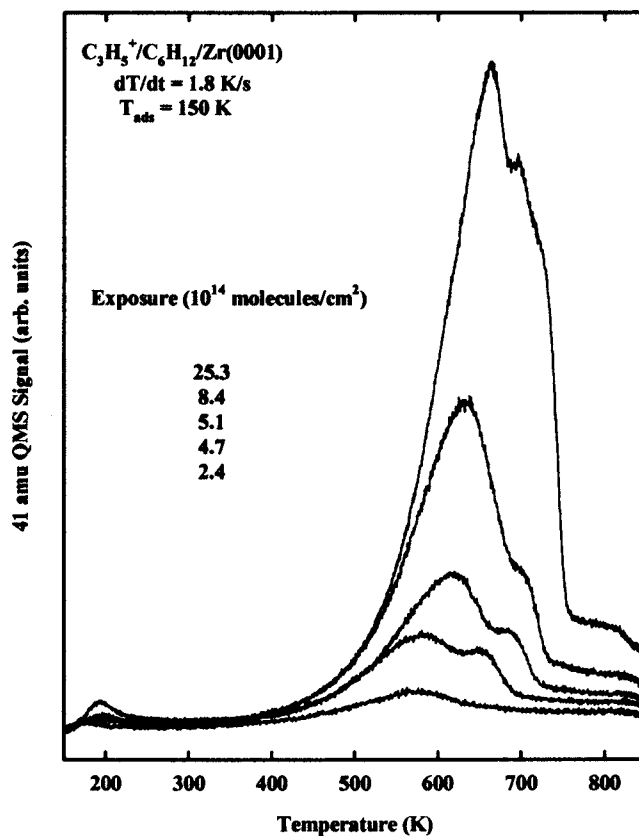


Fig. 1. Thermal desorption spectra of C₃H₅⁺ following C₆H₁₂ adsorption on Zr(0001) at 150 K. The unusually high desorption temperature is indicative of strongly chemisorbed cyclohexane. The high-temperature shoulder reflects the presence of more than one C₆H₁₂-Zr(0001) binding state.

lower and tend toward saturation at approximately the same exposure as in the case without electron bombardment (Fig. 1).

Figure 3 clearly shows the effect of exposure and electron bombardment on the desorption peak temperature. Hollow data points are from the case when no electron bombardment is performed. As the cyclohexane exposure is increased, the desorption peak shifts toward higher temperatures. Interestingly, the difference can be as high as approximately 100 K. Beyond 20 $\times 10^{14}$ molecules/cm² no further increase in desorption temperature is observed, which is consistent with the fact that the TPD yields saturate. The solid data points in Fig. 3 reflect desorption peak temperatures after electron bombardment of C₆H₁₂/Zr(0001) and subsequent heating. For exposures in the range studied, electron bombardment shifts the desorption peak maxima about 50 K higher with respect to the case without electronic excitation. For exposures above 15 $\times 10^{14}$ molecules/cm² the desorption peak maxima exceed 700 K.

However, unlike the C₆H₆/Zr(0001) system, electron bombardment of C₆H₁₂/Zr(0001) produces small quantities of hydrogen in subsequent TPD experiments. Figure 4 shows H₂ integrated peak areas versus electron fluence for a C₆H₁₂ exposure of approximately 3.8 $\times 10^{14}$ molecules/cm². Electron bombardment slightly reduced the amount of desorbing parent molecules and resulted in H₂ desorption near 310 K in

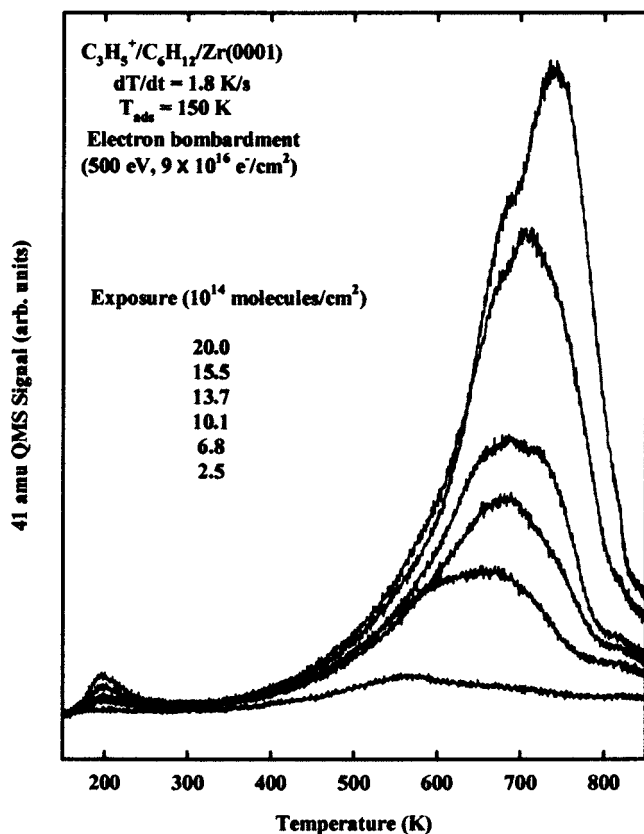


Fig. 2. Thermal desorption spectra of $C_3H_5^+$ following C_6H_{12} adsorption and 500 eV electron bombardment at 150 K. For various exposures the electron fluence has been kept constant at 9×10^{16} electrons/cm². Electron bombardment affects both the desorption profiles and temperatures.

TPD. The inset to Fig. 4 shows one such TPD spectrum of hydrogen. Note the rapid desorption of hydrogen above 800 K. This high-temperature hydrogen desorption from zirconium has also been observed by others.¹²

It is interesting that electron bombardment of $NH_3/Zr(0001)$ ¹³ and $D_2O/Zr(0001)$ ¹⁴ also induced hydrogen desorption at approximately the same temperature as we find for the cyclohexane case. It is not clear what mechanism is responsible for this hydrogen desorption. Almost exactly the same desorption temperature for hydrogen in these three different systems suggests that they originate from the same type of surface-bound intermediate. Presumably this involves some type of Zr–H interaction, since it seems unlikely that N–H, O–H, and C–H intermediates on Zr(0001) would all liberate H_2 at similar temperatures. However, the lack of hydrogen desorption in the case of benzene⁴ indicates that electron bombardment of hydrogen-containing species is not sufficient to guarantee subsequent H_2 production in TPD. Therefore the nature of the adsorbed species and its binding to the surface plays an important role.

Data from AES studies of the $C_6H_{12}/Zr(0001)$ system exhibit similar trends to those reported for $C_6H_6/Zr(0001)$ ^{3,4} and are therefore not shown here. To summarize, the presence of carbon is more pronounced after high-temperature (870 K) annealing of a cyclohexane covered surface than immediately after exposure. This is due to shielding effects

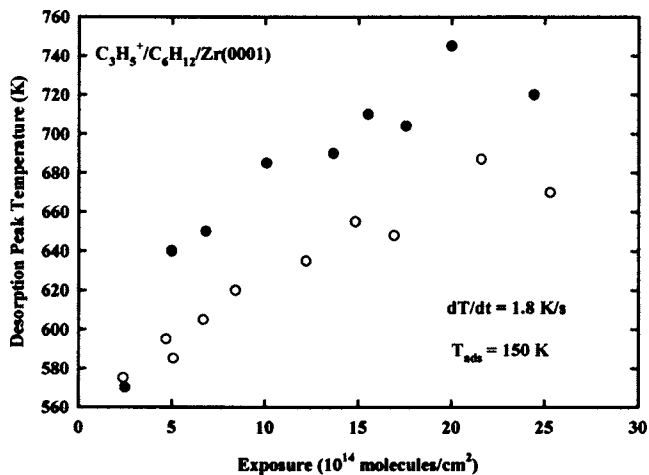


Fig. 3. Desorption temperature versus cyclohexane exposure when no electron bombardment is applied (hollow data points) and following exposure to 500 eV electrons (solid data points). The electron fluence was 9×10^{16} electrons/cm² for the latter data set. The electron bombardment primarily affects adsorbed molecules with tilted geometry.

that are reduced after hydrogen desorption takes place close to the annealing temperature. No effects of 500 eV electron bombardment on the surface carbon content are observed in AES experiments. This is consistent with the fact that TPD yields are slightly reduced only at higher exposures, and therefore that electron bombardment does not directly remove carbon-containing species from the surface at lower exposures. This interpretation is in agreement with early work of Madey and Yates,⁹ who demonstrated that only H^+ desorbed via ESD mechanisms from $C_6H_{12}/Ru(001)$ at low coverages.

LEED experiments of the $C_6H_{12}/Zr(0001)$ system were performed in stepwise annealing fashion. Adsorbed cyclohexane did not exhibit ordering upon adsorption or after stepwise annealing to various temperatures and subsequent

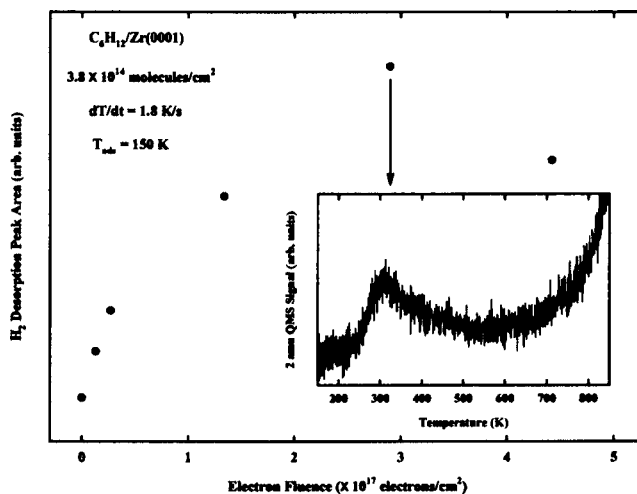


Fig. 4. Integrated hydrogen TPD areas, following electron bombardment of $C_6H_{12}/Zr(0001)$ at 150 K, versus electron fluence. The inset shows the H_2^+ desorption profile for the data point indicated by the arrow. The cyclohexane exposure was 3.8×10^{14} molecules/cm² in all cases presented here.

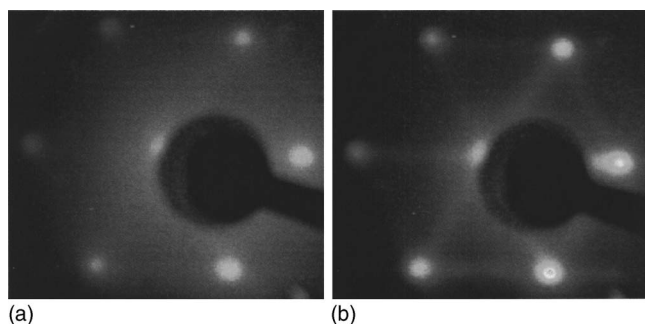


FIG. 5. LEED images (A) after cyclohexane exposure (12.6×10^{14} molecules/cm²) and electron bombardment (9×10^{16} electrons/cm²), and (B) after annealing. Only a 1×1 carbon superstructure can be inferred in these data from a Zr(0001) surface.

cooling. Diffuse patterns are observed after adsorption in cases without or with electron bombardment as shown in Fig. 5(a). High-temperature annealing results in 1×1 patterns like that of Fig. 5(b), which resembles patterns from a cleaned surface. The presence of carbon following annealing, which was clearly detected by AES, is only reflected in an increased brightness of the LEED spots. LEED intensity analysis has confirmed an ordered (1×1)-C structure in a study of C₂H₄ on Zr(0001),¹⁵ and it is likely that similar structures are present in our work.

The main findings of this work are:

(1) Cyclohexane partially dissociates on Zr(0001), especially at low coverages, depositing carbon and leading to the desorption of H₂ during high-temperature annealing. No other desorbing species are detected.

(2) Molecular cyclohexane desorption dominates after higher exposures. The exceptionally high desorption temperatures increase further with exposure.

(3) Electron bombardment further increases the desorption temperature of C₆H₁₂, alters the TPD profiles, and results in small amounts of H₂ desorption just above room temperature.

In comparison, for the C₆H₆/Zr(0001) system, we have observed that (see Refs. 3 and 4):

(1) Benzene partially dissociates on Zr(0001), especially at low exposures, depositing carbon and leading to the desorption of H₂ during high-temperature annealing. However, C₂H₂ and C₄H₄ products are detected during TPD, and are relatively more abundant at low coverages.

(2) Molecular benzene desorption dominates at higher exposures, at exceptionally high desorption temperatures, which increase with exposure. These temperatures are higher than in the cyclohexane case.

(3) Electron bombardment alters the TPD profiles, but does not result in H₂ desorption near room temperature.

Therefore, we see similarities and differences between these two molecules adsorbed on Zr(0001). It is not surprising that we see decomposition at low coverages in both systems, since zirconium is very reactive. In addition, the behavior of the carbon and hydrogen remnants is consistent with the literature. Our interpretation for C₆H₁₂/Zr(0001) is that at low coverages, irreversible dissociation occurs. This

carbon-modified surface then becomes less aggressive toward dissociation but still strongly binds subsequent adsorbates. Eventually, the effect saturates as the sticking coefficient approaches zero.

Both of these systems exhibit high desorption temperatures, with benzene slightly higher presumably due to its pi-bonding ability. Similar to the case of propylene adsorption on Si(100),¹⁶ the desorption features shift to higher temperatures with increasing exposure. This can be attributed to an attractive interaction between the adsorbates. In the absence of electron bombardment, both systems exhibit coverage-dependent overlapping desorption features, presumably due to different adsorption geometries (e.g., flat versus tilted) with similar activation energies. Electron bombardment alters these TPD profiles, possibly indicating molecular reorientation induced by electronic excitation. This reorientation is primarily a result of electron bombardment effects on tilted C₆H₁₂ molecules. Since an electron beam energy of 500 eV is sufficiently high to dissociate the molecules completely, this energy must be rapidly distributed into other channels. The shift to higher desorption temperatures following electron bombardment is consistent with the electron-induced dissociation of C–H bonds and subsequent recombination in TPD, which delays desorption of the parent molecules.

In addition, low-temperature hydrogen desorption is observed for cyclohexane but not for benzene. This difference may indicate that the delocalized pi system of benzene dissipates energy quicker than the alkane ring, leading to a lower probability of electron-induced dissociation. The higher desorption temperature of benzene with respect to cyclohexane indicates stronger binding to the zirconium surface, therefore making it more stable. In addition, cyclohexane has twice the number of hydrogen atoms as benzene. This increases the likelihood of their liberation by electron impact, and the probability that they will recombine via surface diffusion to form H₂ during TPD.

It is clear from the work of Xu and Koel¹⁷ that cyclohexane, in the physisorbed state, has a very high cross section for electron induced C–H bond scission. The C–C bonds are much more stable, as are cyclohexyl radicals that strongly bind to the surface (Pt in the case of Ref. 17). Our results are consistent with these findings, except that in our case we are using a highly reactive getter surface (Zr). This promotes thermally induced dissociation at low coverage, and very strong binding of subsequently adsorbed molecules. This strong adsorption, with the associated electronic coupling to the surface, quenches the excitations produced by electron bombardment.

IV. SUMMARY

Our ultimate goal is understanding and controlling the surface chemistry of adsorbed molecules on zirconium surfaces. We have observed that organic molecules on the surface of this gettering material behave quite differently than carbon-free molecules. Here, we report unusually high desorption temperatures for cyclohexane from zirconium

(0001) surfaces, which indicate strong chemisorption. This is accompanied by irreversible dissociation at low coverages, leaving carbon on or just beneath the surface. As exposure is increased the desorption features shift toward higher temperatures and the peak profiles change, presumably indicating intermolecular attractive interactions and orientational differences, respectively. Electron bombardment of adsorbed cyclohexane affects primarily tilted molecules. These changes, together with only a small effect on desorption yields, indicate that the 500 eV electrons stimulate C–H scission rather than C–C bond breaking, and induce molecular rearrangements. Additionally, exposure to electrons results in low-temperature hydrogen desorption, the yield of which depends on electron fluence.

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