

Effects of electron bombardment on the thermal desorption of cyclic hydrocarbons from zirconium surfaces

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Received 13 July 2004; in final form 8 September 2004

Available online 26 October 2004

Abstract

In this Letter, we compare the effects of 500 eV electron bombardment on the thermal desorption of benzene (C_6H_6) and cyclohexane (C_6H_{12}) from $Zr(0\ 0\ 0\ 1)$ surfaces. In both cases, unexpectedly high desorption temperatures above 600 K indicate strong adsorbate-substrate interaction. Two desorption states are observed for each molecule, presumably due to tilted and flat molecular orientations. Electron fluence does not significantly alter the amount of desorbing species, but for $C_6H_{12}/Zr(0\ 0\ 0\ 1)$ results in small amounts of H_2 desorption near 310 K. Electron bombardment seems to affect the tilted species more than the flat-lying species.

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1. Introduction

This report considers the use of electron bombardment to modify the thermal desorption behavior of benzene and cyclohexane adsorbed on $Zr(0\ 0\ 0\ 1)$. Our previous studies of electron bombardment effects on the $NH_3/Zr(0\ 0\ 0\ 1)$ [1] and $D_2O/Zr(0\ 0\ 0\ 1)$ [2] systems at low temperatures reveal molecular hydrogen desorption just above room temperature as a result of electronic excitation. This electron-induced thermal desorption of hydrogen is interesting since previous studies reported desorption of hydrogen, but only at much higher temperatures [3,4]. Zirconium surface chemistry is often influenced by surface-subsurface exchange, especially in cases involving O, N and H species. The fact that we observe molecular hydrogen desorption at low temperatures following electron bombardment of adsorbed water and ammonia is indicative of a surface-stabilized form of hydrogen that does not undergo sub-surface diffusion.

We have also shown that carbon-containing molecules [5,6] exhibit drastically different desorption kinetics than carbon-free species [7] on $Zr(0\ 0\ 0\ 1)$, possibly due to differences in the surface-subsurface exchange process. An exceptionally strong interaction of benzene with $Zr(0\ 0\ 0\ 1)$, reflected in benzene desorption above 700 K, also results from the unique surface chemistry of zirconium [6]. Low-energy electron diffraction (LEED) data did not reveal any superstructure patterns in these previous experiments, consistent with the fact that carbon only forms 1×1 patterns on $Zr(0\ 0\ 0\ 1)$ [8]. In the present study, we investigate the $C_6H_6/Zr(0\ 0\ 0\ 1)$ and $C_6H_{12}/Zr(0\ 0\ 0\ 1)$ systems, specifically with regard to electron bombardment effects. Since we did not observe electron bombardment effects in Auger electron spectroscopy (AES) and LEED experiments this Letter will focus on temperature programmed desorption (TPD) results only.

2. Experimental details

The zirconium single crystal used in this study has a cylindrical shape with a radius of 3.0 mm and a thickness

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of 1.0 mm. The crystal was polished on one side with the uncertainty in orientation of the (0 0 0 1) plane less than 1° . Experiments were conducted at pressures of 2.0×10^{-10} Torr or below. Benzene (Fisher, purity >99.0%) and cyclohexane (B&J, purity >99.9%) were further purified from atmospheric gases by several freeze-pump-thaw cycles. The gas-handling system was pumped by a turbo-molecular pump prior to each experiment.

The sample temperature was increased at the rate of 1.8 K/s by resistive heating. For TPD experiments the sample was facing the mass spectrometer in a line-of-sight geometry. Exposing the sample to hydrocarbon gases via a line-of-sight molecular beam doser raised the background pressure by a factor of approximately 10. Before each zirconium exposure to benzene or cyclohexane, the surface was cleaned by several sputtering and annealing cycles. Surface cleanliness was verified by AES, as discussed in a previous report [9]. The electron gun (VG Scientific, LEG 41) for electron bombardment studies was operated in Mode 2 with a fixed beam energy of 500 eV. The spot size, determined with a phosphor screen mounted on the back side of the sample manipulator, was larger than the Zr(0 0 0 1) crystal to ensure uniform electron flux.

3. Results and discussion

Fig. 1a shows TPD spectra of benzene following benzene adsorption on Zr(0 0 0 1) at 150 K. For expo-

sure below 15.0×10^{14} molecules/cm², the high-temperature desorption state, β , is more pronounced. As exposure is increased further the low-temperature desorption state, α , starts to dominate. The presence of two desorption states is most likely a result of two geometries of adsorbed benzene molecules, similar to what was reported for Ru(0 0 1) [10]. We propose that the orientation of adsorbed benzene molecules on Zr(0 0 0 1) is coverage dependent, which would explain the change in TPD profiles. We would assign the high temperature β state to flat-lying benzene, which is thermally more stable than the tilted α state. Following benzene desorption the zirconium surface retains carbon, as confirmed by AES experiments. This indicates that some irreversible dissociation occurs. Saturation coverage does not appear to be reached with exposures up to 35.0×10^{14} molecules/cm².

Fig. 1b presents benzene TPD spectra following electron bombardment of adsorbed benzene. The electron fluence was constant at 2.0×10^{17} electrons/cm², with a 500 eV electron beam energy. With respect to Fig. 1a, we observe changes in the peak profiles as a consequence of electronic excitation. We emphasize here the overall trends in our data throughout the exposure range, and have not attempted to use exactly the same molecular exposures for direct, detailed comparisons. The β state dominates throughout all exposures studied here when electron bombardment is used, and does not shift very much in temperature. It is evident that electronic excitation alters the orientation of adsorbed benzene

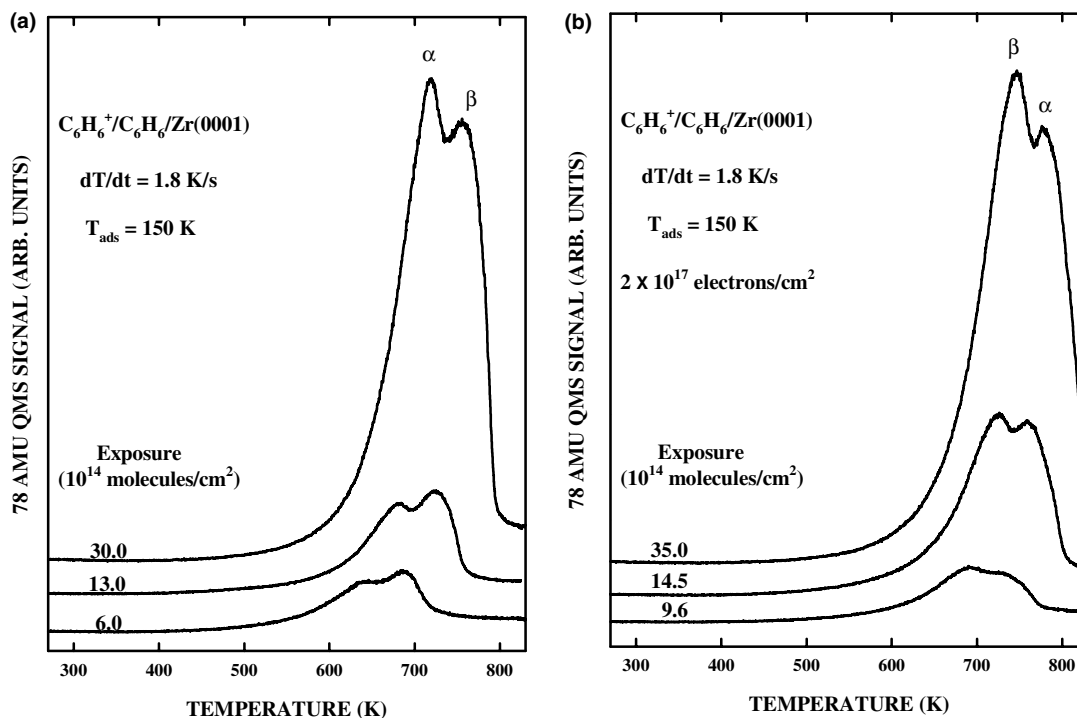


Fig. 1. (a) Desorption of benzene following benzene adsorption on Zr(0 0 0 1) at 150 K. (b) Desorption of benzene following benzene adsorption on Zr(0 0 0 1) at 150 K and electron bombardment (500 eV, 2.0×10^{17} electrons/cm²).

molecules, pushing the desorption of the more weakly-bound α state to higher temperatures.

It is interesting to note that calculation of the area below the desorption features indicates that electron bombardment does not influence the amount of desorbing benzene significantly. Possibly, electron bombardment results in the production of more flat-lying (β state) benzene, and the dissociation of C–H bonds in the tilted α state. Most likely during heating, hydrogen recombines with phenyl fragments and desorbs as benzene, as was reported for $C_6H_6/Au(111)$ subjected to electron bombardment [11]. The shift in the α state desorption temperature is consistent with electron-induced dissociation of C–H bonds and subsequent recombination in TPD, which delays desorption of the parent molecules. However, such a shift was not observed for the $Au(111)$ system. It should be noted that we did not observe biphenyl in TPD, however we detect C_2H_2 and C_4H_4 at low exposures even without electron bombardment. This system is discussed in more detail elsewhere [12].

Fig. 2a shows $C_3H_5^+$ TPD spectra following adsorption of C_6H_{12} at 150 K. The $C_3H_5^+$ signal is shown since it has a higher intensity than $C_6H_{12}^+$. Similar to benzene, cyclohexane desorbs via two desorption states. The desorption features are relatively broad and the desorption peak maxima above 600 K indicate strong interactions of the adsorbed molecules with the $Zr(0001)$ surface. The α state is more pronounced for all exposures. Saturation is reached by exposures of about 20×10^{14} molecules/cm².

Following C_6H_{12} desorption the surface retains some carbon, similar to what was observed in experiments with C_6H_6 . Fig. 2b shows how electron bombardment of $C_6H_{12}/Zr(0001)$ changes subsequent TPD spectra. Note that only one broad peak is detected, and it is shifted toward higher temperatures. Integrated TPD peak areas indicate that electron bombardment only slightly reduces the amount of desorbing species.

Unlike the benzene case, Fig. 3 shows H_2 desorption from $C_6H_{12}/Zr(0001)$ near 310 K, induced by electronic excitation. For a constant cyclohexane exposure of $\sim 3.8 \times 10^{14}$ molecules/cm², varying the electron fluence changes the amount of desorbing hydrogen. No increase in hydrogen desorption is observed above a fluence of 3.0×10^{17} electrons/cm². It is interesting that similar desorption of hydrogen near room temperature has been seen from $Zr(0001)$ following adsorption of ammonia [1] and isotopic water [2]. However, electron bombardment of $C_6H_6/Zr(0001)$ does not induce hydrogen desorption. Note that above 800 K rapid hydrogen desorption takes place, consistent with earlier studies of zirconium surface chemistry [3,4].

It is the comparison of these two cyclic hydrocarbon systems, and the effects of electron bombardment, that is the main purpose of this Letter. Both benzene and cyclohexane desorb at unexpectedly high temperatures indicating strong interactions with the zirconium surface. In both experiments zirconium retains some carbon following desorption, indicating partial irreversible dissociation. In the absence of electron bombardment, two

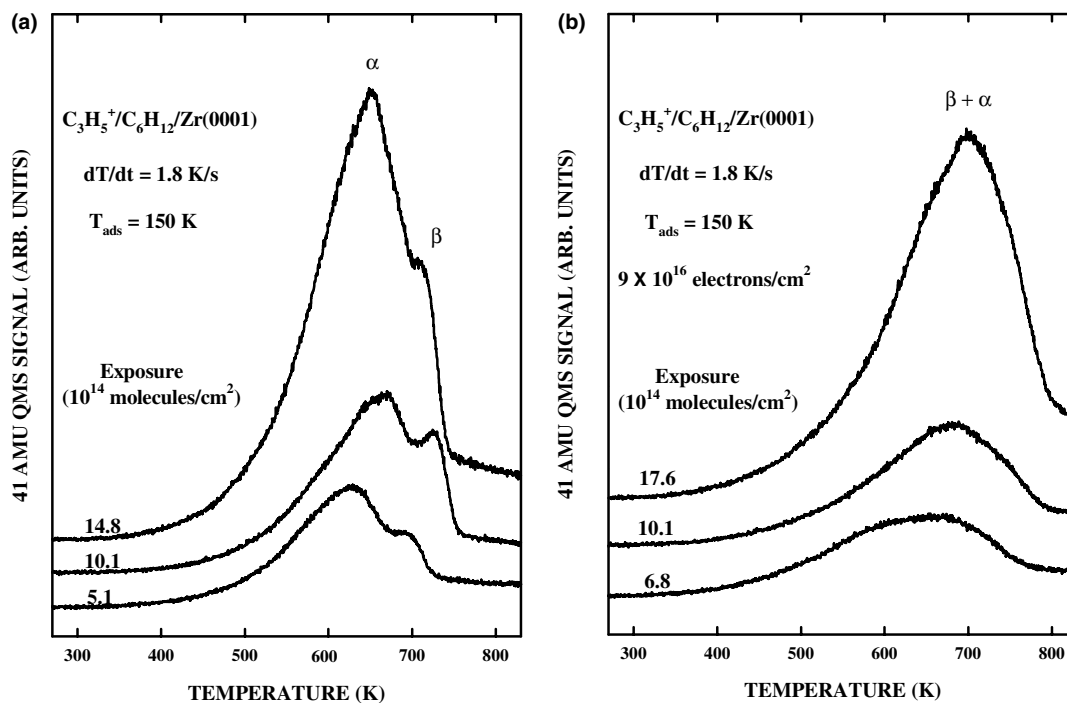


Fig. 2. (a) Desorption of cyclohexane following cyclohexane adsorption on $Zr(0001)$ at 150 K. (b) Desorption of cyclohexane following cyclohexane adsorption on $Zr(0001)$ at 150 K and electron bombardment (500 eV, 9.0×10^{16} electrons/cm²).

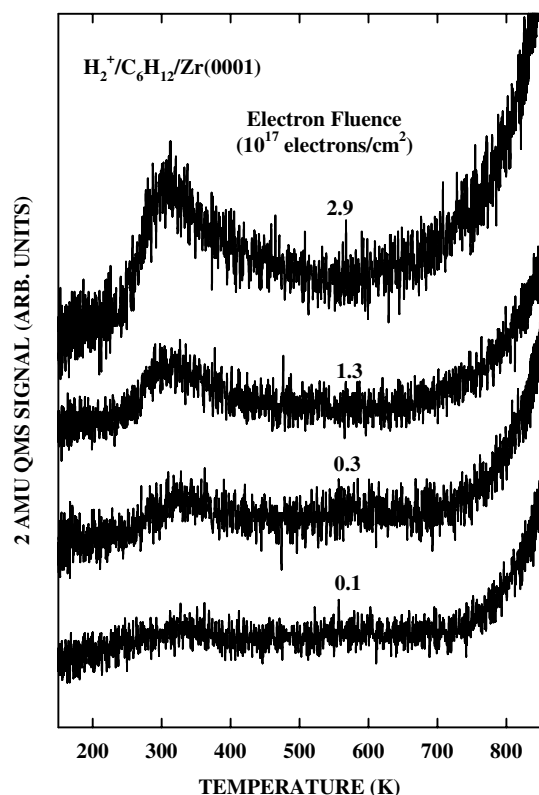


Fig. 3. Desorption of molecular hydrogen following 150 K adsorption of C_6H_{12} and electron bombardment. The figure indicates how H_2 desorption near room temperature depends on electron fluence. For the spectra presented here the C_6H_{12} exposure was $\sim 3.8 \times 10^{14}$ molecules/cm².

desorption features are identified in both cases, presumably due to different adsorption geometries (e.g., flat vs. tilted). Presumably, our adsorption temperature of 150 K is too high to allow for the condensation of multilayers of benzene and cyclohexane. We can not conveniently cool our sample below 150 K, so that the formation of multilayers is not part of our study.

Electron bombardment of benzene does not seem to affect the β state, but changes the α state significantly. For the case of cyclohexane, electron bombardment significantly alters the TPD profiles, eliminating the distinction of the two molecular desorption states. This possibly indicates molecular reorientation induced by electronic excitation. These differences may be attributed to the different bonding of the flat vs. tilted geometries of these two ring systems to the surface. The flat-lying β states may allow for dissipation of the energy provided to their electronic manifold by electron impact. Inferring that the higher temperature β states of both species indicate stronger binding and back-donation from the zirconium surface, these ring/Zr complexes are presumably stabilized more than the tilted α states with respect to electron-induced dissociation.

Finally, cyclohexane has twice as many H-atoms as benzene. This increases the probability that more

protons will be liberated by electron impact, and also the likelihood that they will encounter one another to form H_2 during heating. Recall that we observe H_2 in TPD from cyclohexane, but not from benzene. This is consistent with the fact that hydrogen atoms are bound to aromatic rings more strongly than to alkane rings.

4. Summary

Both C_6H_6 and C_6H_{12} exhibit strong interactions with Zr(0 0 1) surfaces as indicated by unexpectedly high desorption temperatures. Electron bombardment of both $C_6H_6/Zr(0 0 1)$ and $C_6H_{12}/Zr(0 0 1)$ alters TPD profiles, with the more stable (flat-lying) rings desorbing near the same temperature but with the tilted species shifting to higher temperatures. This is presumably due to the time it takes for C–H recombination to occur during TPD ramping, and needs further investigation. Electronic excitation of the alkane system results in desorption of molecular hydrogen near 310 K. On the other hand, electron-bombardment-induced hydrogen desorption is not observed from $C_6H_6/Zr(0 0 1)$. This comparison of aromatic vs. alkane molecules adsorbed on Zr(0 0 1) points to the role of energy dissipation mechanisms of electronically-excited species interacting strongly with a reactive metal system.

Acknowledgements

Acknowledgement is made to the Donors of the American Chemical Society Petroleum Research Fund for partial support of this research. We are grateful for the insightful comments of an anonymous reviewer that helped us improve this manuscript significantly.

References

- [1] N. Stojilovic, Y.C. Kang, R.D. Ramsier, *Surf. Interface Anal.* 33 (2002) 945.
- [2] S. Ankrah, Y.C. Kang, R.D. Ramsier, *J. Phys.: Condens. Matter.* 15 (2003) 1899.
- [3] J.S. Foord, P.J. Goddard, R.M. Lambert, *Surf. Sci.* 94 (1980) 339.
- [4] J.-M. Lin, R.E. Gilbert, *Appl. Surf. Sci.* 18 (1984) 315.
- [5] N. Stojilovic, D.W. Weber, R.D. Ramsier, *Appl. Surf. Sci.* 218 (2003) 188.
- [6] N. Stojilovic, R.D. Ramsier, *Solid State Commun.* 130 (2004) 623.
- [7] Y.C. Kang, R.D. Ramsier, *Surf. Sci.* 519 (2002) 229.
- [8] J.R. Lou, P.C. Wong, K.A.R. Mitchell, *Can. J. Chem.* 66 (1988) 3157.
- [9] N. Stojilovic, J.C. Tokash, R.D. Ramsier, *Surf. Sci.* 553 (2004) 23.
- [10] J. Günster, J. Stultz, S. Krischok, D.W. Goodman, *Chem. Phys. Lett.* 306 (1999) 335.
- [11] D. Syomin, J. Kim, B.E. Koel, G.B. Ellison, *J. Phys. Chem. B* 105 (2001) 8387.
- [12] N. Stojilovic, J.C. Tokash, R.D. Ramsier, *Surf. Sci.* 565 (2004) 243.