Footprints of a Surface Chemical Reaction: Dissociative Chemisorption of *p*-Diiodobenzene on Cu{111}[†]

G. S. McCarty and P. S. Weiss*

Department of Chemistry, The Pennsylvania State University, 152 Davey Laboratory, University Park, Pennsylvania 16802-6300

p-Diiodobenzene dissociatively chemisorbs on Cu{111} into three products—two iodine atoms and a surface-stabilized phenylene intermediate—at room temperature. The phenylene intermediates are mobile on copper terraces at 77 K, but can be trapped at atomic steps and impurity sites. Because of their rapid motion, no stable intermediates are observed by the scanning tunneling microscope on clean Cu{111} terraces. The I atoms remain in pairs on the surface, presumably at the site of dissociation. Initially, the phenylene intermediates preferentially adsorb at monatomic step sites. After saturating the step sites, additional phenylene intermediates adsorb at impurity sites on the atomic terraces.

Introduction

The mechanisms for many heterogeneously catalyzed reactions remain unknown. The determination of the active sites of the catalyst and the geometry of the adsorbed species are a key aspect of these reaction mechanisms. Defect sites, such as atomic steps, have long been speculated to be essential in heterogeneous catalysis.[1,2] Additionally, the geometry of the adsorbed species plays a key role in determining its reactivity, as the geometry determines which functional groups are available for direct reaction and which are not. Direct visualization of the atomic-scale morphology of the reactants, intermediates, and products provides valuable insights into these important factors and thus aids in the elucidation of the reaction mechanism. We use low-temperature scanning tunneling microscope (STM) to obtain this view. We are further able to measure the electronic perturbations of the surface and thus the substrate-mediated interactions between the adsorbates, and the electronic environment viewed by the molecules involved in the reaction.[3−7]

The interactions between copper surfaces and alkyl halides have been studied through a variety of surface techniques.[3,7−12] Many alkyl halides dissociate on copper surfaces forming an alkyl intermediate and a chemisorbed halide. The alkyl intermediates can then undergo coupling reactions and subsequently be desorbed.[8−11] Industrially, this method is used to join alkyl groups in procedures such as the Muller-Rochow production of organochlorosilanes and the Ullmann reaction.[13,14] Using similar chemistry, copper surfaces can be exploited for the disposal of halogenated hydrocarbons.

Copper cleaves carbon-halide bonds, especially C−I bonds.[9,10] In previous work, the C−I bond was cleaved when iodobenzene adsorbed to Cu{111} at temperatures above 175 K.[9,10] STM images have revealed that the resulting adsorbed I atoms produce a surface site at which phenyl intermediates are stabilized.[3,7] It is speculated that these sites may play a key role in coupling aryl groups from aryl halides on copper surfaces by stabilizing complexes of aryl intermediate pairs.[3,7]

Benzene on Cu{111} has also previously been studied using scanning tunneling microscopy and temperature-programmed deposition (TPD) on Cu{111}.[8,15,16] These studies have revealed that benzene preferentially adsorbs at step edges and defect sites. The STM investigations have also determined benzene to be mobile on Cu{111} at 77 K.[8,15,16] The studies of benzene and iodobenzene on Cu{111} have served as a guide for this work. We have chosen to study *p*-diiodobenzene here in the hopes of exploiting the interactions of the phenylene intermediates to self-assemble chains of polyphenylene and to elucidate the process by which these chains form. Here we present the results of the initial step in this process: the dissociative chemisorption of the reactant molecules.

Experimental Section

All experiments were performed with a STM in ultrahigh vacuum (UHV). The base pressure is $<4 \times 10^{-10}$ Torr at room temperature and substantially lower in the low-temperature STM chamber. The STM has been described in detail elsewhere.[17] Briefly, two room-temperature UHV chambers for sample preparation and analysis are mounted on an optical table. The actual STM is contained within an UHV chamber suspended from the optical table. The chamber containing the STM is surrounded by a liquid helium dewar.

The room temperature stage is equipped with a mass spectrometer for residual gas analysis as well as other surface preparation equipment. After the sample is prepared by a series of ion sputters and anneals, it is lowered approximately one meter to the UHV cryostat, where it is placed in an elevator that governs the sample motion onto and off of the STM itself. The chamber is also equipped with leak valves for dosing adsorbates.

The Cu{111} sample was electrochemically polished and prepared in a vacuum by repeated cycles of argon ion bombardment and annealing. A resistive heater maintained the sample at 600 K during Ar$^+$ bombardment. After 45 min, Ar$^+$ bombardment was halted and the crystal was maintained at 600 K and annealed for 15 min. The crystal quality was verified by using the STM prior to exposure to diiodobenzene.

A small amount of *p*-diiodobenzene was introduced into the system through a sapphire leak valve. Before dosing, the diiodobenzene was heated to ∼325 °C to increase its vapor
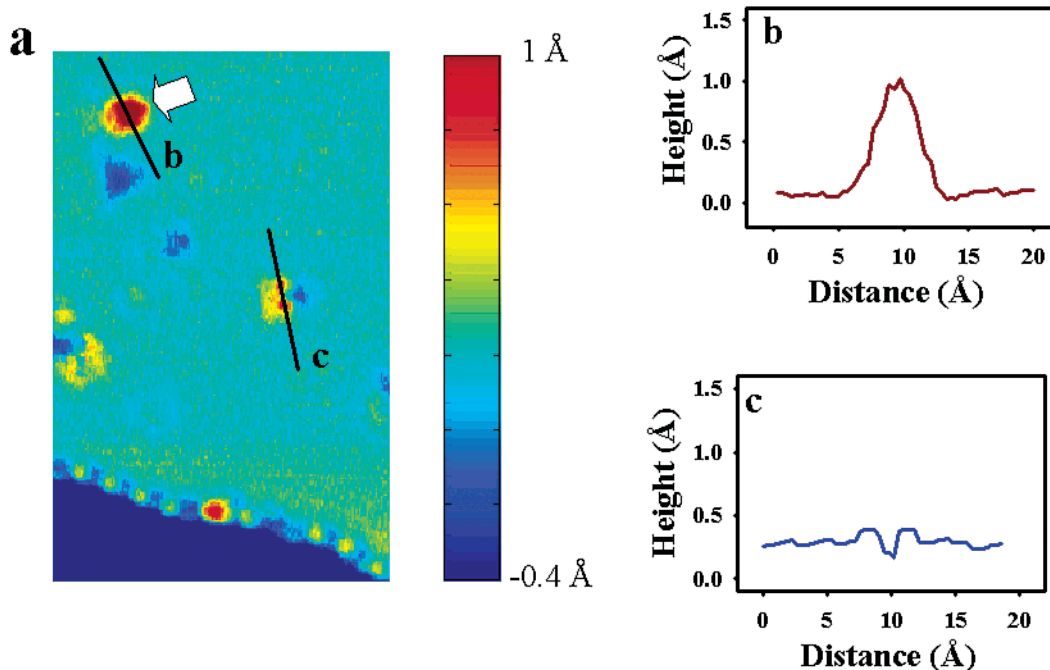
Figure 1. (a) STM image of Cu{111} exposed to 2 Langmuirs of *p*-diiodobenzene at room temperature. The diiodobenzene has dissociated into phenylene intermediates and I atoms on the surface. The image area is 70 Å × 110 Å, and a sample bias (V_s) of 200 mV and a tunneling current (i_t) of 30 pA. Note that the color scale is saturated, so that the lower terrace is beyond the lowest hue shown. (b) A cross section extracted from Figure 1a at the position marked **b** showing the apparent topographic profile of a phenylene intermediate as imaged by STM. (c) A cross section extracted from Figure 1a at the position marked **c** showing the apparent topographic profile of two I atoms as imaged by STM.

pressure. Also, prior to dosing the purity of the *p*-diiodobenzene was verified by mass spectrometry. In UHV, Cu{111} was exposed to *p*-diiodobenzene at room temperature so as to establish a submonolayer coverage of surface species. The sample remained at room temperature for approximately 10 minutes allowing the surface species to dissociate and to diffuse across the substrate prior to lowering the sample onto the STM, which was maintained at 77 K.

All images were acquired at 77 K in UHV. All imaging experiments lasted 3 days due to the low contamination rate in this low-temperature chamber.

Result and Discussion

Figure 1a shows the Cu{111} substrate after exposure to 1 L (1 × 10⁻⁶ Torr-seconds) of *p*-diiodobenzene. The I atoms (the small protruding features highlighted by the line marked **c**) are not mobile, and we conclude that they are strongly adsorbed to the copper surface. We typically find the I atoms in pairs separated by 3−5 Å. We assign the larger protruding feature in Figure 1a under the line marked **b** as an adsorbed phenylene. This phenylene has preferentially adsorbed on a Cu{111} terrace adjacent to at least one I atom. This I atom, highlighted by the white arrow, appears as a small protrusion adjacent to the phenylene intermediate. A number of phenylene intermediates have adsorbed to the atomic step propagating across the lower portion of the image. The observation of these surface species indicates that the *p*-diiodobenzene has indeed dissociated. An analogous result has been reported previously for phenyl pairs associating with iodine on Cu{111} as studied with the STM.[3,7] At low exposure (for our sample preparation an exposure of 1−2 L), *p*-diiodobenzene dissociates on the copper crystal resulting in two strongly adsorbed stationary I atoms and a mobile phenylene. The proximity of the pairs of I atoms indicates that the two dissociation reactions occur close both on the surface and in time. The second dissociation occurs

either simultaneously with the first or at least before the iodophenyl fragment can diffuse away from the site of the first dissociation.

Figure 1b displays a cross section of a single phenylene intermediate extracted from Figure 1a at the position marked **b**. These data indicate the apparent topographic height, ∼0.9 Å, and length, ∼5.0 Å, of the phenylene intermediate. The size of this surface species is comparable with our earlier STM images of benzene on Cu{111}.[3−5,7,15,16,18]

An analogous cross section was also extracted at position **c** in the image, showing the apparent topographic size of the I atoms as imaged by the STM. This cross section (Figure 1c) shows two I atoms in close proximity, each appearing as a protrusion approximately ∼0.2 Å high and ∼2.0 Å wide. The I atoms are separated by 4.0 Å. It is interesting to note that this distance is less than the 7.2 Å separation of the I atoms in *p*-diiodobenzene. This may be due to the atoms moving toward one another upon reaction due to substrate-mediated interactions, such interactions are apparent in the electronic structure as measured by STM of the I atoms.[4,5] Isolated I atoms on Cu{111} appear as protrusions surrounded by a depressed ring.[7,19] The two I atoms in proximity reduce the local density of states between them, apparent as the depression.

At low coverage the phenylene intermediates are mobile on the Cu{111} terraces, even at 77 K, preferentially adsorbing to atomic steps and defects. Other aromatics studied on Cu{111}, benzene and phenyl, have exhibited similar behavior.[3,7,16] Figure 2a−c shows a series of STM images of a Cu{111} atomic step after a 1 L exposure to *p*-diiodobenzene. In these images, seven phenylene intermediates are adsorbed at an atomic step. Figure 2d shows a cross section of data taken from Figure 2a at position **d**. The phenylene intermediate, highlighted by the circle in the cross section, has adsorbed at the atomic step and appears as a protrusion. Phenylene intermediates adsorb at monatomic substrate steps on the bottom copper terrace, parallel to the
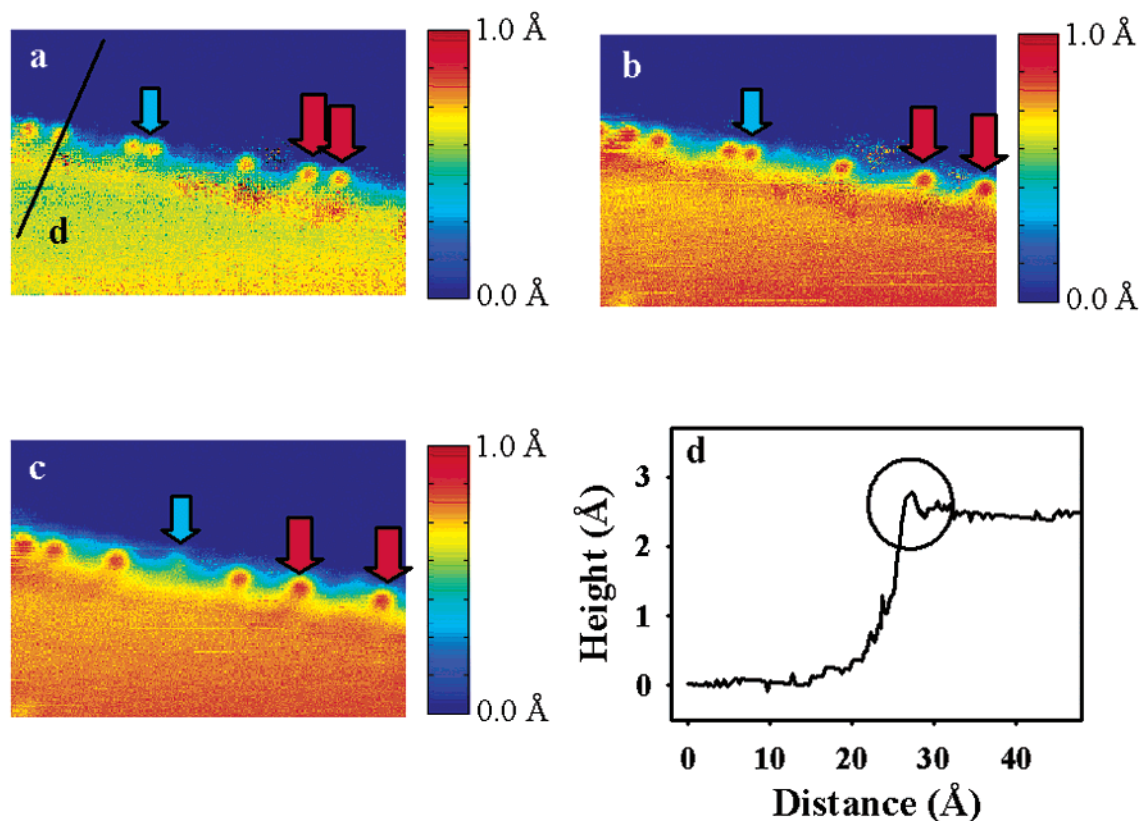
Figure 2. (a-c) A series of STM images of a Cu{111} monatomic step. Seven phenylene intermediates are adsorbed adjacent to the atomic step on the lower terrace. Each imaged area is 60 Å × 40 Å, and $i_t = 100$ pA. Note that the color scales are saturated, so that the lower terrace is beyond the lowest hue shown. The V_s values were (a) 200 mV, (b) 300 mV, and (c) 250 mV. (d) A cross section extracted from Figure 2a at the position marked **d** showing the profile of a phenylene intermediate adsorbed adjacent to an atomic step.

surface, to maximize the interaction between the phenylene and the atomic step. Similar results have previously been reported for benzene and phenyl on Cu{111}.[3,7,12,16]

At atomic steps and atomic defects (the preferential binding sites), tip-induced motion of individual phenylene species is observed even under mild tunneling conditions (sample bias of −200 mV and tunneling current of 100 pA). In each image in Figure 2a−c, a red vertical arrow highlights two of the phenylene intermediates adsorbed at the atomic step. In Figure 2a, the two phenylene intermediates are in close proximity, separated by ∼5 Å. In the next image, Figure 2b, collected 15 min later and after three scans, the phenylene intermediate on the right side of the pair has been moved, resulting in a separation increased to ∼10 Å. In Figure 2c, collected 5 min later, the phenylene intermediate on the left of the highlighted pair has moved, resulting in a separation of ∼12.5 Å.

In the same series of images, Figure 2a−c, a blue vertical arrow highlights an individual phenylene. In Figure 2a,b, this phenylene intermediate is adsorbed at the step edge and appears similar in size and shape to the other six phenylene intermediates in the images. In Figure 2c, however, this phenylene intermediate has moved to an adsorption site ∼2 Å from the atomic step. At this site, the interaction with the step has been reduced, resulting in a phenylene that appears elongated perpendicular to the step direction, and to be reduced in apparent height by ∼0.8 Å as compared to the phenylene intermediates adsorbed adjacent to the atomic step. The elongation and height of the phenylene intermediate support the conclusion that the atomic step influences the observed electronic properties of this phenylene. It is interesting to note that phenylene on sites in the middle of Cu{111} terraces appears in STM images as a protrusion ∼0.9 Å high, while this phenylene (∼2 Å from an atomic step) appears ∼1.6 Å high. Adjacent to an atomic step, phenylenes appear as protrusions 2.4 Å high. We have previously described how the strongest electronic perturbations on such surfaces are at atomic steps.[4,5] This electronic perturbation strongly influences the electronic structure and thus also the STM images of the molecules.

Figure 3 shows two STM images of a portion of the Cu{111} crystal with a low coverage (after 2 L exposure to diiodobenzene) of adsorbed phenylene. The white horizontal arrow in Figure 3a highlights a group of three phenylene intermediates. These three phenylenes are clustered around a surface defect. In the upper left-hand corner of Figure 3a, a mobile phenylene intermediate is highlighted with a vertical arrow. The streaks in the Figure 3a are created by the phenylene moving across the surface more quickly than the STM can image it.[15] By increasing the tunneling current, the substrate beneath the phenylene intermediates can be probed.[6] Figure 3b shows a STM image of a portion of the area in Figure 3a, acquired at a significantly higher tunneling current. The white horizontal arrow marks the same position on Figure 3a as it does in Figure 3b. In Figure 3b, the white horizontal arrow now highlights a depression in the surface corresponding to a substrate defect. When the tunneling current is increased, the tip moves closer to the surface and probes the states of the substrate rather than those of the adsorbates, in the corresponding STM images the adsorbates are transparent.[6] After imaging the substrate in this way, going back to the previous tunneling conditions confirms that the adsorbates are still there. This enables us to determine the adsorption sites without displacing the adsorbates. Phenylenes preferentially adsorb to step edges and to defects on the surface; no stationary phenylene intermediates were observed on the perfect areas of the Cu{111} terraces at 77 K.
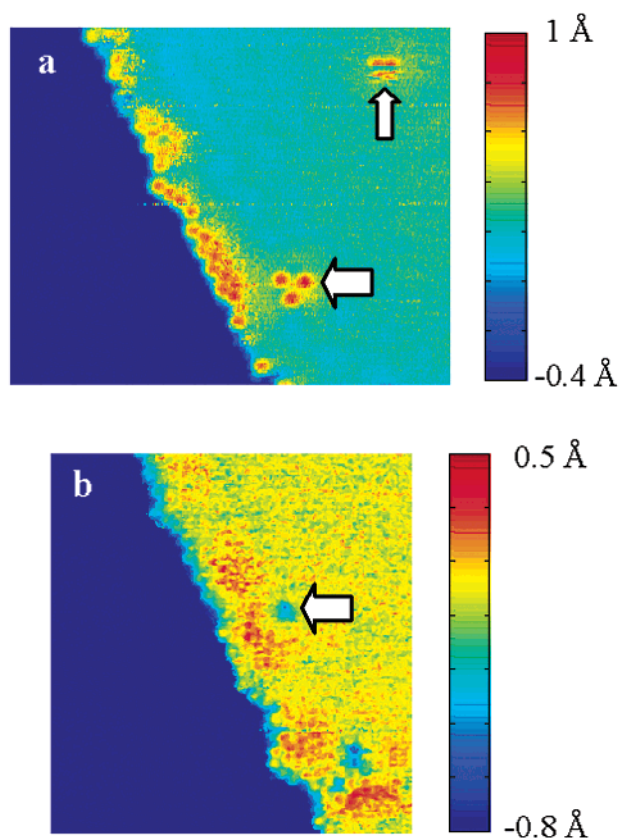
Figure 3. Two STM images of a low coverage of phenylene intermediates on Cu{111}. (a) The phenylene intermediates preferentially bond to the atomic steps and atomic defects. The image area is 85 Å × 75 Å, and V_s = 100 mV and i_t = 50 pA. (b) An overlapping area to that imaged in Figure 3a acquired with a higher tunneling current. The step edge and atomic defects where the phenylene intermediates are bound can be seen (horizontal arrow), but the adsorbates become transparent. The image area is 75 Å × 70 Å, and V_s = 100 mV and i_t = 1.2 nA. In both cases, the color scale is saturated so that the lower terrace is beyond the lowest hue shown.

Conclusions

On Cu{111}, *p*-diiodobenzene dissociates simultaneously into three products—two strongly adsorbed I atoms and a mobile phenylene intermediate. The I atoms appear to have some slight mobility upon reaction on Cu{111} at room temperature and most commonly to be drawn together. The I atoms are observed in pairs at random positions across the surface and are found to

interact electronically. They thus mark the locations at which the dissociative chemisorption takes place. Further, their proximity indicates that the two dissociation reactions occur close in time and space, i.e. either simultaneously or at least before the first molecular fragment can move away from the site of the first dissociation. In contrast, the phenylene intermediates preferentially adsorb at or near atomic defects, atomic steps, and adsorbed iodine on the surface. Even at these preferential adsorption sites at 77 K, the phenylene intermediates remain mobile and can be moved easily by the probe tip under typical STM imaging conditions.[20]

References and Notes

(1) Zambelli, T.; Wintterlin, J.; Trost, J.; Ertl, G. *Science* **1996**, *273*, 1688−1690.
(2) Somorjai, G. A. *Introduction to Surface Chemistry and Catalysis*; John Wiley & Sons: New York, 1994.
(3) Kamna, M. M.; Graham, T. M.; Weiss, P. S. In preparation.
(4) Kamna, M. M.; Stranick, S. J.; Weiss, P. S. *Isr. J. Chem.* **1996**, *36*, 59−62.
(5) Kamna, M. M.; Stranick, S. J.; Weiss, P. S. *Science* **1996**, *274*, 118−119.
(6) Pascual, J. I.; Jackiw, J. J.; Kelly, K. F.; Conrad, H.; Rust, H. P.; Weiss, P. S. *Phys. Rev. B* **2000**, *62*, 12632−12635.
(7) Weiss, P. S.; Kamma, M. M.; Graham, T. M.; Stranick, S. J. *Langmuir* **1998**, *14*, 1284−1289.
(8) Xi, M.; Bent, B. E. *J. Vac. Sci. Technol., B* **1992**, *10*, 2440−2446.
(9) Xi, M.; Bent, B. E. *Surf. Sci.* **1992**, *278*, 19−32.
(10) Xi, M.; Bent, B. E. *J. Am. Chem. Soc.* **1993**, *115*, 7426−7433.
(11) Xi, M.; Bent, B. E. *Langmuir* **1994**, *10*, 505−509.
(12) Hla, S. W.; Bartels, L.; Meyer, G.; Rieder, K. H. *Phys. Rev. Lett.* **2000**, *85*, 2777−2780.
(13) Ullmann, F.; Bielecki, J. *Ber. Dtsch. Chem. Ges.* **1901**, *34*, 2174−2185.
(14) Rochow, E. G. *J. Am. Chem. Soc.* **1945**, *115*, 963−965.
(15) Stranick, S. J.; Kamna, M. M.; Weiss, P. S. *Science* **1994**, *266*, 99−102.
(16) Stranick, S. J.; Kamna, M. M.; Weiss, P. S. *Surf. Sci.* **1995**, *338*, 41−59.
(17) Stranick, S. J.; Kamna, M. M.; Weiss, P. S. *Rev. Sci. Instrum.* **1994**, *65*, 3211−3215.
(18) Stranick, S. J.; Kamna, M. M.; Weiss, P. S. *Nanotechnology* **1996**, *7*, 443−446.
(19) Eigler, D. M. Personal communication.
(20) McCarty, G. S.; Weiss, P. S. In preparation.