

Mechanisms of the Ullmann Coupling Reaction in Adsorbed Monolayers

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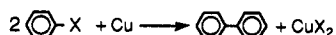
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Abstract: Ninety years ago, Ullmann and co-workers discovered that copper powder catalyzes the coupling of aromatic halides to produce biaryls, yet the role of the copper surface in this reaction remains controversial today. Recently, it has been shown that Ullmann coupling of submonolayer coverages of iodobenzene to form biphenyl occurs with 100% selectivity on a Cu(111) single crystal surface under ultrahigh-vacuum conditions (Xi, M.; Bent, B. E. *Surf. Sci.* **1992**, *278*, 19). We report here on studies in which surface analysis techniques have been applied to determine the mechanism of this reaction. Two mechanisms are found. At low surface coverages (<1 monolayer), iodobenzene dissociates at ~175 K on the Cu(111) surface to form adsorbed phenyl groups, which subsequently couple at 300–400 K to form biphenyl. At high surface coverage (1–2 monolayers), biphenyl is also formed by a second pathway at temperatures as low as 210 K. Isotope labeling and surface vibrational spectroscopy are used to show that this low-temperature pathway involves a reaction between adsorbed phenyl groups and molecular iodobenzene. A key aspect of the high coverages required for this low-temperature coupling pathway is that the molecular iodobenzene assumes an orientation in which its π -ring is tilted significantly away from the surface plane. It is suggested that such a tilted configuration allows phenyl radicals formed by C–I bond scission to react with adjacent phenyl groups as opposed to bonding directly to the copper surface. Potential implications of these results for the solution-phase Ullmann coupling reaction are discussed.

Introduction

In 1901, Ullmann and Bielecki discovered that finely divided copper (Naturkupfer C) catalyzes the coupling of aromatic halides to produce symmetrical biaryls:¹



In the 90 years since this discovery, the Ullmann reaction has proven to be of general synthetic utility for forming both symmetric and asymmetric biaryls.^{2–5} The reaction mechanism, however, remains unknown. While it is generally accepted that copper initiates the reaction by abstracting the halogen atom, subsequent steps are less clear. Among the most frequently proposed mechanisms are those shown in Scheme I for the case of iodobenzene coupling to form biphenyl.

A basic difference between these mechanisms is whether biphenyl is formed in solution or on the copper surface. In the first two mechanisms, for example, phenyl radicals^{6,7} and Cu-phenyl species,⁸ respectively, are released into solution where they react homogeneously with iodobenzene to form biphenyl. Alternatively, the phenyl groups may remain bound to the copper surface with biphenyl being formed either by coupling adsorbed phenyl groups³ or by direct reaction between an adsorbed phenyl group and an iodobenzene molecule.²

If the entire Ullmann reaction occurs on the copper surface as suggested by the latter two mechanisms above, then the potential exists for carrying out the reaction in monolayers of aromatic

halides on copper surfaces under vacuum conditions. The advantage of such an approach is that the many surface analytical techniques developed for vacuum conditions^{9,10} can be applied to study the surface reaction mechanism.

We have taken this approach and have applied surface analysis techniques under ultrahigh-vacuum (UHV) conditions to study the Ullmann coupling of iodobenzene in adsorbed monolayers on a single crystal Cu(111) surface. We find that iodobenzene undergoes Ullmann coupling on this copper surface to form biphenyl with 100% selectivity and that two reaction mechanisms are involved: (1) a low-coverage, high-temperature (300–400 K) pathway in which iodobenzene dissociates to form adsorbed phenyl groups which subsequently couple and (2) a high-coverage, low-temperature (<210 K) coupling reaction between adsorbed phenyl groups and molecularly intact iodobenzene.

Experimental Section

Details of the ultrahigh-vacuum (UHV) apparatus and the experimental procedures have been described previously.^{11,12} Briefly, the chamber is equipped with an ion sputtering gun for surface cleaning, an Auger electron spectrometer (AES) for determining the surface atomic composition, a high-resolution electron energy loss spectrometer (HREELS) for surface vibrational spectroscopy, and two 0–300-amu quadrupole mass spectrometers (QMS) for identifying reaction products evolved from the surface. The copper crystal (a 1-cm-diameter wafer from Monocrystals Inc., 99.999%) was cleaned by cycles of Ar⁺ sputtering and annealing in vacuum, and the surface cleanliness was confirmed by AES. Surface temperature control from 110 to 1100 K was achieved by resistive heating and by cooling with liquid nitrogen. Surface temperatures were measured using a chromel-alumel thermocouple with the junction wedged into a 3-mm-deep hole drilled into the side of the crystal.

* Presidential Young Investigator, A. P. Sloan Fellow, and Camille and Henry Dreyfus Teacher-Scholar.

- (1) Ullmann, F.; Bielecki, J. *Ber. Dtsch. Chem. Ges.* **1901**, *34*, 2174.
- (2) Fanta, P. E. *Chem. Rev.* **1946**, *38*, 139; **1964**, *64*, 613; *Synthesis* **1974**, 9.
- (3) Bacon, R. G. R.; Hill, H. A. O. *Q. Rev., Chem. Soc.* **1965**, *19*, 95; *Proc. Chem. Soc., London* **1962**, 113.
- (4) Goshayev, M.; Otroshchenko, O. S.; Sadykov, A. S. *Russ. Chem. Rev. (Engl. Transl.)* **1972**, *14*, 1046.
- (5) Posner, G. H. *An Introduction to Synthesis Using Organocopper Reagents*; John Wiley: New York, 1980.
- (6) Rapson, W. S.; Shuttleworth, R. G. *Nature* **1941**, *147*, 675.
- (7) Nursten, H. E. *J. Chem. Soc.* **1955**, 3081.
- (8) Paine, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 1496 and references therein.

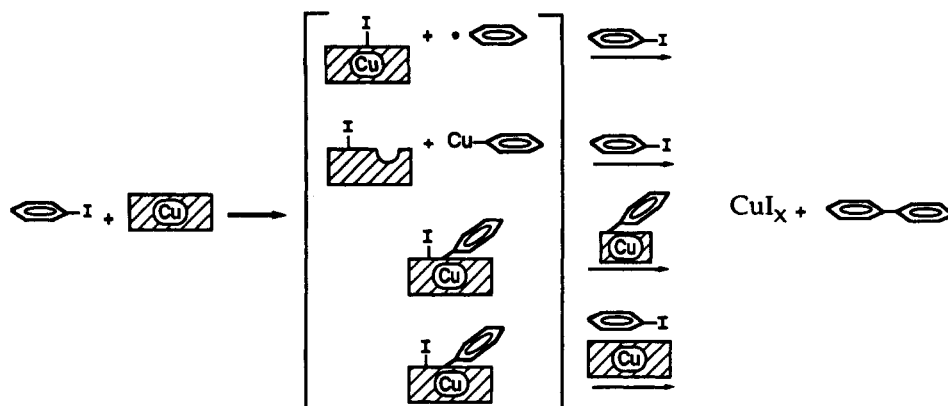
(9) Somorjai, G. A. *Chemistry in Two Dimensions: Surfaces*; Cornell University Press: Ithaca, 1981.

(10) Ertl, G.; Kuppers, J. *Low Energy Electrons and Surface Chemistry*; Verlag Chemie: Weinheim, 1974.

(11) Xi, M.; Bent, B. E. *Surf. Sci.* **1992**, *278*, 19.

(12) Chiang, C.-M.; Wentzlaff, T. H.; Bent, B. E. *J. Phys. Chem.* **1992**, *96*, 1836.

Scheme I



Gases were adsorbed onto the crystal by back-filling the chamber. Exposures are reported in langmuirs ($1 \text{ langmuir (L)} = 1 \times 10^{-6} \text{ Torr}\cdot\text{s}$) and are uncorrected for differing ion gauge sensitivities. $\text{C}_6\text{H}_5\text{I}$ (99%, Aldrich) and $\text{C}_6\text{D}_5\text{I}$ (97 atom % D, Icon) were purified by several freeze-pump-thaw cycles with liquid nitrogen prior to dosing, and sample purities were confirmed *in situ* by mass spectrometry. D atoms, which have been generated and applied to titrate adsorbed phenyl groups, were adsorbed line-of-sight onto the Cu(111) surface by dissociating D_2 (99.5 atom % D, Matheson) with a hot ($\sim 1800 \text{ K}$) tungsten filament.¹³ The D atom exposures are reported as the D_2 exposure to the filament since the D atom flux is not accurately known.¹³

In this study, the temperature-programmed reaction (TPR) experiments were conducted using two mass spectrometers (Vacuum Generators SXP 300) with different experimental configurations. One of the mass spectrometers was installed behind a differentially-pumped stainless steel shield containing a 2-mm-diameter aperture. In TPR experiments with this QMS, the sample was held $\sim 2 \text{ mm}$ from the aperture so that only molecules evolved from the central portion of the 1-cm-diameter crystal were detected. We have found, however, that this conventional setup for TPR experiments has a low detection efficiency for less volatile compounds such as biphenyl.^{11,14} Because biphenyl is readily condensed onto the chamber walls upon collision, it is appropriate to use an unshielded mass spectrometer to detect the desorbing flux of this "self-pumping" compound during TPR experiments. In this study, all the TPR spectra for biphenyl were acquired with the unshielded QMS, while for other species the spectra were acquired with the shielded QMS. The heating rates were 4 K/s in the TPR experiments, and up to three masses were monitored simultaneously by computer-controlled multiplexing of the mass spectrometer. All the HREELS spectra were taken in the specular direction ($\theta_{\text{in}} = \theta_{\text{out}} = 60^\circ$ from the surface normal) at 120 K .

Results and Interpretation

Ullmann Coupling in Adsorbed Monolayers. Submonolayer coverages of iodobenzene react on Cu(111) to form biphenyl with 100% selectivity. Previous temperature-programmed reaction (TPR) studies combined with integrated desorption mass spectrometry (IDMS) over the temperature range $120\text{--}550 \text{ K}$ have shown that biphenyl is the only volatile product besides a small amount ($<1\%$) of impurity benzene in the iodobenzene source.¹¹ Auger electron spectra taken after TPR experiments show that iodine remains on the surface, but all carbon is removed. Figure 1 shows the TPR spectra for biphenyl evolved from Cu(111) as a function of iodobenzene exposure at 120 K . The yield

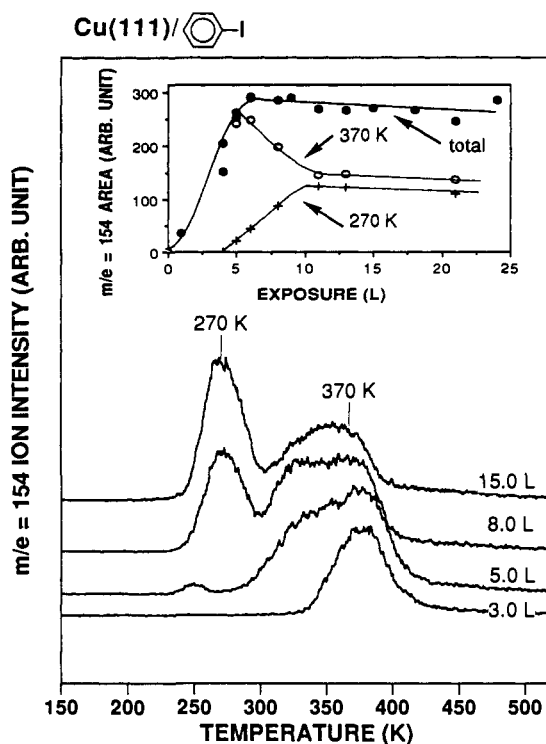


Figure 1. Temperature-programmed reaction spectra of biphenyl ($m/e = 154$) evolved from Cu(111) as a function of increasing exposures of iodobenzene at 120 K . The heating rates were 4 K/s . The inset shows the TPR peak areas for biphenyl as a function of iodobenzene exposure.

of biphenyl, as derived from the TPR peak area and shown in the inset, increases linearly with iodobenzene exposure and reaches a saturation value at 5–6 langmuirs. For exposures less than 5 langmuirs, biphenyl evolves from the surface above 300 K with a single desorption peak, which shifts to lower temperature with increasing iodobenzene exposure. This submonolayer chemistry of iodobenzene on Cu(111) has been discussed in detail in a previous paper.¹¹ Briefly, by the combination of TPR results, work function change measurements, surface vibrational spectroscopy, and H atom titration experiments, it was established that a 5-langmuir exposure corresponds to one monolayer of iodobenzene adsorbed with its π -ring parallel to the surface plane. The adsorbed iodobenzene dissociates on Cu(111) at $\sim 175 \text{ K}$ to form iodine atoms and adsorbed phenyl groups, which are thermally stable to above 300 K . Surface vibrational spectra as well as near edge X-ray absorption fine structure (NEXAFS) results¹⁵ indicate that the phenyl intermediates bond to Cu(111)

(13) Xi, M.; Bent, B. E. *J. Vac. Sci. Technol.* **1992**, *B10*, 2440.

(14) Feulner, P.; Menzel, D. *J. Vac. Sci. Technol.* **1980**, *17*, 662.

(15) Xi, M.; Yang, M. X.; Jo, S.-K.; Bent, B. E.; White, J. M.; Stevens, P. Manuscript in preparation.

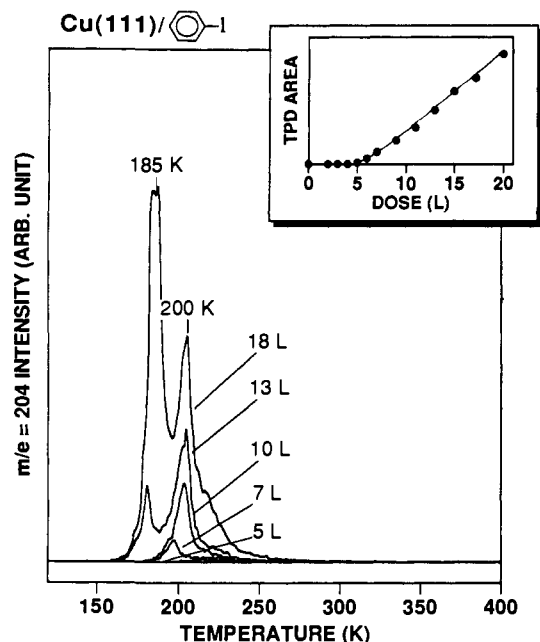


Figure 2. Molecular desorption of iodobenzene ($m/e = 204$) from Cu(111) for increasing exposures at 120 K. The inset shows the TPD peak area as a function of iodobenzene exposure. The heating rates were 4 K/s.

with their π -rings approximately parallel to the surface. The rate-determining step in biphenyl evolution above 300 K is coupling of the adsorbed phenyl groups, and this reaction occurs at 30–50 K higher temperature than for desorption of a comparable coverage of biphenyl from Cu(111).

For exposures above 5 langmuirs, biphenyl is also formed below 300 K as evidenced by the appearance of the peak at 270 K in TPR spectra of Figure 1. As shown in the inset to Figure 1, the total yield of biphenyl remains constant for exposures above 5 langmuirs, but the yield of the 370 K pathway decreases while that of the 270 K pathway increases. Above 12 langmuirs, the total yield of biphenyl and the relative yield of the two channels remain constant.

Consistent with the constant total yield of biphenyl for exposures >5 langmuirs, molecular desorption is observed to increase linearly for these exposures. As shown in Figure 2, molecular desorption peaks are observed at 200 and 185 K with increasing exposure. The two molecular desorption peaks for iodobenzene on Cu(111) are analogous to benzene desorption at above monolayer coverage from this surface, where peaks at 155 and 152 K have been attributed to desorption from the second layer and multilayers, respectively.¹⁶ Analysis of the 185 K peak using zero-order kinetics as suggested by the alignment of the leading edges of the 185 K peaks yields a desorption energy of 13.1 kcal/mol, with an uncertainty of ± 0.4 kcal/mol from the statistical analysis.

The fact that the relative yields of biphenyl at 270 and 370 K in the TPR spectra change while the total yield remains constant for iodobenzene exposures between 6 and 12 langmuirs suggests that biphenyl is formed by two different reaction pathways for high surface coverages of iodobenzene. This assumption is confirmed by the following experiment. Iodobenzene (7.0 langmuirs) was adsorbed at 120 K and annealed at 210 K to induce C–I bond dissociation and molecular desorption. The surface was then titrated with 20 langmuirs of D atoms to scavenge unreacted phenyl groups. The subsequent TPR spectrum for biphenyl is compared in Figure 3 with that for 7.0 langmuirs of iodobenzene without annealing or exposure to D atoms. Annealing and titrating with D atoms almost completely removes the 370

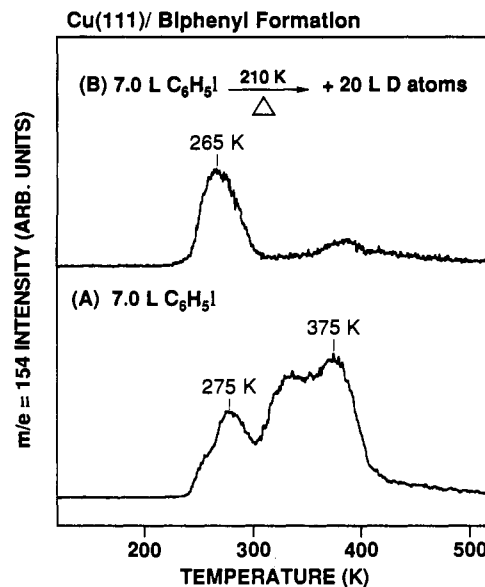


Figure 3. TPR spectra monitoring biphenyl ($m/e = 154$) evolved from Cu(111) after (A) a 7.0-langmuir exposure of iodobenzene at 120 K and (B) a 7.0-langmuir exposure of iodobenzene which was annealed at 210 K and titrated with 20 langmuirs of D atoms.

K peak, but the 270 K peak is unaffected. Having previously found that D atom titration scavenges surface phenyl groups to form benzene- d_1 , but reacts only slightly with biphenyl,^{11,13} we conclude that the biphenyl evolved at 270 K is already formed upon annealing the iodobenzene layer to 210 K. The 270 K peak temperature is consistent with that for molecular desorption of biphenyl from Cu(111) at monolayer coverage.¹¹ The remainder of this paper will focus on the mechanism for forming biphenyl below 210 K. We will also address why this low-temperature pathway is only observed for high coverages of iodobenzene.

The Orientational Requirement for Formation of Biphenyl below 210 K. Surface vibrational spectra indicate that, concurrent with the appearance and increase of the 270 K biphenyl peak in the TPR spectra, there is a change in the average orientation of the adsorbed iodobenzene. Specular HREELS spectra for iodobenzene adsorbed molecularly intact at 120 K on Cu(111) for 5-, 7-, and 12-langmuir exposures are shown in Figure 4. All the modes observed have frequencies consistent with those measured by infrared spectroscopy for liquid-phase iodobenzene, and we assign the peaks to vibrational modes by comparison with the liquid-phase spectra.¹⁷ A detailed assignment of the vibrational spectra of C_6H_5I adsorbed on Cu(111) can be found in ref 11. Briefly, the intense 715–720- cm^{-1} peak is an out-of-plane (γ_{CH}) bending mode, and the 900–1200- cm^{-1} peaks are primarily in-plane (β_{CH}) bending modes; two ring-stretching modes are observed at 1470 and 1575 cm^{-1} , and the CH stretching modes occur at 3040 cm^{-1} .

The most dramatic changes in the HREELS spectra with increasing iodobenzene exposure are the significant increase of the intensities of the in-plane bending and stretching modes. The HREELS spectrum for 5 langmuirs of iodobenzene adsorbed on Cu(111) is shown in Figure 4A. This spectrum is similar to those for lower iodobenzene exposures in which the dominant peak is the intense out-of-plane C–H bending mode at 715 cm^{-1} . Since dipole scattering (which predominates in the specular HREELS spectrum) selects against dynamic dipole moments parallel to the surface plane,¹⁸ the large relative intensity of this mode in the specular HREELS spectrum implies that iodobenzene bonds with its π -ring approximately parallel to the surface. With increasing iodobenzene exposure, the intensities of the in-plane C–H bending

(17) (a) Whiffen, D. H. *J. Chem. Soc.* **1956**, 1350. (b) Nanney, T. R.; Lippincott, C. R.; Hamer, J. C. *Spectrochim. Acta* **1966**, *22*, 737.

(18) Ibach, H.; Mills, D. L. *Electron Energy Loss Spectroscopy and Surface Vibrations*; Academic: New York, 1982.

(16) Xi, M.; Yang, M. X.; Jo, S.-K.; Bent, B. E.; Stevens, P. To be submitted to *J. Chem. Phys.*

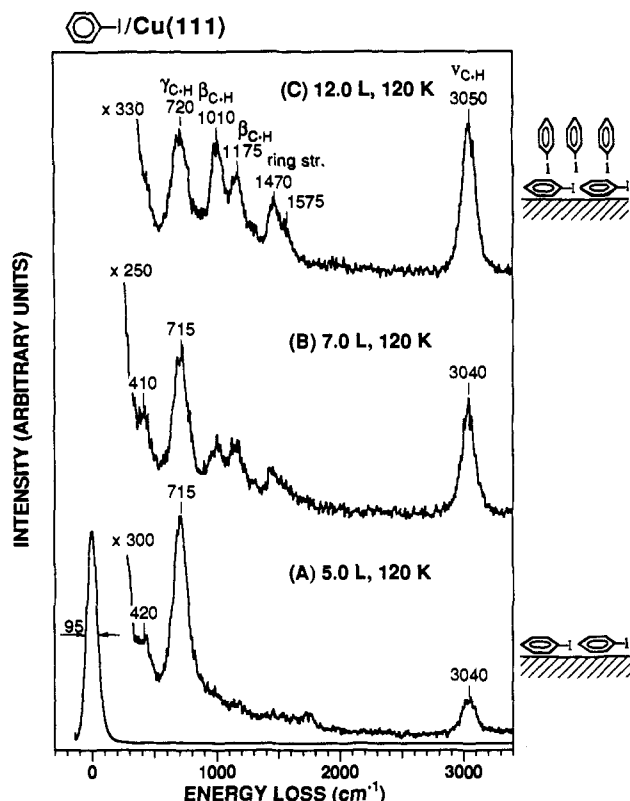


Figure 4. Specular HREEL spectra of C_6H_5I on $Cu(111)$ at 120 K after (A) 5.0-langmuir, (B) 7.0-langmuir, and (C) 12.0-langmuir exposures. The relative intensities of the vibrational modes for the adsorbed species suggest the adsorption geometries shown adjacent to the spectra. The observed vibrational frequencies are consistent with those for C_6H_5I in solution.¹⁸

modes (β_{CH}) at 995 and 1155 cm^{-1} , the in-plane ring-stretching mode at 1455 cm^{-1} , and the in-plane C–H stretching mode (ν_{CH}) at 3040 cm^{-1} increase significantly. The comparably high intensities for the in-plane modes and the out-of-plane γ_{CH} mode at 12 langmuirs indicate that at this coverage the average ring orientation is neither along the surface normal nor in the surface plane. This tilting of the average π -ring orientation away from the surface plane for exposures above 5 langmuirs correlates with the appearance of the low-temperature reaction channel for forming biphenyl.

To investigate if all the adsorbed iodobenzene molecules adopt the same orientation at high coverages and if the reaction occurs uniformly among the adsorbed iodobenzene, isotope-labeling experiments have been performed. In these studies, 5 langmuirs of iodobenzene was adsorbed on $Cu(111)$ at 120 K. For this exposure, the molecules bond with their π -rings parallel to the copper surface. The top panels of Figure 5 show the TPR and HREELS spectroscopic signatures: biphenyl evolution above 300 K, no molecular desorption, and weak intensity in the C–H stretching region of the vibrational spectrum. If 5.0 langmuirs of iodobenzene- d_5 is then added to this C_6H_5I monolayer, the TPR and HREELS results in the middle panels of Figure 5 are obtained. All three isotopomers of biphenyl ($C_{12}H_{10}$, $C_{12}D_{10}$, and $C_{12}H_5D_5$) are observed at both 260 and 360 K; both iodobenzene isotopes show molecular desorption in comparable amounts, and the HREELS spectrum shows substantial intensities in both the C–H and C–D stretching regions. These results are characteristic of 10 langmuirs of iodobenzene adsorbed on $Cu(111)$ as evidenced by the reference spectra in the bottom panel in Figure 5. The fact that both iodobenzene isotopes show the same high-coverage behavior indicates that the adsorbed molecules become equivalent regardless of the dosing sequence.

The extent of equilibration between the iodobenzene isotopes can be quantified from the TPR yields in Figure 5. From the

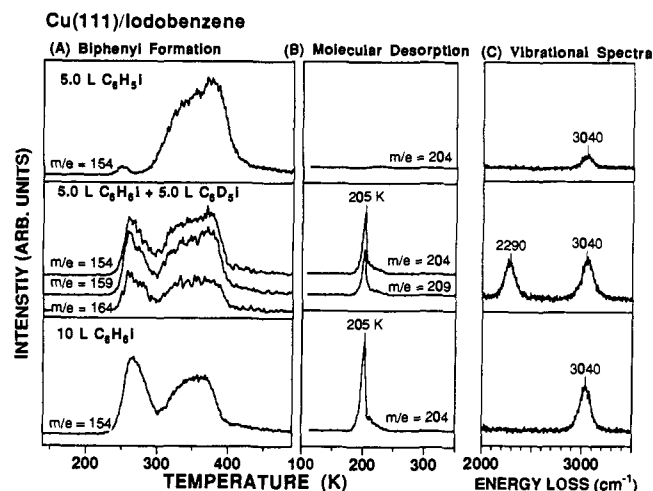


Figure 5. TPR spectra monitoring biphenyl evolution (column A), iodobenzene evolution (column B), and the surface HREEL spectra (column C) after 5.0 langmuirs of C_6H_5I (top panel), 5.0 langmuir of C_6H_5I followed by 5.0 langmuirs of C_6D_5I (middle panel), and 10 langmuir of C_6H_5I (bottom panel) were dosed onto $Cu(111)$ at 120 K. Only the ν_{CH} and ν_{CD} regions of the HREEL spectra are shown, and the intensities have been normalized with respect to the elastic peak in each case.

molecular desorption yields for $C_6H_5I:C_6D_5I$ of 1.0:0.75, we can conclude either that the isotopes are not completely randomized and an excess of C_6D_5I reacts to form biphenyl leaving excess C_6H_5I to desorb molecularly intact or (if the isotopes are completely randomized) that the surface composition is actually 43% C_6D_5I and 57% C_6H_5I as opposed to the 50:50 ratio suggested by the nominal 5-langmuir exposures. The biphenyl TPR results in Figure 5 confirm the latter possibility. The 154:159:164 peak areas of 1.8:2.5:1 for the three biphenyl isotopes correspond to 58% C_6H_5 and 42% C_6D_5 , which is virtually identical to that suggested by the molecular desorption spectra. Furthermore, random combination of 58% C_6H_5 and 42% C_6D_5 to form biphenyl leads to a biphenyl product ratio of 1.9:2.8:1 for $C_{12}H_{10}:C_{12}H_5D_5:C_{12}D_{10}$, which, to within the experimental uncertainty, is the same as that measured experimentally. We conclude that the iodobenzene isotopes completely equilibrate upon sequential 5-langmuir exposures at 120 K on $Cu(111)$.

To explain similar results for benzene on $Cu(111)$ ¹⁶ and on $Ru(001)$,¹⁹ bilayer adsorption models with interlayer exchange have been proposed. It was suggested that the aromatic rings of benzene in the first layer lie parallel to the surface while those in the second layer bond upright on top of the first layer. The resulting "T" configuration for the first- and second-layer benzene molecules is analogous to the packing configuration in crystalline benzene.²⁰ Exchange between the layers at the adsorption temperature accounts for the HREELS and TPR isotope labeling results. The TPR, HREELS, and recent NEXAFS results¹⁵ for iodobenzene are all remarkably similar to those for benzene on $Cu(111)$, and accordingly, we suggest the presence of two distinct molecular orientations in the high-coverage iodobenzene structure. The important point for the studies here is that the tilting of the π -ring away from the surface plane at high coverage correlates with the formation of biphenyl below 210 K.

Mechanism for the Low-Temperature Ullmann Coupling Pathway. To summarize the results to this point, the TPR and H atom titration results indicate that, for high coverages of iodobenzene (above 5 langmuirs in exposure), biphenyl is formed by two pathways: one below 210 K and the other above 300 K. The high-temperature pathway corresponds to coupling of adsorbed phenyl groups. Branching to the lower temperature pathway for exposures above 5 langmuirs correlates with a

(19) Jacob, P.; Menzel, D. *Surf. Sci.* **1988**, *201*, 503; **1989**, *220*, 70.

(20) Cox, E. G. *Proc. R. Soc.* **1932**, *A135*, 491.

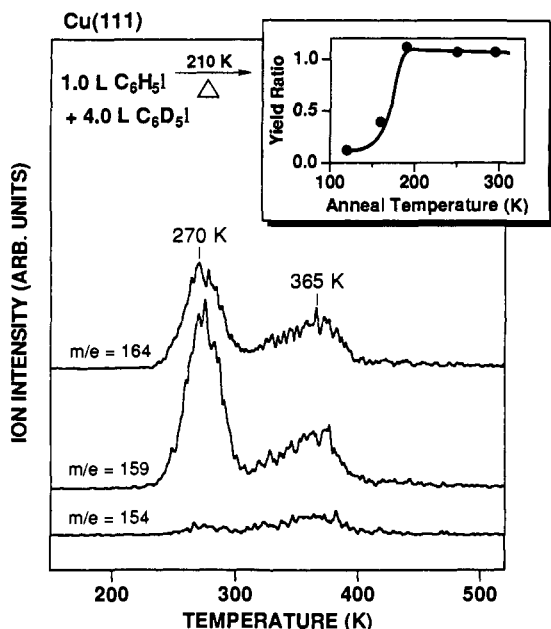


Figure 6. TPR spectra monitoring biphenyl ($m/e = 154$), biphenyl- d_5 ($m/e = 159$), and biphenyl- d_{10} ($m/e = 164$) evolved from Cu(111) after adsorbing 1.0 langmuir of C_6H_5I which was annealed at 210 K, followed by 4.0 langmuirs of C_6D_5I . The inset shows the ratio of the biphenyl- d_5 ($m/e = 159$) yield in the 270 K peak to that in the 370 K peak as a function of annealing temperature after 2.0 langmuirs of C_6H_5I was annealed and reacted with 4.0 langmuirs of C_6D_5I . The heating rates were 4 K/s.

dramatic increase in the average tilt angle of the π -rings with respect to the surface plane.

Two possibilities for the low-temperature Ullmann pathway can be envisioned: direct coupling of two iodobenzene molecules or coupling between an iodobenzene molecule and an adsorbed phenyl group. These two possibilities can be distinguished by isotope-labeling experiments. First, 1 langmuir of iodobenzene is adsorbed at 120 K and annealed to 210 K to form phenyl (C_6H_5) groups on Cu(111). Subsequent exposure to 4.0 langmuirs of iodobenzene- d_5 (C_6D_5I) at 120 K followed by a TPR experiment produces the spectra in Figure 6. As opposed to the case without preannealing where biphenyl is formed almost exclusively above 300 K, a significant amount of biphenyl- d_5 ($m/e = 159$) is evolved at 270 K. As shown in the inset to Figure 6, the yield of the 260 K biphenyl- d_5 peak as a function of preannealing temperature for a 2-langmuir C_6H_5I exposure shows a dramatic increase for annealing temperatures between 160 and 190 K. The 10-fold increase in the yield ratio upon annealing above 190 K agrees with previous work function change measurements and H atom titration experiments which indicated C-I bond dissociation at ~ 175 K. Thus, the evolution of cross-coupled biphenyl (C_6H_5 - C_6D_5) at 270 K demonstrates that the low-temperature coupling mechanism involves the reaction of adsorbed phenyl groups with molecular iodobenzene.

To confirm this conclusion and to show that the role of annealing the iodobenzene submonolayer first is to initiate carbon-iodine bond scission as opposed to, for example, inducing diffusion to achieve a particular configuration on the surface, we have generated phenyl groups on Cu(111) at 120 K by electron beam-induced dissociation of iodobenzene. Recent studies by Zhou and White have shown that electrons with energies of 5–12 eV selectively decompose chlorobenzene to phenyl groups on Ag(111).²¹ In our experiments, a beam of electrons with energies up to 18 eV and flux of 4×10^{11} e⁻/s was used.²² TPR spectra taken after 1.0 langmuir of C_6H_5I is adsorbed at 120 K, exposed to the electron beam for 4 min, and then exposed to 4.0 langmuir

(21) Zhou, X.-L.; White, J. M. *J. Chem. Phys.* **1990**, *92*, 5612.

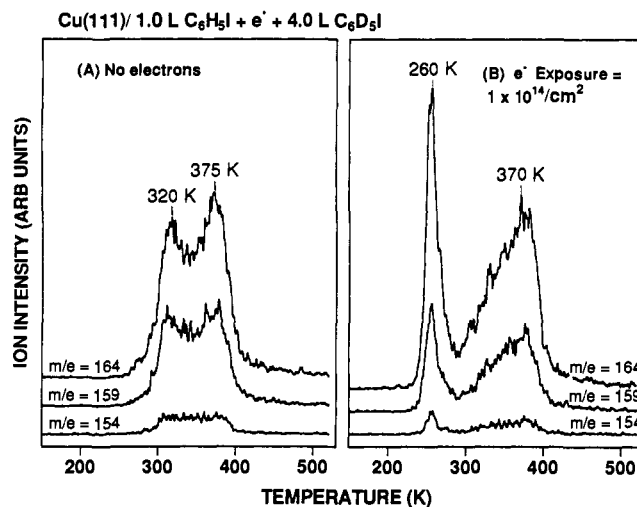


Figure 7. TPR spectra of biphenyl ($m/e = 154$), biphenyl- d_5 ($m/e = 159$), and biphenyl- d_{10} ($m/e = 164$) formed by adsorbing 4.0 langmuir of C_6D_5I onto a Cu(111) precovered at 120 K with (A) 1.0 langmuir of C_6H_5I and (B) 1.0 langmuir of C_6H_5I exposed to $1 \times 10^{14}/cm^2$ electrons at ~ 18 eV. The surface heating rates were 4 K/s.

of C_6D_5I are shown in Figure 7B. It is evident that biphenyl, biphenyl- d_5 , and biphenyl- d_{10} are all formed through the low- and high-temperature pathways. By contrast, with no electron exposure, biphenyl is only formed above 300 K (Figure 7A). We infer that some of the preadsorbed C_6H_5I molecules are dissociated by the electron beam to form phenyl- h_5 , which subsequently reacts with molecular C_6D_5I before it forms phenyl- d_5 on the surface.

An interesting aspect of the results in both Figures 6 and 7 is that no biphenyl is evolved at 260 K unless phenyl groups are formed prior to adsorbing the 4.0 langmuir of C_6D_5I . Why should it matter whether phenyl groups are formed before adsorbing all of the iodobenzene or during the TPR experiment after all of the iodobenzene is adsorbed? By comparing the differences between high (>5 langmuir) and low (<5 langmuir) exposures, we believe that the key is the effective surface coverage, which in turn determines the orientation of adsorbed iodobenzene. Forming phenyl groups by dissociating the C-I bond in iodobenzene increases the total adsorbate coverage so that some of the subsequently adsorbed iodobenzene molecules adopt a tilted orientation. This point is illustrated by the HREELS spectrum in Figure 8B. The large intensity for the ν_{CD} mode at 2290 cm^{-1} for C_6D_5I indicates a tilted orientation. This is to be contrasted with the HREELS spectrum in Figure 4A, where for the same total exposure (5 langmuirs) of iodobenzene, essentially all of the molecules lie approximately flat on the surface. That the tilted configuration evident in the HREELS spectrum of Figure 8B is not simply due to forming phenyl groups prior to iodobenzene adsorption is evidenced by the HREELS spectrum in Figure 8A for a lower total exposure of iodobenzene. Here, the absence of the ν_{CH} and ν_{CD} stretching modes as well as other in-plane vibrational modes (even those that are dipole-allowed) indicates that both the phenyl groups and molecular iodobenzene- d_5 bond with their π -rings flat on the surface. As shown in Figure 9A, such a monolayer produces no biphenyl at 260 K, even though phenyl groups are formed prior to iodobenzene adsorption. These results confirm that a tilted orientation for the iodobenzene molecules is necessary for them to react with adsorbed phenyl groups by the low-temperature Ullmann coupling pathway.

The importance of coverage is further illustrated by the TPR results in Figure 9B for the other extreme. Here, the first layer has been completely saturated with phenyl groups and iodine

(22) On the basis of the results of Zhou and White²¹ for the electron-induced dissociation of chlorobenzene on Ag(111), the 18-eV electron energies in our experiments probably induce C-H as well as C-I bond scission, but phenyl groups are still likely to be the major dissociation product.

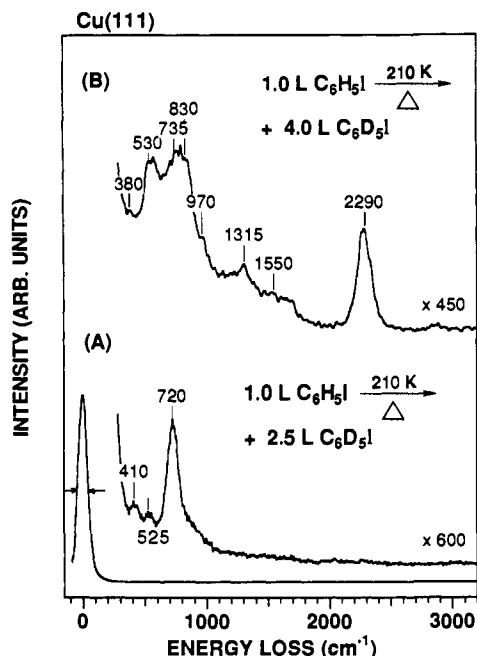


Figure 8. Specular HREEL spectra of Cu(111) after exposure at 120 K to 1.0 langmuir of C_6H_5I which was annealed to 210 K, followed by (A) 2.5 langmuirs and (B) 4.0 langmuirs of C_6D_5I at 120 K.

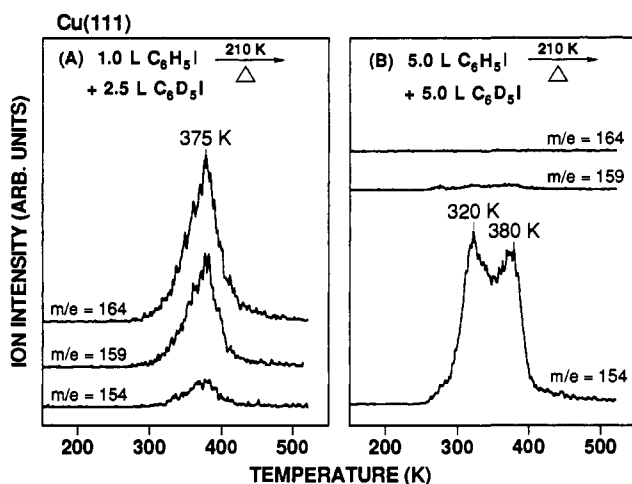


Figure 9. TPR spectra of biphenyl ($m/e = 154$), biphenyl- d_5 ($m/e = 159$), and biphenyl- d_{10} ($m/e = 164$) formed by adsorbing (A) 1.0 langmuir of C_6H_5I at 120 K and annealing to 210 K followed by 2.5 langmuirs of C_6D_5I and (B) 5.0 langmuirs of C_6H_5I at 120 K and annealing to 210 K followed by 5.0 langmuirs of C_6D_5I at 120 K.

atoms by annealing 5.0 langmuirs of C_6H_5I to 260 K. Subsequent adsorption of 5.0 langmuirs of C_6D_5I produces no biphenyl at 260 K even though a tilted orientation is observed by HREELS. Presumably there is no space on the copper surface to abstract the iodine atom from C_6D_5I . In fact, virtually none of the C_6D_5I is incorporated into the biphenyl evolved above 300 K as well. We conclude that the low-temperature Ullmann coupling pathway involves adsorbed phenyl groups and molecular iodobenzene that bonds with its π -ring tilted away from the surface plane. Furthermore, coupling requires that the iodine atom in the molecular iodobenzene have access to the copper surface.

Discussion

Mechanisms of the Ullmann Coupling Reaction of Iodobenzene on Cu(111). From the results above and those previously published,¹¹ we conclude that iodobenzene reacts to form biphenyl by two mechanisms on Cu(111). These two pathways, which are

distinguishable by the dramatically different temperatures at which they occur, are summarized in Figure 10. For exposures less than 5 langmuirs, all biphenyl is evolved at temperatures above 300 K as a result of coupling of adsorbed phenyl groups, as shown in the top panel of Figure 10. For higher exposures, biphenyl is also formed at temperatures as low as 210 K by reaction of adsorbed phenyl groups with molecular iodobenzene. This pathway is shown in the bottom of Figure 10. If we assume that both mechanisms occur with typical pseudo-first-order preexponential factors of 10^{13} s^{-1} , then their rates at 300 K differ by more than 10^6 .²³

Key experimental evidence for these reaction pathways can be summarized as follows. HREELS studies show that, for exposures less than 5 langmuirs, iodobenzene bonds to Cu(111) with its π -ring parallel to the surface plane (see Figure 4A). Work function measurements and D atom titration experiments reported elsewhere¹¹ indicate that iodobenzene dissociates at ~ 175 K to form adsorbed phenyl groups and iodine atoms and that the phenyl groups are thermally stable to above 300 K. While the details of the phenyl group bonding to Cu(111) are not yet fully understood, both NEXAFS¹⁵ and HREELS spectra¹¹ indicate that phenyl groups bond with their π -rings approximately parallel to the surface plane. We have previously suggested that this unexpected bonding orientation may be due to formation of either Cu-phenyl species or phenyl anions;¹¹ for clarity in Figure 10, we show these flat-lying phenyl groups with a nonbonded hybrid orbital to distinguish them from iodobenzene. In the low-coverage mechanism, biphenyl is formed by coupling of the adsorbed phenyl groups at temperatures above 300 K, while the iodine remains adsorbed on the surface until temperatures above 900 K. For exposures above 5 langmuirs, however, the iodobenzene adsorbs with the average orientation tilted significantly away from the surface plane. In this case, some of the iodobenzene dissociates to form adsorbed phenyl groups, and some of the phenyl groups react directly with undissociated iodobenzene to form biphenyl, which remains on the surface until ~ 260 K, where it desorbs molecularly intact.

The low-coverage phenyl coupling channel is relatively straightforward. Here, we focus on the details of the high-coverage pathway which produces biphenyl at temperatures of 210 K or below. The evidence that biphenyl is formed below 210 K from this mechanism comes from the D atom titration results shown in Figure 3. A second feature of the low-temperature Ullmann coupling pathway which is definitively established by the results above is that it involves adsorbed phenyl groups. This aspect is demonstrated by cross-coupling experiments such as those shown in Figure 6. Specifically, if a submonolayer of C_6H_5I is annealed above 170 K to dissociate the C-I bond and form adsorbed phenyl groups, then subsequent reaction with C_6D_5I at exposures sufficient to saturate the monolayer produces the cross-coupled biphenyl ($C_6H_5-C_6D_5$) by both the low-temperature and high-temperature pathways. Since temperatures above 300 K are required to couple two adsorbed phenyl groups, it is reasonable to conclude that the <210 K pathway must involve the reaction of adsorbed phenyl groups with molecular iodobenzene.

Since the low-temperature Ullmann coupling reaction involves reaction between adsorbed phenyl groups and molecular iodobenzene, the question arises as to why this pathway is observed only for high surface coverages of iodobenzene. Even at submonolayer coverages these two species must be present together on the surface at some point during a TPR experiment since all C-I bonds in the adsorbed layer do not dissociate simultaneously. One possibility is that high adsorbate coverages are required to push the reactants close to one another so that the bimolecular reaction can occur. The results here show that an additional reason for the high-coverage requirement is a change in the

(23) Second-order preexponential factors (units = $\text{cm}^2 \text{ molecule}^{-1} \text{ s}^{-1}$) are converted to pseudo-first-order (units = s^{-1}) by multiplying by the surface coverage.

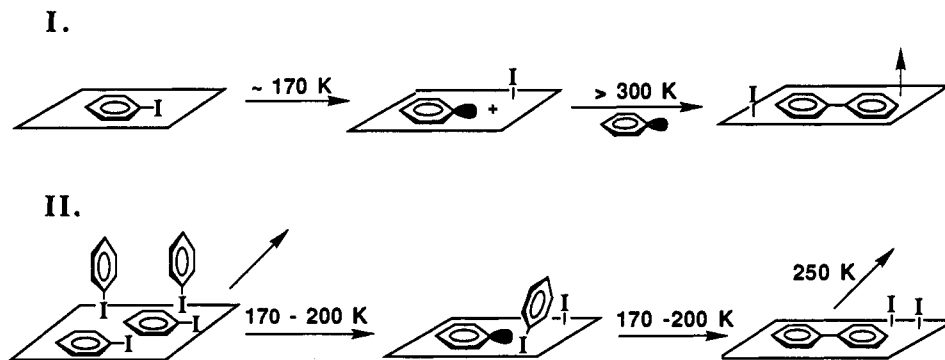


Figure 10. Schematic summary of the mechanisms for the Ullmann coupling reaction of iodobenzene in adsorbed monolayers on Cu(111). Panel I shows the low-coverage, high-temperature (300–400 K) pathway in which iodobenzene dissociates to form adsorbed phenyl groups which subsequently couple to form biphenyl. Panel II shows the high-coverage, low-temperature (<210 K) coupling reaction between adsorbed phenyl groups and molecularly intact iodobenzene. Upward-pointing arrows indicate desorption into the gas phase.

orientation of iodobenzene. As indicated by the TPR and HREELS results in Figures 7–9, formation of biphenyl below 210 K is restricted to monolayers where molecular iodobenzene is adsorbed with its π -ring tilted substantially away from the surface plane, a configuration which does not exist at low coverage. While the results here do not definitively establish the structure of these high-coverage layers, recent TPR, HREELS, and NEXAFS results,¹⁵ as well as studies on similar layers formed by benzene adsorption on Cu(111),¹⁶ indicate that a bilayer is formed on the surface.

The details of how molecular iodobenzene in a second layer can react with phenyl groups in the first layer to form biphenyl remain to be established, but several features of the mechanism are clear from the results here. For example, it is clear from the TPR results in Figure 9B that the molecular iodobenzene must have access to the surface in order for the low-temperature pathway to occur. Presumably, access to the surface is necessary in order to abstract the iodine atom from the molecular iodobenzene. Such an abstraction reaction has precedence in the chemistry of CH_3I on Cu(111), where it has been found that methyl radicals are formed during C–I bond scission at 140 K.²⁴ Some of the radicals are trapped on the surface to form adsorbed methyl groups, but some are ejected into the gas phase. Radical formation is possible because the C–I bond in CH_3I is only 56 kcal/mol, which is comparable to the strength of the Cu–I bond being formed.

Taken together with the results here, this observation suggests that the low-temperature Ullmann coupling pathway involves reaction between adsorbed phenyl groups and transient phenyl radicals formed during C–I bond dissociation. The 10 kcal/mol stronger C–I bond in iodobenzene relative to that in iodomethane²⁵ may account for dissociation at 175 K as opposed to 140 K. Such a radical pathway can also account for the importance of iodobenzene orientation in the low-temperature coupling pathway. When iodobenzene bonds in a tilted configuration with the iodine end toward the surface, phenyl radicals formed by C–I bond scission can react directly with an adjacent adsorbed phenyl group before bonding to the surface and becoming surface-bound phenyl groups. At low coverages where iodobenzene lies flat on the surface, transient phenyl radicals would probably have too short a lifetime to couple with adjacent phenyl groups. While there is no direct evidence for formation of phenyl radicals during C–I bond dissociation of iodobenzene (i.e. no phenyl radicals were detected desorbing from the surface analogous to the methyl radicals from iodomethane), there is evidence that adsorbed phenyl groups can “pick up” radicals at this low temperature. Recent studies have shown that iodomethane and other iodoalkanes including 1-iodo-2,2-dimethylpropane (neopentyl iodide) can be

cross coupled with adsorbed phenyl groups to form iodoalkanes at the temperature where alkyl radicals are formed by C–I bond dissociation of the iodoalkane.²⁶

A final important observation about the high-coverage pathway is that, over the coverage range where it is observed (5–12 langmuir of exposure), the total yield of biphenyl stays approximately constant. In other words, part of the first 5 langmuirs of iodobenzene adsorbed on the surface (which would normally form adsorbed phenyl groups that couple above 300 K) reacts with molecular iodobenzene at low temperature to form biphenyl, and yet the total yield of biphenyl does not increase.

On the basis of this result and the observations discussed above, our picture of the low-temperature Ullmann coupling pathway is as follows. The high exposures required for this reaction pathway lead to formation of an iodobenzene bilayer in which the first-layer molecules lie flat on the surface and the second-layer molecules stand upright. As the surface is heated above 175 K, C–I bond scission commences in the flat-lying layer directly adjacent to the copper; dissociation of the C–I bonds to form adsorbed phenyl groups and iodine atoms increases the effective surface coverage, and some first-layer molecules are pushed to the second layer. Concurrently, some second-layer molecules gain access to the copper through disruption of the monolayer. As the second-layer molecules approach the copper surface, iodine end down, the iodine atom can be abstracted by the copper surface to produce phenyl radicals which either couple immediately with phenyl groups in the first layer or bond to the surface themselves to form strongly adsorbed phenyl groups. Phenyl groups that do not react with phenyl radicals remain on the surface to above 300 K, where they eventually couple to form biphenyl.

Implications for the Ullmann Coupling Reaction in Solution. In discussing the possible implications of the results above for the Ullmann coupling reaction of aryl halides over copper powder in solution, it is useful to first review some of the key observations about the solution-phase reaction. With regard to the copper surface, it should be noted that the types of copper used have been quite diverse, ranging from Baker’s copper powder to Ullmann’s copper bronze, to copper bronze pretreated with iodine/acetone, and to copper freshly precipitated *in situ*.²⁴ Most recent work suggests that either clean copper metal²⁷ or copper(I) species generated in solution by dissolution of the copper metal or oxide²⁸ are the active constituent. Particularly significant in the context of the current study is the conclusion of Suslick et al. that the dramatic enhancement in the Ullmann coupling rate by the use of ultrasound results from removal of a surface oxide from the copper powder to expose copper metal.²⁷

Given the uncertainty over the type of copper important for efficient Ullmann coupling, it is not surprising that the solution-

(24) Lin, J. L.; Bent, B. E. *J. Am. Chem. Soc.* 1993, 115, 2849.

(25) Sanderson, R. T. *Chemical Bonds and Bond Energy*; 2nd ed.; Academic: New York, 1976.

(26) Xi, M.; Bent, B. E. Submitted to *Langmuir*.

(27) Suslick, K. S.; Casadonte, D. J.; Doktycz, S. J. *Chem. Mater.* 1989, 1, 6.

phase mechanism is still debated. There is, however, general agreement that a highly reactive intermediate is involved in the reaction. For example, it is found that aryl halides which are not themselves active in the Ullmann reaction can be cross coupled with aryl halides which are active.^{2,28-30} The explanation is that the more active halide reacts with the copper to generate a reactive intermediate which subsequently reacts with the less active halide.

The controversy over the mechanism for the Ullmann reaction centers around the nature of the reactive intermediate. The favored candidates are phenyl free radicals,⁶ copper-phenyl species dissolved in solution,^{2,8} and phenyl groups bound to the copper surface.²⁻⁴ The evidence for radicals includes the observation that the Ullmann product yield drops precipitously when a "radical trap" is added to the reaction mixture,^{7,30,31} and the finding that highly sterically hindered products can be formed.⁷ The latter are difficult to explain with copper-phenyl or surface-bound phenyl groups given the steric constraints. On the other hand, aryl copper compounds generated by alternative methods (for example by reacting Grignard reagents with copper halides)³³ show many of the same products with similar product distributions to those found in the Ullmann reaction.⁸ Furthermore, these product distributions are sometimes different from those expected for aryl free radicals.² There is also evidence that the Ullmann reaction continues after filtration of the copper catalyst from solution, an observation that supports the formation of discrete copper-aryl species.⁸ It should be noted, however, that aryl copper compounds are known to react with carbonyl (C=O) and NO₂ groups attached to the aryl ring, a pathway not observed in Ullmann coupling.³⁴⁻³⁶ In short, no one mechanism can account for all the experimental observations.

Although the reaction conditions in the present study are quite different from those in solution-phase Ullmann reactions, the studies here establish chemical precedence for reactions that occur on the copper surface and provide insight into the types of intermediates that may be involved in the solution-phase reaction. For example, the results above definitively establish that metallic copper surfaces can carry out the Ullmann reaction, that the reaction for submonolayer coverages on atomically clean surfaces is 100% selective for the Ullmann product, and that the reaction occurs at quite low temperature (<400 K). More importantly, it has been established that reaction on the surface occurs by two mechanisms which have dramatically different kinetics. The existence of these two mechanisms may explain why no single mechanism can successfully account for all the solution-phase results.

It should be emphasized that the finding of two mechanisms for Ullmann coupling on the copper surface under vacuum conditions does not rule out additional homogeneous pathways in the solution-phase reaction. In fact, the intermediates in the surface reactions provide some support for proposed solution-

phase pathways. For example, the low-temperature reaction between adsorbed phenyl groups and molecular iodobenzene occurs at the same temperature as C-I bond scission in iodobenzene, suggesting a radical mechanism. In the experiments here, these phenyl radicals are captured by adsorbed phenyl groups to form biphenyl, but in solution there is also the possibility of solvation and transport away from the surface. Such a process, which is analogous to that proposed and successfully modeled as a side reaction in the formation of Grignard reagents,³² may account for the radical-type reaction products observed in the Ullmann reaction. Likewise, the adsorbed phenyl groups isolated on the copper surface in the vacuum reaction may be precursors to formation of solubilized copper-phenyl species in the solution reaction. The unusual bonding geometry for these adsorbed phenyl groups in which the π -ring lies approximately parallel to the surface plane could indicate formation of a copper-phenyl species in which the necessary copper atom is pulled from the bulk lattice or abstracted from a step edge.¹¹ Alternatively, the adsorbed phenyl groups may bind to the surface as anions^{11,37} and coupling may occur at the surface of the metal even in the solution-phase reaction. We note in particular that phenyl anions would be analogous to the "bound radicals" postulated for the Ullmann reaction^{2,31} and that the flat-lying geometry for these species may account for the ability of the Ullmann reaction to form quite sterically hindered products.

Conclusions

The results above show that when iodobenzene is reacted with a Cu(111) single crystal surface under vacuum conditions, Ullmann coupling occurs to produce biphenyl and adsorbed iodine atoms. Temperature-programmed reaction studies, surface vibrational spectra by high-resolution electron energy loss, and titration of the adsorbed monolayer with deuterium atoms establish that the coupling reaction occurs by two mechanisms. At submonolayer coverages, iodobenzene bonds with its π -ring parallel to the surface plane, carbon iodine bond scission occurs at ~175 K, and the adsorbed phenyl groups remain on the surface until temperatures above 300 K, where they couple to form biphenyl. At high coverages, adsorbed phenyl groups react directly with molecular iodobenzene below 210 K to form biphenyl. The onset of this low-temperature reaction correlates with a change in the average orientation of the adsorbed molecular iodobenzene from lying flat to tilting away from the surface plane. In addition, the 175-200 K temperature for the phenyl/iodobenzene reaction correlates with the temperature for C-I bond scission in iodobenzene. On the basis of studies of CH₃I dissociation which show that methyl radicals are formed during C-I bond scission,²⁴ we postulate that the phenyl/iodobenzene reaction involves the addition of transient phenyl radicals formed during C-I bond scission to the adsorbed phenyl groups. Competition between phenyl radical reaction with adsorbed phenyl groups and bonding to the copper surface may explain why the low-temperature pathway is observed only at high surface coverage.

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- (28) Foster, J. *J. Chem. Soc.* **1960**, 594.
(29) Lewin, A. H.; Cohen, T. *Tetrahedron Lett.* **1965**, 50, 4531.
(30) Rule, H. G.; Smith, F. R. *J. Chem. Soc.* **1937**, 1096.
(31) Hasimoto, H.; Nakano, T. *J. Org. Chem.* **1966**, 31, 891.
(32) Whitesides, G. M.; Casey, C. P. *J. Am. Chem. Soc.* **1961**, 83, 4541.
(33) Tamura, M.; Kochi, J. K. *J. Organomet. Chem.* **1972**, 42, 205.
(34) Gilman, H.; Straley, J. M. *Recl. Trav. Chim. Pays-Bas.* **1936**, 55, 821.
(35) Costa, G.; Camus, A.; Catti, L.; Morsich, N. *J. Organomet. Chem.* **1966**, 5, 568.
(36) Gilman, H.; McCracken, R. *J. Am. Chem. Soc.* **1929**, 51, 821.

- (37) Lindley, J. *Tetrahedron* **1984**, 40, 1433.