Cross Coupling of Phenyl Groups with Alkyl Iodides on Copper Surfaces: A Radical Mechanism?

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The cross coupling of phenyl groups (C_6H_5) with alkyl iodides in adsorbed monolayers on single-crystal Cu(110) and Cu(100) surfaces under ultrahigh-vacuum conditions has been studied by a combination of temperature-programmed reaction techniques and isotope labeling. In these experiments, phenyl groups were generated on the surface by the dissociative adsorption of iodobenzene. Detailed studies in the case of the CH₃I + phenyl reaction to form toluene show that there are two mechanisms for the process: a low-temperature pathway (<160 K; activation energy <10 kcal/mol), in which phenyl groups react directly with CH₃I, and a much higher temperature pathway (\sim 400 K, activation energy \sim 27 kcal/mol), in which adsorbed methyl groups produced by C-I bond scission couple with coadsorbed phenyl groups. The mechanism of the lowtemperature reaction has yet to be fully resolved, but experimental evidence for a radical mechanism is presented. The relevant observations in this regard include the following: (1) when methyl radicals are impinged onto a phenyl precovered Cu(100) surface at 100 K, toluene is produced by an Eley-Rideal mechanism; (2) independent studies have shown that methyl radicals are produced during CH₃I dissociation on Cu(111); (3) the upper limit of 160 K for the phenyl + CH_3I reaction temperature on Cu(110) is quite close to the temperature for C-I bond scission in CH_3I on this surface; and (4) neopentyl iodide, which is much more sterically hindered than CH₃I, also shows a direct reaction with coadsorbed phenyl groups, suggesting that the process is C-I dissociation followed by coupling as opposed to phenyl attack at the C-Ibond.

I. Introduction

Bimolecular reactions at the gas-solid interface have traditionally been classified as occurring by one of two broad classes of mechanisms. The Langmuir-Hinshelwood mechanism, which involves a reaction between two chemisorbed species that have thermally accommodated to the underlying surface,¹ has been the most prevalent mechanism in previous studies. Several experimental and theoretical studies have, however, also provided evidence for reactions occurring by an Eley-Rideal mechanism,²⁻²¹ which involves reaction between gas phase and surface-bound species prior to thermal accommodation of the gas phase species with the surface.^{22,23} Although these two limiting cases provide a framework for the classification of most reactions occurring on surfaces, there have been a number of recent reports of a variant of the Eley-Rideal mechanism in which the "hot" reactant is produced on the surface instead of in the gas phase. For example, it has been shown that radicals generated photochemically at surfaces by irradiation of photoactive monolayers can react with coadsorbed species prior to thermal accommodation with the surface.²⁴⁻²⁶ Experimental evidence for analogous Eley-Rideal reactions in which "hot" radicals are produced in the thermal dissociation of adsorbed molecules is less definitive, although recent results^{19,27-38} have suggested that these processes may be more prevalent than previously supposed. Indeed, it is now clear^{39,40} that the exothermic dissociation of adsorbed species on surfaces can lead to "hot" radical fragments, which might react with coadsorbed species before bonding with and accommodating to the surface. The current work provides evidence for such a direct Eley-Rideal reaction of methyl radicals, produced in the thermal dissociation of methyl iodide on Cu(110) and Cu(100) surfaces, with coadsorbed phenyl groups to form adsorbed toluene.

Eley-Rideal reactions of radicals produced in the thermal dissociation of an adsorbate are uncommon and relatively unstudied largely because the thermodynamics of adsorbate bond dissociation reactions generally prevent the formation of free radical species. As Figure 1 indicates, most chemical bonds within stable molecules are relatively strong (approximately 80-100 kcal/mol) compared with the chemical bonds between surface metal atoms and adsorbate fragments (which are generally 20-70 kcal/mol). Since entropy changes for adsorption are usually negative or at most slightly positive, the thermodynamic driving force for adsorption is generally the exothermicity of the reaction. Given that the strengths of bonds to metal surfaces are generally significantly weaker than the bonds within molecules (as indicated above), an exothermic dissociative adsorption reaction generally requires making two bonds to the surface for each bond broken within the dissociatively adsorbed molecule. This general rule of two bonds made per one bond broken is the reason that both fragments produced by dissociative adsorption at metal surfaces remain bound to the surface. We note, also, that this "normal" dissociative adsorption process corresponds to the microscopic reverse of a Langmuir-Hinshelwood process, whereas free radical formation during dissociative adsorption corresponds to the microscopic reverse of an Eley-Rideal process. The lack of evidence for Eley-Rideal reactions of radicals produced in adsorbate thermal dissociation on metal surfaces results largely from the fact that free radicals are not generally produced in thermal dissociation.

Although this general rule of the production of two surfacebound species in the dissociation of an adsorbate on a metal surface accounts for most previously studied surface reactions, alkyl iodides provide an exception to this rule. Using methyl iodide adsorbed on copper as a model system, Figure 2 indicates

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Figure 1. Schematic of the two extreme mechanisms for dissociative adsorption of molecules on metal surfaces. The "normal" mechanism, depicted by the products in the upper right, results in the formation of two chemisorbed species by a thermodynamically favorable reverse Langmuir—Hinshelwood process. The radical pathway, depicted by the products in the lower right, results in the formation of one chemisorbed species and one gas phase radical species by a reverse Eley–Rideal process, which is generally thermodynamically unfavorable.



Figure 2. Schematic of the two possible dissociative adsorption pathways (alkyl radical production and metal alkyl formation) for methyl iodide on Cu(111). Because of the weak CH_3 -I bond and the strong Cu-I bond, alkyl radical production during dissociative adsorption is thermodynamically possible, as discussed in the text.

that the C–I bond energy of 55 kcal/mol in methyl iodide is unusually weak for a chemical bond.⁴¹ In addition, the 60–70 kcal/mol bond energy of I chemisorbed on Cu is unusually strong for a chemisorption bond.⁴¹ Consequently, it is energetically feasible for C–I bond cleavage in methyl iodide adsorbed on Cu to result in chemisorbed I and methyl free radicals. In fact, previous experiments in our laboratory have detected methyl radicals desorbing into the gas phase at the same surface temperature as C–I bond cleavage in methyl iodide adsorbed on Cu(111).^{41,42} Atom,⁴³ radical,⁴⁴ and carbene^{36,45–48} evolution during the dissociative adsorption of halogen-containing molecules on other surfaces has also been reported.

In each of these radical-generating dissociative adsorption processes, there is a branching between radical ejection to the gas phase and radical adsorption on the surface. There is also evidence in several cases for surface reactions of these radicals prior to either thermal accommodation on the surface or desorption into the gas phase. Examples include ethylene formation during CH₂I₂ dissociative adsorption on aluminum surfaces^{35,36} and octane formation during 1-C₄H₉I dissociation on Cu(111) (ref 34) as well as toluene (C₆H₅CH₃) formation during dissociative adsorption of CH₃I on a Cu(111) surface precovered with a partial monolayer of adsorbed phenyl (C_6H_5) groups.^{19,33} Analogous reactions of hot atoms or radicals have also been inferred for systems where atom or free radical evolution from the surface is not detected concurrently but where the surface reaction products and kinetics^{27-32,37,38} are suggestive of such pathways.

The present work is concerned with the reactions of methyl iodide and other alkyl iodides with coadsorbed phenyl groups (C_6H_5) on Cu(110) and Cu(100) surfaces. Previous studies of these reactions on a Cu(111) surface have indicated two mechanisms for this reaction: a high-temperature pathway at \sim 350 K involving coupling of surface-bound methyl and phenyl groups and a low-temperature (<160 K) pathway involving some type of direct reaction between phenyl groups and the alkyl iodides.^{19,20,33} The detection of gas phase methyl radicals during CH₃I dissociation at ~140 K on Cu(111) (refs 41, 42) led to the suggestion that the low-temperature toluene formation pathway involves a free radical mechanism. In the studies presented here, it is shown that reactions directly analogous to those described above for Cu(111) also occur on Cu(110) and Cu(100) surfaces. It is also demonstrated that both the direct and indirect mechanisms occur not only when CH₃I is the reactant but also when methyl radicals generated with a gas phase pyrolysis source are impinged onto copper surfaces precovered by a partial monolayer of phenyl groups. The kinetics of the low-temperature reaction for both methyl radicals and methyl iodide have been investigated using a chemical displacement technique. The results provide further support for the hypothesis of Eley-Rideal-type processes involving free radical or hot radical intermediates in the low-temperature cross coupling reactions of alkyl iodides and adsorbed phenyl groups on copper surfaces.

II. Experimental Section

The experiments were performed in a UHV system at Columbia University. Details of the Columbia UHV chamber and of experimental protocol for TPD studies are described elsewhere.²⁰ Briefly, the Cu(110) and Cu(100) crystals (Monocrystals, 99.999%) were cleaned by cycles of Ar⁺ sputtering and annealing. Reactants were adsorbed onto the crystal by back-filling the chamber. Iodobenzene (Aldrich, 99%), iodobenzene-d₅ (Icon, 97 atom % D), methyl iodide (Aldrich, 99.5%), and toluene (Aldrich, 99.8%) were purified by several freeze-pump-thaw cycles with liquid nitrogen prior to dosing, and sample purities were confirmed by in situ mass spectrometry. All exposures are reported in Langmuirs (1 Langmuir (L) $= 1 \times 10^{-6}$ Torr·s) and are uncorrected for differing ion gauge sensitivities. The quadrupole mass spectrometer (QMS) is installed behind a differentially pumped shield containing a 2 mm diameter aperture. In TPD studies, the sample was held 1-2 mm from the aperture so that only molecules evolved from the central portion of the 1 cm diameter crystal contribute to the detected signal. The heating rate in all TPD experiments was 3 K/s.

Methyl radicals were generated in these studies by pyrolyzing azomethane using a source similar to the one developed by Peng Cross Coupling of Phenyl Groups with Alkyl Iodides

et al.⁴⁹ Briefly, azomethane (synthesized by D.-H. Sun and A. Gurevich,⁵⁰ using the procedure of Renaud and Leitch⁵¹) was passed into the vacuum system through a 3 mm i.d. quartz tube with a 4 cm zone at the tip of the tube heated resistively to 1000 K. Pyrolysis of azomethane in this heated zone produced a flux of methyl radicals along with some methane, ethane, nitrogen, hydrogen, and unreacted azomethane. Previous studies have shown that the species other than methyl radicals do not stick to copper surfaces held at room temperature.⁵² In the studies here, methyl radicals were adsorbed line-of-sight by positioning the surface approximately 2 cm in front of the dosing tube. Exposures are reported in Langmuirs where the dose pressure corresponds to the pressure rise in the chamber during pyrolysis. For reference, a 1.0 L exposure in these units corresponds to 80% saturation of the Cu(100) surface with methyl groups (as determined by calibration TPD experiments that monitor the ethene coupling product desorption yield).

III. Results and Interpretation

As mentioned in the Introduction, the results presented below concern the reaction of phenyl groups with coadsorbed methyl iodide and with methyl radicals incident on the surface from the gas phase. In both cases the coupling product is toluene. The studies of the methyl radical reactions were carried out on a Cu(100) surface, while the studies of the phenyl + CH₃I reaction were carried out on Cu(110). The reason for studies on two different surfaces is that the Cu(100) sample was inadvertantly melted during the course of the research, and a (110) sample was available. However, aside from small kinetic differences between the two surface geometries, we find no structure sensitivity of the reaction mechanisms discussed. In particular, the phenyl + CH₃I reactivity we report here for Cu(110) is directly analogous to that reported previously for Cu(111), and we therefore expect Cu(100) to behave similarly with respect to this chemistry.

IIIA. Adsorbed Phenyl Groups + Gas Phase Methyl Radicals on Cu(100). Throughout the studies in this paper, adsorbed phenyl groups (C_6H_5) have been generated on the single-crystal copper surfaces by the dissociative adsorption of iodobenzene (C_6H_5I). Extensive studies on Cu(111) surfaces have documented, by high-resolution electron energy loss spectroscopy,²⁰ near edge X-ray absorption fine structure measurements,⁵³ work function change measurements,²⁰ and titration with hydrogen atoms,²⁰ that annealing a monolayer of iodobenzene to temperatures above 180 K results in C–I bond scission to form surface phenyl groups that are stable to temperatures above 300 K. Similar surface chemistry also appears to be valid for Cu(100) and Cu(110),⁵⁴ and in the studies here, iodobenzene monolayers have been annealed to temperatures of 200–300 K to generate adsorbed phenyl groups.

The results in Figure 3 demonstrate that gas phase methyl radicals (CH₃) react with adsorbed phenyl groups (C₆H₅) on Cu(100) to form toluene (C₆H₅-CH₃) by both the Langmuir-Hinshelwood and Eley-Rideal mechanisms. Figure 3A (lower trace) displays a temperature-programmed reaction (TPR) spectrum for the Langmuir-Hinshelwood pathway, which is the sole mechanism observed when a Cu(100) surface is first exposed to 1.0 L of methyl radicals (80% of monolayer saturation) followed by 2.0 L of iodobenzene (40% of monolayer saturation). The resulting TPR spectrum shows toluene evolution at 360 K as a result of phenyl + methyl coupling by a Langmuir-Hinshelwood mechanism. Since toluene desorbs from Cu(100) at temperatures below 350 K (see Figure 4 results described below), we conclude that toluene evolution at 360 K and above is due to rate-determining coupling of phenyl +



Figure 3. Temperature-programmed desorption spectra monitoring toluene evolution at $m/e^+ = 91$ on Cu(100). The top trace shows results following addition of 1.0 L of methyl radicals to a surface, which had been previously exposed to 2.0 L of iodobenzene and briefly annealed to 200 K to generate adsorbed phenyl groups. The bottom trace shows results following sequential adsorption of 1.0 L of methyl radicals and 2.0 L of iodobenzene at 100 K. As discussed in the text, the low temperature toluene desorption peak at 240 K in the top spectrum results from a direct Eley–Rideal reaction of gas phase methyl radicals, while the higher temperature peaks at 360 and 380 K in the two spectra result from a Langmuir–Hinshelwood reaction of surface-bound methyl and phenyl groups.

methyl followed by rapid desorption of the product toluene. (For reference, methyl + methyl coupling to produce ethane occurs at 400-450 K on Cu(110).^{55,56}) Virtually identical results are obtained if the order of addition is reversed and methyl radicals are adsorbed onto a surface precovered at 100 K with a parital monolayer of iodobenzene, which remains molecularly intact at this temperature.

To observe the Eley-Rideal mechanism for phenyl + methyl coupling on Cu(100), the order of reactant addition is reversed and methyl radicals are impinged onto a Cu(100) surface precovered with a partial monolayer of phenyl groups. Selected results of these studies are shown in Figure 3B. In the results shown, adsorbed phenyl groups were generated on Cu(100) by exposing the surface to 2.0 L of iodobenzene at 100 K and then briefly annealing to 200 K to induce C-I bond dissociation. Subsequent exposure to "1.0 L" of methyl radicals from the pyrolysis source saturates the surface with methyl groups. Note that the toluene produced in a subsequent TPR experiment is evolved from the Cu(100) surface in two distinct temperature regimes (240 and 380 K). The higher temperature (380 K) peak reflects that coupling of adsorbed phenyl and methyl groups analogous to what is shown in Figure 3A when the order of reactant addition was reversed. The lower temperature (240 K) peak is observed only when methyl radicals are dosed after phenyl groups have been generated on the surface. (For example, this peak is also absent when iodobenzene is preadsorbed but the surface has not been annealed to dissociate the C-I bond and generate surface phenyl groups prior to methyl radical adsorption.) The origin of the 240 K toluene evolution



Figure 4. Temperature-programmed desorption spectra monitoring toluene molecular desorption at $m/e^+ = 91$ on Cu(110) following (A) adsorption of several different exposures of toluene alone and (B) sequential adsorption of 2.0 L of toluene and 10.0 L of iodobenzene at 100 K. The spectrum in B indicates that iodobenzene quantitatively displaces toluene from the monolayer on Cu(110).

peak is not obvious from the single experiment in Figure 3B, but the results below suggest an Eley-Rideal mechanism.

We note first that the 240 K peak temperature for toluene evolution in Figure 3B is indicative of toluene molecular desorption from Cu(100). While we have not obtained TPD spectra for toluene on Cu(100), we have studied toluene adsorption on Cu(110), where one would expect a similar, if not stronger, molecule/surface interaction because of the increased surface corrugation. As shown by the temperatureprogrammed desorption (TPD) results in Figure 4A, toluene desorbs from monolayers on Cu(110) over a wide temperature range from 200 to 350 K (multilayers are evolved at temperatures below 200 K; for example, note the peak temperature of 160 K in Figure 4). The temperature for the onset of desorption shifts down with increasing surface coverage, and it is reasonable that toluene evolution in the phenyl + methyl experiments of Figure 3B should commence near 200 K since the surface is saturated with phenyl, methyl, and iodine in these studies. That toluene evolution maximizes at 240 K and ceases for temperatures above 300 K in Figure 3B is also reasonable since the surface remains covered with adsorbed species (CH₃, unreacted phenyl, and iodine) after all toluene has desorbed.

Confirmation that the 240 K desorption temperature in the experiment of Figure 3B for Cu(100) is determined by the rate of toluene desorption and that this toluene is actually formed at temperatures below 160 K comes from chemical displacement studies. The basis for these experiments is illustrated schematically in Figure 5 and demonstrated experimentally as shown by the spectra presented in Figure 4B. As shown in Figure 5, the idea is to use iodobenzene- d_5 to displace weakly adsorbed molecules such as toluene while leaving strongly chemisorbed reaction intermediates such as phenyl and methyl on the surface. The ability of iodobenzene to displace toluene at very low temperatures is demonstrated by the TPR results in Figure 4B. In this experiment 2.0 L of toluene has been adsorbed on Cu-(110) at 100 K followed by 10.0 L of iodobenzene. On the



Figure 5. Schematic chemical displacement experiment in which a relatively large exposure of iodobenzene- d_5 is added to a surface initially covered with molecular toluene (top) or chemisorbed methyl and phenyl groups (bottom). As indicated, iodobenzene- d_5 displaces the weakly adsorbed toluene molecules from the monolayer to the second or multilayer, resulting in toluene desorption at 160 K in a subsequent TPD experiment. As also indicated, iodobenzene- d_5 fails to displace more strongly chemisorbed methyl and phenyl groups.

basis of the TPD results in Figure 4A, 2.0 L of toluene would be expected to desorb at 200-350 K in the absence of any effect of coadsorbed iodobenzene. However, as shown by the toluene TPD spectrum in Figure 4B, the addition of iodobenzene displaces 100% of the toluene from the monolayer to the multilayer, where it is evolved at 160 K, consistent with the multilayer peak temperature in Figure 4A. This displacement phenomenon is discussed more fully in other publications;⁵⁷ the important point for the studies here is that toluene produced in the phenyl + methyl reaction can be displaced from the monolayer by iodobenzene.

Figure 6 presents the results for the application of chemical displacement to the phenyl + methyl coupling reaction. The TPR spectrum in Figure 6A is directly analogous to that in Figure 3B except for the fact that 1.0 L rather 2.0 L of iodobenzene has been adsorbed and annealed to generate phenyl groups prior to methyl radical adsorption. (It should also be noted that the studies in Figures 3 and 6 were performed on a Cu(100) crystal that had been remounted several times in between, so peak temperatures are probably only comparable to within 10-20 K.) The experiment in Figure 6B is the same as that in Figure 6A except that after phenyl generation and methyl radical exposure, 10 L of iodobenzene- d_5 has been added prior to desorption to displace any product toluene to the multilayer. (Fully deuterated iodobenzene was used as the displacing agent to verify that none of the phenyl groups from the displacing agent are incorporated in the product toluene.) As shown by the TPR spectrum in Figure 6B, this displacement procedure shifts the 221 K toluene peak in Figure 6A to the 160 K multilayer desorption temperature (compare Figure 4B). [The precise yields and temperatures in Figures 6A,B cannot be compared because the experiments were performed weeks apart; it should also be noted that the kinetics of the hightemperature phenyl + methyl coupling reaction are perturbed (e.g. note the split peak at \sim 320 K in Figure 6B) by the presence of the coadsorbed iodobenzene displacing agent on the surface.] The shift of the low-temperature toluene peak from 221 to 160 K upon displacement implies that the 221 K toluene peak temperature in Figure 3A is indicative of the kinetics of toluene desorption (from the monolayer) and that the toluene is actually formed below 160 K. Since this temperature is so much lower than the 350-400 K temperature range for Langmuir-Hinshelwood coupling of phenyl and methyl on Cu(100), we



Figure 6. Temperature-programmed desorption spectra monitoring toluene evolution at $m/e^+ = 91$ following (A) no addition and (B) addition of 10.0 L of iodobenzene- d_5 to a Cu(100) surface that had been previously exposed to 1.0 L of iodobenzene- h_5 , annealed to 200 K, and then exposed to 1.0 L of methyl radicals. The decrease in the low-temperature toluene evolution temperature from 221 K, without the addition of the iodobenzene- d_5 , to 160 K, upon addition of the iodobenzene- d_5 , indicates that these toluene products are formed below 160 K and suggests an Eley–Rideal mechanism as discussed in the text.

conclude that the low-temperature toluene formation pathway involves an Eley-Rideal reaction between phenyl and methyl at the methyl adsorption temperature of 100 K. It should be noted, however, that the displacement studies in Figure 6B only place an upper limit of 160 K on the reaction temperature; these studies do not definitively establish that reaction occurs during dosing at 100 K since the iodobenzene displacing agent remains adsorbed in the multilayer to 160 K and would therefore also displace any toluene formed up to 160 K during the TPR experiment. On the other hand, the absence of this lowtemperature reaction channel when the order of phenyl and methyl addition is reversed provides strong evidence in support of an Eley-Rideal mechanism.

IIIB. Adsorbed Phenyl Groups + Coadsorbed Methyl Iodide on Cu(110). Having established that gas phase methyl radicals react with adsorbed phenyl groups by both Langmuir-Hinshelwood and Eley-Rideal mechanisms on Cu(100), the TPR results in Figure 7 address the possibility of analogous processes for the reaction of phenyl with coadsorbed methyl *iodide* on Cu(110). As noted in the Introduction, the basis for these studies is the observation that methyl iodide produces methyl radicals during carbon-iodine bond dissociation on Cu(111).41,42 Figure 7A shows the toluene product TPD spectrum obtained after coadsorbing 1.0 L of methyl iodide and 1.0 L of iodobenzene- d_5 at 100 K on Cu(110). The single peak in the TPR spectrum at 435 K is indicative of the kinetics of phenyl + methyl coupling on Cu(110). The 50-75 K higher peak temperature for this reaction on Cu(110) compared with Cu(100) (compare Figure 3) indicates a higher barrier for this Langmuir-Hinshelwood coupling reaction on Cu(110), although



Figure 7. Temperature-programmed desorption spectra monitoring toluene- d_5 evolution at $m/e^+ = 96$ on Cu(110) following (A) sequential adsorption of 1.0 L of iodobenzene- d_5 and 1.0 L of methyl iodide at 100 K and (B) addition of 1.0 L of methyl iodide to a surface that had been previously exposed to 1.0 L of iodobenzene- d_5 and briefly annealed to 230 K to form phenyl groups.

10-20 K of this peak difference may be due to differences in thermocouple contact with the two surfaces.

The absence of a low-temperature toluene evolution peak in the iodobenzene + methyl iodide study of Figure 7A is not surprising since previous studies have shown that the C–I bond in methyl iodide dissociates at ~140 K (refs 41, 42, 58, 59) on Cu surfaces, while the C–I bond in iodobenzene does not dissociate until ~180 K (refs 20, 53, 54). As a result, iodobenzene molecules, not phenyl groups, are present on the surface when methyl radicals are generated by C–I bond scission in CH₃I. This experiment is therefore analogous to the studies in which methyl radicals were impinged onto an iodobenzene-covered Cu(100) surface and only Langmuir– Hinshelwood coupling was observed.

To determine whether methyl radicals generated upon CH₃I dissociation will react with phenyl groups prior to thermal accommodation with the surface, adsorbed iodobenzene must be annealed to generate phenyl groups prior to CH₃I adsorption. The TPD spectrum in Figure 7B results from dosing 1.0 L iodobenzene- d_5 on Cu(110) and briefly annealing at 200 K to produce adsorbed phenyl groups before cooling back to 100 K and dosing 1.0 L of methyl iodide. As shown, toluene is now evolved at both 430 and 315 K, evidencing two different toluene formation pathways. In analogy with the coadsorption experiment in Figure 7A, the 426 K peak in Figure 7B results from coupling of surface-bound methyl groups with surface-bound phenyl groups. The new peak at 315 K reflects a different pathway for toluene formation that is only detected when phenyl groups exist on the surface prior to C-I bond cleavage in methyl iodide. This low-temperature toluene desorption channel is suggestive of an Eley-Rideal mechanism analogous to that responsible for the low-temperature toluene desorption channel in the gas phase methyl radical experiments presented above.

While the TPR spectrum in Figure 7B for toluene evolution from phenyl + CH₃I looks reasonably straightforward, this spectrum is atypical of the TPR results for this reaction. For higher coverages of phenyl, the low-temperature toluene evolution channel shifts to lower temperature and multiple peaks (up to 3) are observed. Selected TPR results for iodobenzene- d_5 exposures of 1.0, 2.0, and 3.0 L are shown in Figure 8A. Similar



Figure 8. Temperature-programmed desorption spectra monitoring toluene- d_5 evolution at $m/e^+ = 96$ following (A) no addition and (B) addition of 10.0 L of iodobenzene- h_5 to a Cu(110) surface that had been previously exposed to several different exposures of iodobenzene- d_5 , annealed to 230 K, and then exposed to 1.0 L of methyl iodide. In (B) the surface was also annealed to 150 K after exposure to the 1.0 L of methyl iodide and before exposure to 10.0 L of iodobenzene- h_5 . The single low-temperature toluene desorption feature at 160 K (after addition of the iodobenzene- h_5 chemical displacing agent) in B indicates that the toluene, which results in the low temperature desorption features at 316, 297, 238, and 176 K (when the iodobenzene- h_5 chemical displacing agent is not added in A), is actually formed below 160 K. This toluene formation below 160 K is strongly suggestive of an Eley–Rideal mechanism involving methyl radicals produced in the thermal dissociation of methyl iodide, as discussed in the text.

complex peak structure was also reported previously in studies of analogous cross coupling reactions on Cu(111).³³ In that work, the multiple peak structure was attributed to complex, coverage-dependent product desorption kinetics, and this interpretation is verified here using the chemical displacement protocol described above in connection with Figures 4-6. The results are shown in Figure 8B, which presents TPR spectra for monolayers that are the same as those in Figure 8A except that 10 L of iodobenzene- h_5 has been added as a displacing agent prior to the TPR experiment. Note that while the 430 K phenyl + methyl coupling TPR peaks are relatively unaffected by the addition of this displacing agent, all of the lower temperature toluene peaks that were observed from 176 to 316 K in Figure 8A are now displaced to a common multilayer desorption temperature of 160 K. This result confirms the idea that all toluene evolved between 176 and 316 K in the experiments of Figure 8A was formed at temperatures below 160 K.

IIIC. Adsorbed Phenyl Groups + Alkyl, Vinyl, and Aryl Iodides on Cu(110). In addition to studying the reaction of CH₃I with phenyl groups, we have studied the reactions between phenyl and vinyl iodide, iodobenzene, and longer chain alkyl iodides on Cu(110). The results, which are analogous to those above for CH₃I, are not shown here, but they can be briefly summarized as follows. Like CH₃I, vinyl iodide shows two reaction channels for coupling with phenyl groups: a lowtemperature (<188 K) reaction involving molecular vinyl iodide and a higher temperature (~380 K) pathway involving surfacebound vinyl groups. In the case of the longer chain alkyl iodides, if the alkyl group contains a β -hydrogen atom, then only the low-temperature molecular alkyl iodide pathway is observed. The reason for the absence of the higher temperature alkyl + phenyl coupling reaction is that adsorbed alkyls with β -hydrogens undergo β -hydride elimination at temperatures below 250 K on copper surfaces.^{58,60} Thus, the temperature of alkyl decomposition is significantly lower than the temperature of alkyl + phenyl coupling, which, based on the CH₃I studies, is expected to be ~400 K.

While alkyl iodides like ethyl iodide show only the lowtemperature phenyl + alkyl iodide pathway for coupling on Cu(110), neopentyl iodide, which lacks β -hydrogens, shows both low- and high-temperature pathways. The high-temperature phenyl + *neopentyl* pathway evolves neopentyl benzene, as identified by the parent molecular ion, $m/e^+ = 148$, at 415 K, while neopentyl benzene from the low-temperature phenyl + *neopentyl iodide* pathway can be displaced (by iodobenzene d_5) and desorbed from Cu(110) at temperatures as low as 190 K.

Results on the coupling of phenyl with iodobenzene to form biphenyl are presented elsewhere,⁵⁴ but the significant findings in connection with the present work are that only the hightemperature phenyl + phenyl coupling reaction is observed on Cu(110), while on Cu(111) and Cu(100) both the hightemperature phenyl + phenyl pathway and the low-temperature phenyl + iodobenzene pathways are observed. Possible reasons for this difference are discussed in ref 54.

IV. Implications of the Results for the Mechanism of Reaction between Phenyl Groups and Alkyl Iodides on Copper Surfaces

The results presented above indicate two mechanisms for the cross coupling reaction between phenyl groups and methyl iodide coadsorbed on a Cu(110) surface. One involves C-I bond dissociation in methyl iodide at \sim 140 K followed by coupling of coadsorbed phenyl and methyl groups above 400 K to form toluene, which immediately desorbs from the surface. The second involves a direct reaction between phenyl groups and intact methyl iodide. This reaction occurs at temperatures below 160 K. Attempts to monitor the kinetics of this reaction more precisely by a number of means (chemical displacement, hydrogen atom titration, and near edge X-ray absorption fine structure spectroscopy) were unsuccessful, so there remains a question as to whether CH₃I dissociation and toluene formation are separate events (coupled by a methyl free radical or hot radical intermediate) or whether the phenyl groups interact directly with CH₃I so that C-I dissociation and C-C bond formation occur in concerted fashion.

While the possibility of direct interaction between CH₃I and phenyl cannot be ruled out, several experimental results argue against this possibility and for the free radical or hot radical scenario. First, in connection with the possibility of direct interaction during C–I dissociation, we note that an S_N2 mechanism where the phenyl group attacks the back side of the methyl group in CH₃I ejecting the iodine (a mechanism suggested previously for the reaction of H and CH₃I on Pt(111) to make methane³²) is ruled out on the basis of studies with neopentyl iodide. As shown in Figure 9, the bulky neopentyl group shields the electrophilic pocket opposite the carbon– iodine bond, prohibiting back-side attack by surface phenyl groups. The fact that the low-temperature coupling channel is



Figure 9. Schematic S_N2 displacement reaction of adsorbed phenyl groups (possibly anionic) with methyl iodide (left) and neopentyl iodide (right). The tert-butyl substitution of methyl iodide to form neopentyl iodide provides steric hindrance, which prevents nucleophillic attack by the phenyl group. The finding of similar reactivities for methyl iodide and neopentyl iodide argues against an S_N2 reaction between adsorbed phenyl and molecular methyl iodide as the mechanism for the lowtemperature toluene formation in these studies.



REACTION COORDINATE

Figure 10. Schematic reaction coordinate for the formation of toluene from adsorbed phenyl groups and methyl iodide on Cu surfaces. As shown, the reaction can occur by both the Langmuir-Hinshelwood mechanism (solid line), involving a chemisorbed methyl intermediate, and the Eley-Rideal mechanism (dashed line), involving a methyl free radical intermediate. Because of the relatively large 27 kcal/mol barrier to coupling coadsorbed alkyl and aryl groups on Cu surfaces, the Langmuir-Hinshelwood pathway only occurs at a measurable rate above 375 K. The energetic barrier to the Eley-Rideal pathway is simply the barrier to adsorbed CH₃I bond dissociation, so this reaction pathway occurs below 160 K.

observed for neopentyl iodide is thus inconsistent with nucleophilic attack but consistent with a radical mechanism.

Other evidence in support of a radical mechanism includes (1) the observation that methyl radicals incident on a phenyl precovered surface from the gas phase react by an Eley-Ridealtype pathway to produce toluene, (2) the finding that methyl radicals are generated and evolved from the surface in the thermal dissociation of the C-I bond in methyl iodide on Cu(111),^{41,42} and (3) the determination from chemical displacement studies that the upper limit to the phenyl + CH₃I reaction temperature is 160 K, which is quite close to the temperature of ~ 140 K for C–I dissociation in CH₃I in the absence of phenyl groups.

Thus, while the definitive experiment is still lacking, the studies presented here provide further evidence in support of a radical mechanism in the low-temperature reaction of phenyl groups with methyl iodide on copper surfaces. A schematic diagram of the relative energetics for this type of mechanism is shown in Figure 10. As shown, the barrier for C-I bond scission in CH₃I to produce a methyl radical is less than 10

kcal/mol and the process is approximately thermal neutral. Upon radical formation, there are three possibilities: radical desorption, radical reaction with coadsorbed species, and radical trapping into the \sim 30 kcal/mol (ref 42) potential energy well corresponding to surface-bound methyl groups on copper surfaces. The results presented here provide evidence for a branching between a direct pathway for reaction of methyl radicals with coadsorbed phenyl groups and trapping of methyl radicals on the surface followed by a normal Langmuir-Hinshelwood coupling reaction with a much higher activation energy. It is interesting that the former pathway represents the combination of a reverse Elev Rideal reaction (methyl radical formation from CH₃I dissociation) with an Elev-Rideal process (phenyl + methyl radical coupling). More experimentation is required to establish the extent to which the proximity of CH₃I and phenyl are important and the extent to which CH₃ exists as a free radical intermediate in this low-temperature cross coupling reaction.

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