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Coupling and Disproportionation Reactions of Alkyl Iodides on a Single-Crystal Copper Surface: Alkyl Radicals versus Metal Alkyls

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Abstract: Previous studies of straight-chain alkyl iodides (C_2–C_5) adsorbed on a Cu(111) surface at submonolayer coverages have shown that these molecules dissociate at ~120 K to generate adsorbed alkyl groups and iodine atoms. The surface-bound alkyls (with an alkyl–metal bond energy of ~30 kcal/mol) undergo β-hydride elimination above ~200 K. Here, the thermal chemistry of these alkyl iodides at high surface coverage (up to saturation of the monolayer) is investigated by using temperature-programmed reaction/desorption to identify the surface reaction products and reaction kinetics. The intriguing aspect, which is different from the reaction at low coverage, is the formation of alkyl coupling and disproportionation products at the temperature where the C–I bond dissociates. The relative yields of these products suggest a radical mechanism. The parallel reaction channels for forming alkyl radicals and adsorbed alkyls during C–I bond dissociation on the Cu(111) surface are discussed in the context of analogous reactions of alkyl halides with metal surfaces in solution.

1. Introduction

The reaction of alkyl halides (RX) with metals is well-documented in the synthetic literature as a preparative method for a variety of organic and organometallic compounds. Well-known examples of these reactions to form dialkyl metals, alkyl metal halides, alkylsilanes, and alkanes are shown below:

$$RX \xrightarrow{Zn} ZnR_2 \quad \text{(Frankland,}^1\text{ 1849)}$$

$$RX \xrightarrow{Mg} RMgX \quad \text{(Grignard,}^2\text{ 1901)}$$

$$RX \xrightarrow{Cu/Si} R_2SiX_2 \quad \text{(Rochow,}^3\text{ 1945)}$$

$$RX \xrightarrow{Na} R_2 \quad \text{(Wurtz,}^4\text{ 1855)}$$

While the distribution of the alkyl groups (R) and halogen atoms (X) is different in the primary reaction products shown above, the secondary products of these reactions are frequently directly analogous to the primary products in others. For example, in the Grignard reaction, CH_3MgBr is the desired product, but side reactions to form C_2H_6 (the Wurtz coupling product) and $Mg(CH_3)_2$ (the Frankland-type dialkyl product) are often observed.

A second common feature of the reactions above is that in each case the mechanism of reaction between the alkyl halide and the metal surface has proven controversial. A primary point of contention, which has yet to be unequivocally resolved, is the extent to which free alkyl radicals, surface-bound alkyl radicals, or adsorbed metal–alkyl species are intermediates in these reactions.[5–9] The formation of rearranged, coupled, and disproportionated alkyl groups suggests the participation of alkyl radicals, but the branching ratio between these pathways is sometimes substantially different from that found for alkyl radicals generated in solution by other radical precursors.[5–7] In the case of the Grignard reaction, two explanations for these differences have been offered. Whitesides, Garst, and co-workers have pointed out that different branching ratios are to be expected for the high concentrations of radicals generated at surfaces, and they have proposed a simple free radical model with only one adjustable parameter to account for a wide range of experimental results.[8,9] Walborsky, on the other hand, has suggested that surface-adsorbed alkyl radicals are responsible for these results.[6] The formation of Mg–alkyl species is supported by the formation of the Grignard reagent itself, but the role of such species in generating coupling, disproportionation, and rearrangement products has been difficult to determine.

The advent of ultra-high-vacuum surface preparation and analysis techniques has made it possible to isolate the elementary steps in the reaction of alkyl halides with atomically-clean metal surfaces. Over the past four years, these reactions have received considerable attention as a way to generate and study the chemistry of alkyl species bound to metal surfaces.[17] Most of these studies have focussed on the reaction of methyl halides, but longer chain alkyl halides have also been studied on silver,[12] copper,[13,14] platinum,[15–18] and aluminum[19–21] surfaces. Several general findings have emerged. First, because the alkyl halides are highly reactive with atomically clean surfaces, the surfaces must be cooled

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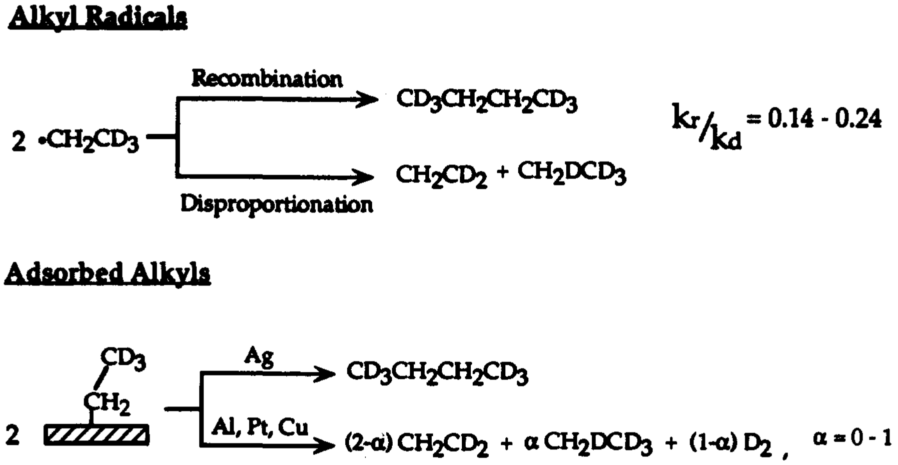

Figure 1. Typical reactions of (top) free alkyl radicals and (bottom) alkyl groups adsorbed on metal surfaces.

to temperatures of 100 K or below to study the carbon–halogen bond dissociation reaction. Second, while the most commonly-reported C–X bond dissociation products are the halogen and an alkyl group bound to the metal surface, recent studies of CH_3Br decomposition on a potassium-precovered Ag(111) surface[10] and of CH_3I decomposition on a clean Cu(111) surface[11] have shown that methyl radicals can be ejected from the surface into the gas phase concurrently with the formation of adsorbed methyl groups. Third, the alkyl groups bond quite strongly to the metal surface, with bond energies being in the range of 25–40 kcal/mol.[22,18] And fourth, while the products and kinetics of the reaction of these adsorbed alkyl groups are highly metal dependent, there are no examples to date where the surface-bound alkyl groups undergo both coupling and disproportionation reactions analogous to the reactions of alkyl radicals in the gas phase and solution. As shown in Figure 1, alkyl coupling has been observed on silver surfaces,[12] and alkyl reaction to form alkenes and alkanes has been reported on copper,[13,14] platinum,[15–18] and aluminum[19–21] surfaces, but these latter reactions are not strict disproportionations; the predominant product is the alkene, and excess hydrogen desorbs as H_2 ($\alpha \ll 1$ in Figure 1).

In this paper, results are reported which show that alkyl coupling and disproportionation products are formed when high coverages of alkyl iodides (near saturation of the monolayer) are reacted with a single-crystal Cu(111) surface under ultra-high-vacuum conditions. The ratio of disproportionation to coupling products is 0.44 ± 0.13, which is consistent with that expected from the reactions of alkyl radicals. A radical mechanism is also supported by cross-coupling studies of alkyl iodides and adsorbed alkyl groups. Taken together with previous results on the reactions of adsorbed groups on Cu(111), these results allow us to distinguish between the role of alkyl radicals and metal alkyls in the chemistry of alkyl iodides with this copper surface.

2. Experimental Section

The experiments were carried out in an ultra-high-vacuum chamber equipped with an Auger electron spectrometer (AES) for determining surface composition, a high-resolution electron energy loss spectrometer (HREELS) for measuring surface vibrational spectra, a shielded and differentially-pumped quadrupole mass spectrometer for detecting and identifying gas-phase reaction products, and an ion sputtering gun for surface cleaning. In the studies reported here, the Cu(111) single crystal (a disk of 1-cm diameter purchased from Monocrystals Inc., 99.999% purity) was mounted on a resistive heating element which was capable of heating the surface to 1100 K and cooling, with liquid nitrogen, to 110 K. The surface temperature was monitored by a thermocouple, the junction point of which was inserted into a hole on the edge of the crystal. The surface was cleaned in vacuum by sputtering with Ar^+ ions and annealing at 950 K.[22]

In the temperature-programmed reaction/desorption (TPR/D) experiments, the clean surface was cooled to 110–120 K and exposed to gas molecules by backfilling the chamber. The exposures are expressed in Langmuirs (L) (1 L = 10^{-6} Torr·s) and are uncorrected for differing ion gauge sensitivities. For the C_1–C_5 alkyl iodides studied here, exposures of between 4 and 8 L are required to saturate the monolayer at 110 K (the exact value depends on the compound, with larger exposures being required for the longer chain molecules where the ion gauge sensitivity is larger). In the experiments in which two different compounds were reacted, separate leak valves and manifolds were used to avoid cross contamination of the dosing gases.

All of the alkyl iodides were purchased from Aldrich and stored in glass vials shielded from light to prevent photodecomposition. The samples were purified by freeze–pump–thaw cycles to remove volatile contaminants, and their purities were confirmed in situ by mass spectrometry. In the TPR/D experiments, the surface, after exposure to the gas molecules, was positioned line-of-sight to the mass spectrometer; the surface was held 2 mm from a 2 mm diameter sampling aperture to the differentially-pumped mass spectrometer. This configuration ensured that the mass spectrometer detected only those species evolved from the center of the surface. The mass spectrometer was multiplexed to detect up to three masses in each TPR/D experiment and was operated at an ionization energy of 70 eV. The surface heating rate was 2.5 K/s throughout these studies.

3. Results and Interpretation

As mentioned in the Introduction, previous studies of alkyl iodides have established that, for *submonolayer* coverages on a Cu(111) surface, C–I bond dissociation occurs between 100 and 150 K to form adsorbed alkyl groups and iodine atoms.[13,14] These alkyl groups subsequently decompose at temperatures *above 200 K*. In this paper, we focus on alkyl iodide reaction products formed at temperatures *below 200 K* and for coverages at *near saturation of the monolayer*. The compounds studied were the straight-chain C_1–C_5 alkyl iodides. We present first the results of alkyl coupling and cross coupling followed by a selected example of the alkyl disproportionation reaction. The relative product yields are then quantified, and the effects of dosing time on the total product yield are discussed.

Alkyl Coupling. Figure 2 shows temperature-programmed reaction (TPR) spectra for the alkyl coupling products from the C_1 to C_5 alkyl iodides on Cu(111). Only one representative mass for each product is shown. The coupling products have been identified by comparing the cracking ratios for at least three diagnostic ions with calibration mass spectra obtained with the same mass spectrometer. These comparisons are summarized in Table I along with values for the cracking ratios from the literature.[23] The highest intensity in each entry of Table I has been set to 1000 for purposes of comparison. The ions monitored

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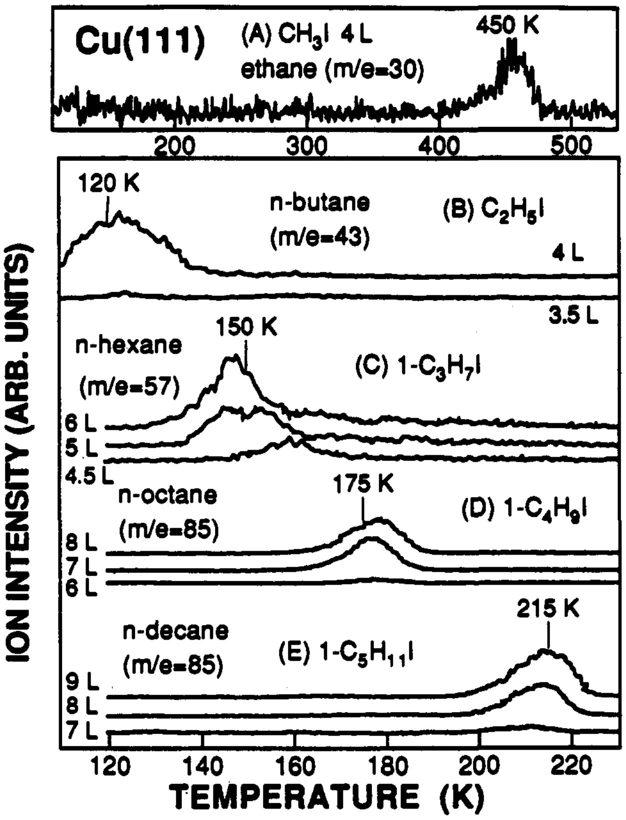

Figure 2. Temperature-programmed reaction (TPR) spectra for alkyl coupling products from the C_1 to C_5 alkyl iodides on Cu(111). The ethane peak at 450 K is due to the coupling of the adsorbed methyl groups. For the longer chain alkyl iodides, the low-temperature reaction channel for alkyl coupling is attributed, as discussed in the text, to a radical mechanism. The increase in peak temperature with increased carbon chain length indicates that the alkane peaks are desorption-limited. In the case of C_2H_5I, alkyl coupling to produce butane may be rate-limited by carbon–iodine bond dissociation which occurs at approximately the same temperature.

Table I. Comparison of the Mass Spectrometer Cracking Patterns for Butane, Hexane, Octane, and Decane from This Work with the Cracking Patterns from Reference 23

	m/e			
butane source	29	41	43	58
literature	448	284	1000	126
C_4H_{10} (TPD)	453	359	1000	82
C_2H_5I (TPR)	410	388	1000	104

	m/e				
hexane source	57	58	71	85	86
literature	1000	45	50	4	141
C_6H_{14} (TPD)	1000			14	160
C_3H_7I (TPR)	1000	45			174
CH_3I (3 L) + $C_5H_{11}I$ (5 L) (TPR)			45	7	160

	m/e			
octane source	70	71	85	114
literature	407	783	1000	230
C_8H_{18} (TPD)	343	537	1000	
C_4H_9I (TPR)		493	1000	97

	m/e			
decane source	71	85	86	142
literature	1000	696	44	203
$C_5H_{11}I$ (TPR)	1000	520	44	
CH_3I (3 L) + $C_5H_{11}I$ (5 L) (TPR)		696		291

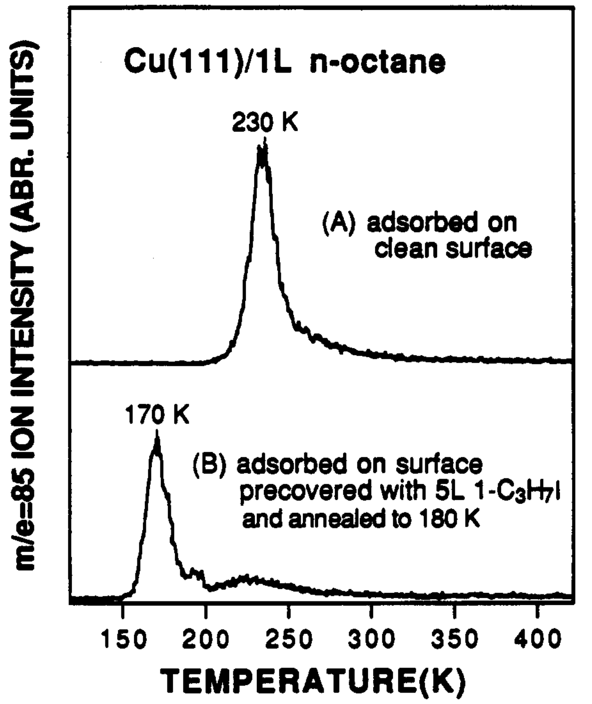

Figure 3. Temperature-programmed octane desorption spectra after 1 L of octane was adsorbed on a Cu(111) surface under the indicated conditions.

in the TPR spectra of Figure 2 were selected to avoid potential interferences from molecular desorption if there is any. In the spectra here there is either no molecular desorption at the selected exposures or it occurs at a different temperature from that where the coupling product is evolved.

There are several interesting aspects to note about the results in Figure 2. First, for the C_2–C_5 alkyl iodides, coupling occurs only at low temperatures (<200 K) and for relatively high exposures (saturation of the monolayer occurs for exposure between 4 and 8 L depending on the compound). CH_3I, on the other hand, produces ethane at temperatures above 400 K. Previous studies by HREELS and TPR have shown that the C–I bond in CH_3I dissociates at ~140 K on Cu(111) to produce methyl groups which are stable on the surface to temperatures above 400 K.[24] The ethane at 450 K in Figure 2A is thus attributable to the coupling of adsorbed methyl groups. In the case of the longer chain alkyl iodides C–I bond dissociation occurs at ~120 K to generate alkyl groups on the surface.[13] On the basis of the methyl coupling temperature of 450 K, it seems unlikely that coupling of the longer chain surface-bound alkyl groups occurs at temperatures as low as 120 K. Apparently other mechanisms are operative in these low-temperature coupling reactions.

The increase in the peak temperature as a function of alkyl chain length for the coupling products in Figure 2 indicates that either the rate is significantly slower for longer chains or molecular desorption is the rate-determining step in product evolution. The results in Figure 3 suggest the latter. As shown in Figure 3A, a submonolayer coverage of octane desorbs from Cu(111) at 230 K. While this temperature is ~50 K higher than that in Figure 2D for octane evolution from the reaction of iodobutane, this difference is attributable to coadsorbed species on the surface. As shown in Figure 3B, if a Cu(111) surface is precovered with 5 L of iodopropane and annealed to 180 K to mimic the surface environment present when the coupling product is formed, then octane desorbs from this surface at ~170 K. This temperature is consistent with that observed for coupling of iodobutane to form octane. Similar agreement is found for hexane desorption and hexane evolution from the coupling of iodopropane. These results indicate that the iodoalkane coupling peaks in spectra C–E of Figure 2 are desorption limited. The unusually low

Scheme I

$$\text{R–Cu} + \text{R–Cu} \longrightarrow \text{R}_2 + 2\text{Cu} \tag{1}$$

$$\text{R–Cu} + \text{R–I} \longrightarrow \text{R}_2 + \text{Cu–I} \tag{2}$$

$$\text{R–Cu} + {}^\bullet\text{R} \longrightarrow \text{R}_2 + \text{Cu} \tag{3}$$

$$\text{R–I} + \text{R–I} + 2\text{Cu} \longrightarrow \text{R}_2 + 2\text{Cu–I} \tag{4}$$

$$\text{R–I} + {}^\bullet\text{R} + \text{Cu} \longrightarrow \text{R}_2 + \text{Cu–I} \tag{5}$$

$${}^\bullet\text{R} + {}^\bullet\text{R} \longrightarrow \text{R}_2 \tag{6}$$

temperature observed for desorption of the coupled product is due to either interactions with coadsorbed species in the monolayer or possibly bonding of the product in a physisorbed second layer (see section 4 for a discussion of how the coupling product may be formed by radical reactions in a second layer). In the case of iodoethane coupling to give butane (Figure 2B) the surface reaction may be rate determining, since the peak temperature (120 K) is about the same as the temperature for C–I bond dissociation.[13] This result suggests that C–I bond dissociation is the rate-determining step in forming the coupled products.

Several mechanistic possibilities can be envisioned for these low-temperature coupling reactions, and we mention them here to place the rest of the experimental results in context. The mechanisms for coupling can be classified according to the species involved in the alkyl coupling step, and these species include the following: molecular alkyl iodides, adsorbed alkyl groups, and alkyl radicals. As shown in Scheme I, there are six possible coupling mechanisms involving all possible pairs of these three species. The first of these mechanisms, coupling of surface-bound alkyl groups, seems unlikely on the basis of the high temperature required for coupling surface-bound methyl groups as shown in Figure 2A. To address the possibility that adsorbed alkyl groups react with either alkyl radicals or molecularly intact alkyl iodides to form the coupled products (eqs 2 and 3 above), cross-coupling reactions have been studied in which one alkyl iodide is dissociated to form alkyl groups followed by adsorption of an alkyl iodide of different chain length. Cross coupling indicates that the reaction involves adsorbed alkyl groups.

Cross Coupling of Alkyl Iodides. Cross coupling between a variety of C_1–C_5 alkyl iodides has been studied; the results are illustrated here for the cross coupling of iodomethane and iodopentane. Figure 4 shows TPR/D spectra for masses 71 (A) and 86 (B) after 3 L of CH_3I followed by 5 L of $C_5H_{11}I$ are dosed onto Cu(111) at 115 K. For these exposures, the total adsorbate coverage on the surface is slightly in excess of monolayer saturation so some molecular desorption (not shown) is observed. The peaks at 155 K in Figure 4 are due to formation of the cross-coupled product, hexane, as evidenced by the partial cracking pattern tabulated in Table I. Note that the hexane peak temperature in Figure 4B is consistent with that observed in Figure 2C for iodopropane coupling, supporting the conclusion that molecular desorption is the rate-determining step in product evolution. The small peaks at higher temperature (185, 210, and 235 K) are cracking fragments from the evolution of molecular $C_5H_{11}I$, decane, and pentane as indicated in the figure. The 185 K peak for $C_5H_{11}I$ is consistent with that observed for the molecular ion (not shown) while the 210 K peak for decane agrees with that in Figure 2E for iodopentane coupling. Pentane evolution at 235 K in Figure 4B is from the decomposition of adsorbed pentyl groups consistent with previous studies at submonolayer coverages.[13]

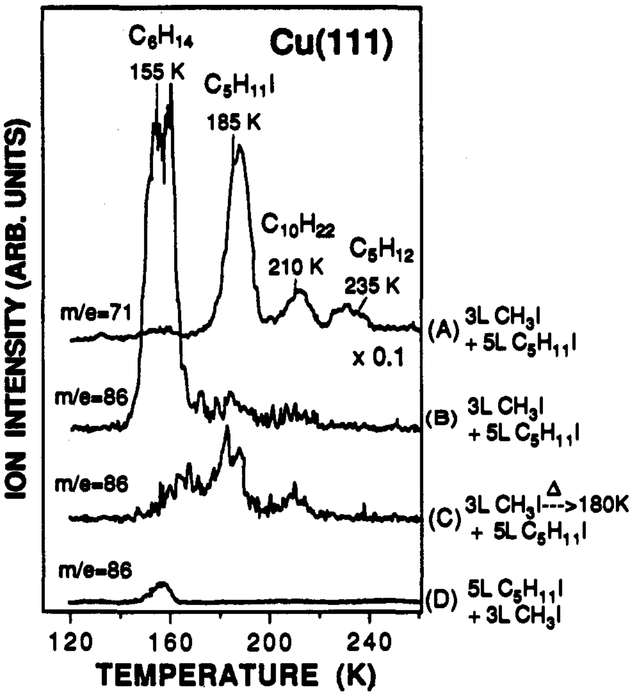

Figure 4. Temperature-programmed reaction/desorption spectra for *m/e* 71 and 86 after CH_3I and $C_5H_{11}I$ are dosed under the indicated conditions. The relatively small C_6H_{14} peaks in (C) and (D) in comparison to that in (B) indicate that surface-bound alkyl groups are not the major species involved in alkyl coupling.

Different results are obtained if the CH_3I dosed at 120 K is annealed to 180 K prior to recooling the surface to condense $C_5H_{11}I$. As shown in Figure 4C, this procedure almost completely eliminates the hexane peak at 155 K; the $C_5H_{11}I$ molecular desorption peak (185 K) increases slightly, and the decane coupling product (210 K) is essentially unchanged. These effects are attributable to the formation of adsorbed methyl groups by annealing the CH_3I to 180 K. The formation of both CH_3 and I from this annealing increases the total adsorbate coverage on the surface, which accounts for the slight increase in the $C_5H_{11}I$ molecular desorption peak at 185 K. The dramatic decrease in the hexane yield upon forming adsorbed methyl groups suggests that the pathway to form hexane does not involve adsorbed CH_3, i.e. surface-bound alkyl groups are not the primary coupling species. This conclusion is supported by the TPR spectrum in Figure 4D where the surface has been exposed to first $C_5H_{11}I$ and then CH_3I. The hexane yield is small in this case because the C–I bond in $C_5H_{11}I$ dissociates at ~120 K, approximately 20 K below where CH_3I dissociates. As a result, only adsorbed pentyl groups are present when CH_3I dissociates at 140 K. [Note that, because the total iodopentane exposure is only 5 L, no molecular desorption or coupling to form decane is observed (compare Figure 2E). Decane is formed in Figure 4B because the total adsorbate coverage on the surface while iodopentane is being adsorbed is increased by the presence of preadsorbed iodomethane. The signal-to-noise ratio is larger in this spectrum because only one ion was monitored in the TPR experiment].

Results similar to those in Figure 4 for iodomethane and iodopentane are obtained for cross coupling of other alkyl iodides. In each case, the yield of cross-coupled products decreases dramatically when either constituent is first dissociated to form adsorbed alkyl groups. We have yet to find conditions where substantial yields of the cross-coupled products are formed by reaction of alkyl iodides with adsorbed alkyl groups. These results suggest that surface-bound alkyl groups are not the primary intermediates for coupling alkyl iodides at low temperatures. Two factors prevent a more definitive conclusion from these results. First, because C–I bond scission occurs at approximately the adsorption temperature in these studies, some surface-bound alkyl groups are formed upon adsorption. Second, despite care to ensure that there is no cross contamination in the iodoalkane sources (separate gas manifolds and leak valves were used for each compound), a small, but finite, yield of cross-coupled products is observed when iodoalkanes are reacted with surface-bound

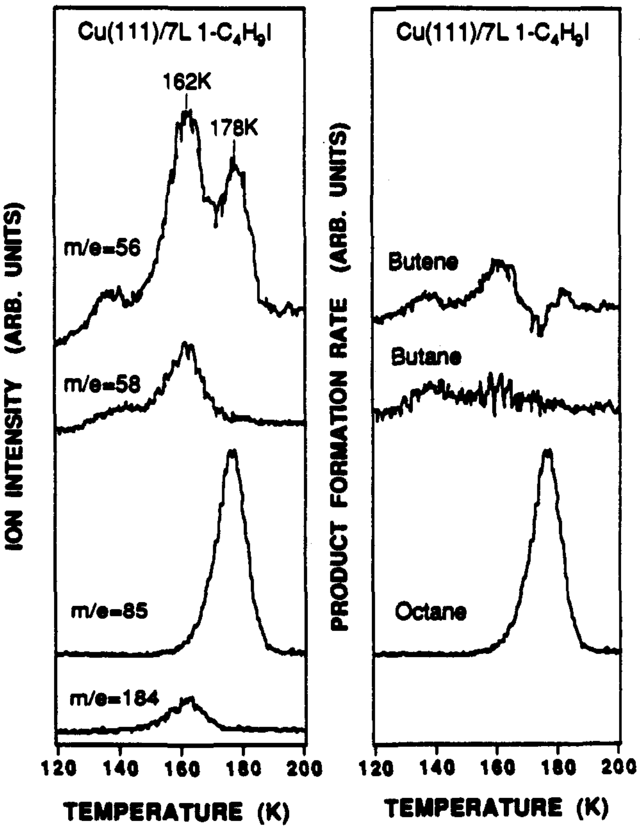

Figure 5. The left panel shows the temperature-programmed reaction/desorption spectra for *m/e* 56, 58, 85, and 184 after 7 L of 1-C_4H_9I was dosed onto Cu(111). The cracking fragments of octane and iodobutane cannot completely account for the peaks observed at ~160 K for *m/e* 56 and 58. The right panel shows the butene, butane, and octane formation rate after the relative mass sensitivities at *m/e* 56, 58, and 85 for these compounds were taken into account.

alkyl groups. We cannot rule out the possibility that the decreased yield in comparison with that of the undissociated alkyl iodides is due to the formation of islands of adsorbed alkyl groups so that subsequently adsorbed alkyl iodides can only react with alkyl groups on the perimeter of the islands.

To address the possibility that radicals are intermediates in the coupling reaction, disproportionation products have been carefully investigated. As shown in Figure 1, disproportionation is one of the characteristic reactions of alkyl radicals in the gas phase and in solution.[25] One would therefore expect both coupling and disproportionation products if alkyl radicals are involved. The results presented below show that both pathways do occur and in about the ratio expected for alkyl radicals.

Alkyl Disproportionation. This reaction pathway is illustrated with results for iodobutane. The left panel of Figure 5 shows TPR/D spectra for masses 56, 58, 85, and 184 after a 7 L exposure of C_4H_9I at 120 K. The peak for *m/e* 184 is due to molecular desorption of C_4H_9I which also has cracking fragments at *m/e* 56 and 58. The peak for *m/e* 85 is due to octane which has a cracking fragment at *m/e* 56. The cracking contributions from C_4H_9I and octane, however, cannot completely account for the peaks observed at *m/e* 56 and 58. The remaining peaks at these masses are attributable to butene and butane, respectively. There is no evidence for butyl radicals at *m/e* 57. While the simultaneous evolution of butene and butane is to be expected if C–I bond scission is the common rate-determining step in their formation, the 140 K peak temperature is 20 K above that for butane evolution from iodoethane in Figure 2B, a reaction that is also presumably limited by C–I bond scission. The reason for this difference has yet to be established.

The evolution of both alkyl coupling and disproportionation products from iodobutane suggests a radical mechanism for their formation. A characteristic feature of gas-phase and solution-phase alkyl radical reactions is the branching ratio for coupling vs disproportionation. As shown in Figure 1, the ratio of the disproportionation/coupling rate constants is typically 0.14–0.24.[25,26] In the case of the surface experiment, the relative rate constants can be approximated by the relative product yields as described below.

Product Yields. To calculate the relative yields of octane, butene, and butane from the results in the left panel of Figure 5, the ion intensities are first corrected for cracking contributions. To convert the resulting ion fractions to relative product yields the mass spectrometer sensitivities must be known. These values were obtained as follows. Standard mass spectra were obtained for each compound at a fixed chamber pressure as measured by an ion gauge. The spectra were then adjusted for differing ion gauge sensitivities with use of relative sensitivity factors based on literature values for similar compounds.[27] For the case here, the relative ion gauge sensitivities for octane, butene, and butane have been taken as 2, 1, and 1, respectively. The resulting correction factors to convert the ion intensities at *m/e* 84, 58, and 56 to relative product yields for octane, butane, and butene are 1.0, 0.69, and 2.1, respectively.

By using these detection sensitivities and correcting for cracking fragments, the ion TPR spectra in the left panel of Figure 5 have been converted to relative product intensities as shown in the right panel. Two factors are significant. First, the butane-to-butene ratio of 1.1 is consistent, to within the experimental uncertainty, with a strict disproportionation reaction where the ratio is 1. Second, the ratio of butene or butane to octane is 0.44 ± 0.13, which is within a factor of 2 of that expected for radical–radical reactions. It is worth noting that since this ratio can range from 0 to infinity, a factor of 2 is small on a global scale.

Figure 6 shows the relative product yields (for those products formed below 200 K) as a function of C_4H_9I exposure. The coupling and disproportionation products are observed over the same coverage range where molecular desorption is first observed, but while the yield of C_4H_9I continues to increase, the yields of octane, butene, and butane all saturate for an exposure of ~7 L. Interestingly, it is found that the maximum total yield of these low-temperature products depends on the dosing time. For exposure times longer than ~20 s, the total yields stay constant. Faster exposures, however, result in larger yields. Figure 7 shows that for the same 7 L exposure of C_4H_9I, the octane yield for a 2-s dose at ~3.5×10^{-6} Torr is about 4 times that for a 35-s dose at 2×10^{-7} Torr. In the former experiment, it was difficult to achieve a fixed pressure for such short times, so the actual exposure is somewhat larger than 7 L as evidenced by a significant molecular desorption peak at 155 K (not shown). This overexposure, however, is not the reason for the increased octane yield, since the octane yield saturates for an exposure of 7 L as shown in Figure 6. The octane peak at 155 K in Figure 7C is concurrent with molecular desorption and probably reflects dissolution of octane in the C_4H_9I multilayer. The inset in Figure 7 shows the relative product yield for octane as a function of dosing time for a 7-L exposure. For dosing times longer than ~20, the octane yield is constant to within the experimental uncertainty. The reasons for the higher yield at short dosing times are discussed further in section 4.

4. Discussion

The results presented above establish that alkyl coupling and disproportionation products are formed concurrently with C–I bond dissociation for high surface coverages of the straight-chain C_2–C_5 alkyl iodides on a Cu(111) surface. These high-coverage

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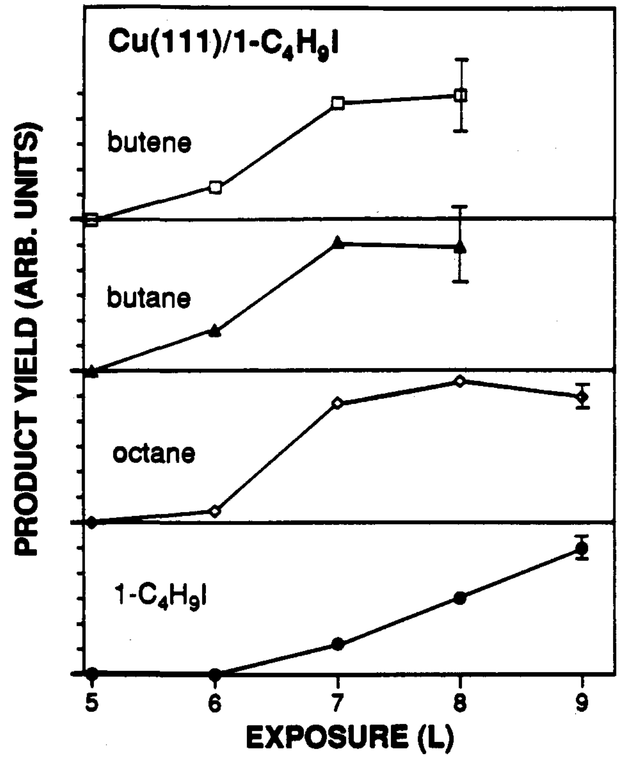

Figure 6. Plot of relative product yields as a function of 1-C_4H_9I exposure to Cu(111). Butene, butane, and octane emerge at near monolayer saturation and show a similar trend as a function of exposure.

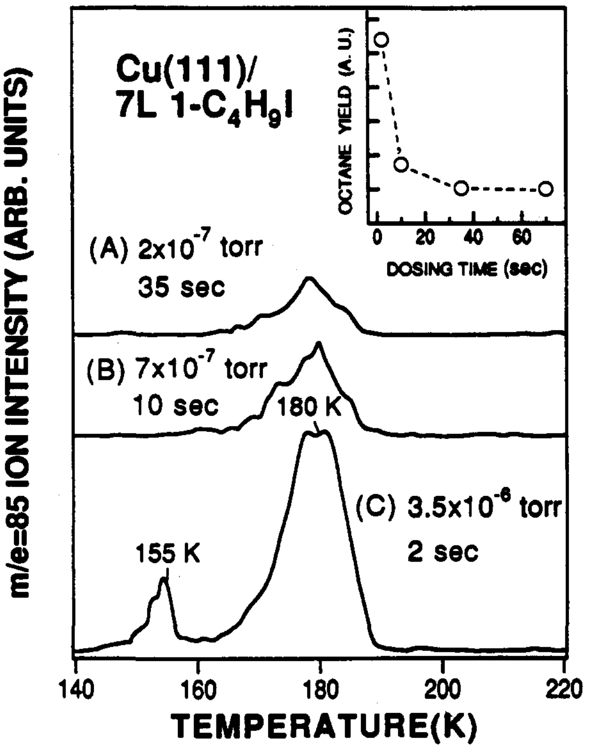

Figure 7. Temperature-programmed reaction spectra for *m/e* 85 after 1-C_4H_9I is dosed for various times to attain a 7-L exposure. The relative octane yield as a function of dosing time for a 7-L exposure is shown in the inset.

reaction channels are summarized in Figure 8 together with those reactions previously determined for the alkyl iodides at lower surface coverages. The primary evidence that C–I bond dissociation is the rate-determining step in forming the coupling products at high surface coverage is the evolution of butane at 120 K for the reaction of iodoethane (see Figure 2B). This is the same temperature, to within experimental uncertainty, as that reported previously for C–I bond scission.[13,14] For the longer chain alkyl iodides, desorption is the rate-determining step in the evolution of coupling products from the surface. The formation of alkyl disproportionation products is evidenced by the evolution of butane and butene is an approximately 1:1 ratio from iodobutane. The formation of these products over the same range of surface coverage where octane is formed (see Figure 6) and in a nearly constant ratio to octane suggests a common intermediate in the surface reaction mechanism to form all three products. This intermediate and the coupling/disproportionation reaction mechanism(s) are discussed below.

As mentioned in the introduction, two species have been proposed as intermediates in the reaction of alkyl iodides with metal surfaces: alkyl radicals and surface-bound alkyl groups. Previous studies of alkyl iodides on single-crystal copper surfaces support the presence of both of these species. For example, adsorbed alkyl groups have been identified by surface vibrational spectroscopy for dissociative adsorption of submonolayer coverages of the C_1–C_5 alkyl iodides.[13] In addition, however, methyl radicals have been detected in the gas phase by mass spectrometry for dissociation of CH_3I on a Cu(111) surface.[11] The concurrent evolution of methyl radicals and formation of adsorbed methyl groups suggests that both reaction channels involve a methyl radical which is either trapped on the surface or ejected into the gas phase.[11] Similar free radical intermediates have also been suggested for the formation of adsorbed alkyl groups from the longer-chain alkyl halides.[13]

The results here allow us to address the relative importance of alkyl radicals and adsorbed alkyl groups in the reactions of the C_2–C_5 alkyl iodides on Cu(111). The alkene and alkane products formed at temperatures above 200 K for submonolayer coverages are the result of surface-bound alkyl intermediates (see Figure 8). While it is possible that a high surface coverages these alkyl groups undergo coupling and disproportionation reactions at much lower temperatures, the results here suggest that this is not the case. Coupling of adsorbed methyl groups to produce ethane does not occur until ~450 K. This temperature corresponds to an activation energy of ~27 kcal/mol,[28] which is more than twice that for the alkyl iodide coupling and disproportionation products formed at ~120 K. Furthermore, the cross-coupling studies presented in section 3 show that cross coupling is virtually eliminated when either of the alkyl iodides is dissociated to form adsorbed alkyl groups prior to adsorbing the other alkyl iodide. Finally, the ratio of the disproportionation and coupling products for iodobutane (0.44 ± 0.13) is approximately that expected from the reactions of alkyl radicals in the gas phase and in solution.[25,26] All of these results lead us to conclude that alkyl radicals and not surface-bound alkyl groups are the primary intermediates in the reaction to form coupling and disproportionation products from the alkyl iodides on Cu(111).

Given the intermediacy of alkyl radicals in forming the alkyl iodide coupling and disproportionation products, the question is whether the alkyl radicals react directly with one another or instead with molecular alkyl iodides (eqs 5 and 6 in Scheme I). In the gas phase, the primary pathway for the reaction of alkyl radicals and alkyl halides is atom abstraction.[25] If the same holds on the surface, then more alkanes and less alkyl coupling would be expected. Radical–radical reactions, on the other hand, yield product distributions for straight-chain alkyl groups quite similar to those found for the alkyl iodides on Cu(111).[25,26] The difficulty is to envision how alkyl radicals can live long enough on the surface to encounter one another. The two reaction channels that can compete with radical–radical reactions are adsorption onto the metal surface to form surface-bound alkyl groups and desorption from the surface as free alkyl radicals (which are not detected). Bonding to the surface is inhibited by the high surface

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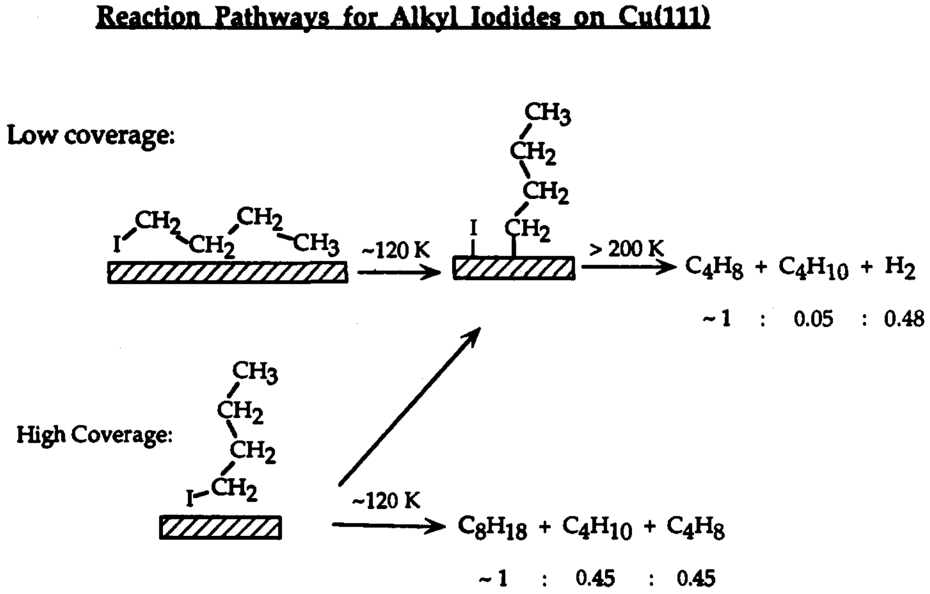

Figure 8. Reaction pathways for straight chain alkyl iodides on Cu(111) as illustrated by 1-iodobutane. At low coverage, the adsorbed alkyls undergo β-hybride elimination to give alkene, alkane, and hydrogen. At high coverage, alkyl coupling and disproportionation also occur at ~120 K where the C–I bond dissociates. The product ratios shown are for a saturation coverage of the alkyl iodide.

coverages required to observe these reactions. In this regard it is also significant that infrared spectroscopy studies of alkyl halides on Pt(111) indicate a tilting of the alkyl chain away from the surface for high coverages.[29] Such an upright adsorption geometry, as shown in the bottom of Figure 8, would allow the alkyl radical formed upon C–I bond scission to become an extrinsic precursor, i.e. a species weakly adsorbed on top of the chemisorbed monolayer.[30] It should be noted that C–I bond scission is approximately thermoneutral on Cu(111) with only a small barrier for the reverse reaction so that little energy need to be dissipated to accommodate radicals physisorbed in a second layer.[11] From such a physisorbed state, there are three possibilities: desorption, reaction with the chemisorbed layer, or reaction with another physisorbed radical. The latter possibility would be expected to produce the coupling and disproportionation products in the observed ratio.

An additional observation in support of the second layer, physisorbed radical scenario described above is the finding that alkyl bromides do not show this high coverage, coupling and disproportionation chemistry. Instead, an additional molecular desorption peak, slightly above the multilayer peak temperature, is observed at the high surface coverages where coupling and disproportionation occur for the alkyl iodides. We attribute this molecular desorption peak to alkyl bromides whose alkyl chains tilt away from the surface at high coverages. Under these conditions, the binding energy to the surface is reduced and becomes methyl bromide-like, i.e., dominated by the bromine end of the molecule. Since CH_3Br desorbs from Cu(111) without dissociation, it is not surprising that longer chain alkyl bromides do not dissociate at high coverage.[13] For alkyl iodides, however, the carbon–halogen bond dissociation temperature is 30–40 K lower, so that CH_3I and high coverages of the longer chain alkyl iodides (whose binding to the surface is CH_3I-like) dissociate as opposed to desorbing from the surface.

While the results here provide strong evidence for radical participation in these low-temperature coupling and disproportionation reactions, many questions remain regarding the details of these reactions. For example, it is not yet clear how iodopentane reacts with iodomethane to form hexane as documented by the TPR results in Figure 4B. The fact that the C–I bond in iodopentane dissociates at ~20 K lower temperature than the C–I bond in CH_3I[13] suggests that a pentyl radical may react with molecular CH_3I. Alternatively, since the coverage of iodopentane that must be added to preadsorbed CH_3I to form this product corresponds to approximately saturation of the monolayer, it may be that some second layer iodopentane that remains molecularly intact gains access to the surface and dissociates when the monolayer is disrupted during C–I bond scission in CH_3I. In such a scenario, radical–radical reactions could still be the source of the cross-coupling product. We cannot, however, rule out the participation of other mechanisms in addition to radical/radical reactions to account for the results. The main argument against these alternatives is the lack of precedence in gas phase and solution chemistry for forming coupling and/or disproportionation products by radical/molecule reactions.

We conclude with several comments about the larger product yields observed for shorter dosing times (see Figure 7). This finding indicates some process in the adsorbed layer that occurs on the time scale of seconds. An intriguing possibility is that this time constant reflects the lifetime of alkyl radicals formed by C–I bond scission at the adsorption temperature. Precedence for bimolecular reactions of radicals formed by thermal dissociation of a molecular precursor on a surface comes from the studies of Houtman and Barteau on formaldehyde polymerization on a Rh(111) surface.[31] Analogous to the results here, the extent of polymerization was found to increase as the exposure time was decreased. Recent results on the photoinduced polymerization of formaldehyde on Ag(111) support a radical mechanism for the polymerization reaction.[32] Long lifetimes for adsorbed radicals are particularly reasonable if the radicals are physisorbed in a second layer as suggested above. Alternatively, the increased coupling yield observed for short dosing times may reflect a change in the 2-dimensional ordering on the surface. It is known that the long-range order in monolayers can be dramatically affected by the rate of collective diffusive motions relative to the rate of adsorption, with faster dosing or dosing at lower temperatures producing smaller ordered domains that have different desorption and/or reaction kinetics.[33-35] Further experiments, particularly

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studies in which lower surface temperatures are accessible, are needed to distinguish these possibilities.

5. Conclusions

The results reported here show that when straight-chain C_2–C_5 alkyl iodides are dissociatively adsorbed at low temperatures on a Cu(111) surface, two processes occur. At low coverages, the carbon–iodine bond dissociates at ~120 K to form adsorbed alkyl groups and iodine atoms. At high coverages, alkyl coupling and disproportionation products as well as adsorbed alkyl groups are formed during C–I bond dissociation. The disproportionation to coupling ratio of 0.44 ± 0.13 is within a factor of 2 of that found for alkyl radicals in the gas phase and in solution, suggesting a radical mechanism for forming these products. A radical mechanism is also supported by previous studies showing that methyl radicals are formed when CH_3I thermally dissociates on a Cu(111) surface. These radical reactions at temperatures below 150 K are quite different from the reactions of surface-bound alkyl groups which occur above 200 K and produce primarily alkenes and hydrogen as a result of β-hydride elimination by the adsorbed alkyl groups.

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