Formation of Methyl Radicals during the Oxidative Addition of Iodomethane to a Single-Crystal Copper Surface

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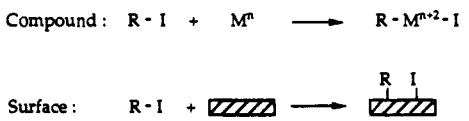
Abstract: Submonolayer quantities of CH_3I have been adsorbed onto an atomically-clean Cu(111) single-crystal surface under ultra-high-vacuum conditions. At 110 K, the molecules remain intact. Upon heating the surface, the carbon–iodine bond dissociates at 140 K to produce adsorbed methyl groups (which have been identified by surface vibrational spectroscopy) and gas-phase methyl radicals (which are detected by mass spectrometry). The activation energy for these processes is ~8.5 kcal/mol. The observation of methyl radicals suggests that the surface reaction is analogous to the oxidative addition of alkyl iodides to metal compounds by atom-transfer or electron-transfer mechanisms. The thermodynamics and kinetics of both mechanisms are discussed in the context of the Cu(111) results.

1. Introduction

Recent studies have shown that iodoalkanes dissociate below 300 K on a number of atomically-clean, single-crystal metal surfaces under vacuum conditions to form surface-bound alkyl groups and iodine atoms.[1] This process is formally analogous to the oxidative addition of alkyl iodides to inorganic compounds,[2] as shown in Scheme I. Beyond this formal analogy there may also be mechanistic similarities. There is evidence from the reactions of alkyl iodides with both metal compounds[2] and metal surfaces[3] *in solution* that alkyl radicals can be formed during dissociation of the carbon–iodine bond. In the case of metal compounds, the evidence for radicals is both chemical (coupling and disproportionation reactions,[2] rearrangement reactions,[4] and radical traps[5]) and spectroscopic (elecron spin resonance[4a,6] and chemically-induced dynamic nuclear polarization[7]). For metal surfaces, however, there is much debate over whether alkyl radicals play a role.[3] Alkyl coupling, disproportionation, and rearrangement products suggest radicals,[8] but the potential role of metal alkyl species has been difficult to rule out, since the ways in which such species would react have been unknown until recently.[1]

In the present work, we present mass spectrometric evidence that methyl radicals are evolved into the gas phase during the oxidative addition of iodomethane to a single-crystal Cu(111) surface under ultra-high-vacuum conditions. The competing reaction channel to form adsorbed methyl groups is also observed, and this pathway has been discussed in a previous publication.[9]

Scheme I



2. Experimental Section

The ultra-high-vacuum system used in these experiments has been described previously.[10] The apparatus with a base pressure of $<2 \times 10^{-10}$ Torr is equipped with capabilities for surface cleaning (ion sputtering), determination of surface composition (Auger electron spectroscopy), detection of desorbed products (mass spectrometry), and measurement of surface vibrational spectra (high-resolution electron energy-loss spectroscopy). The Cu(111) single crystal (Monocrystals Co., 99.999%) is attached to a resistive heating element with a chromel wire wound around the grooved edge of the crystal. The junction of an alumel–chromel thermocouple is wedged into a hole in the side of the crystal to monitor the surface temperature. The surface was cleaned by ion bombardment and annealing in vacuum as previously described,[11] and the cleanliness was confirmed by Auger electron spectroscopy. CH_3I (99.5%) and CD_3I (99.5+ atom %D) were obtained from Aldrich. Prior to introduction into the vacuum system, they were purified and degassed by several freeze–pump–thaw cycles with liquid nitrogen. Their purity was verified in situ by mass spectrometry. Iodomethane was adsorbed onto the Cu(111) surface at 120 K by backfilling the chamber with a specified pressure for the appropriate time to achieve the desired surface coverage. Exposures are reported as Langmuirs (L) (1 L = 10^{-6} Torr·s). In the temperature-programmed reaction (TPR) experiments, the surface was positioned in front of the mass spectrometer and the surface heating rate was 2.5 K/s. A skimmer with a 2 mm diameter aperture ensured that only species evolved from the center of the 1 cm diameter single crystal were detected by the differentially-pumped mass spectrometer. Control experiments with variable exposures to electrons from the mass spectrometer ionizer showed that these electrons do not play a role in the results reported here.

3. Results and Discussion

3.1. Methyl Radicals from CH_3I. High-resolution electron energy-loss spectra show that iodomethane adsorbs molecularly

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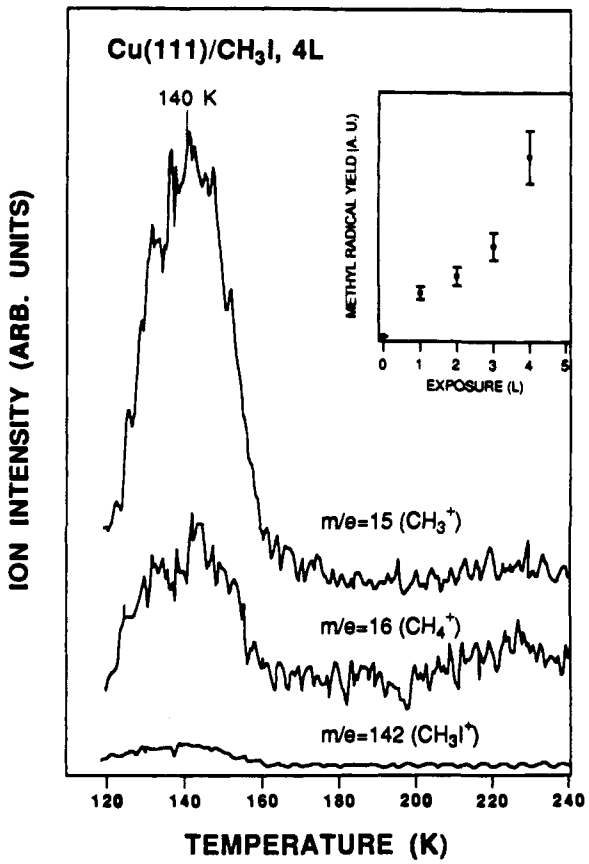

Figure 1. Temperature-programmed reaction spectra for m/e = 15, 16, and 142 after a 4-L exposure of iodomethane to Cu(111) at 120 K. All of the peaks are attributed to the evolution of methyl radicals during C–I bond dissociation. CH_4^+ (m/e = 16) and CH_3I^+ (m/e = 142) are due to hydrogen or iodine abstraction from the walls inside the mass spectrometer shield.

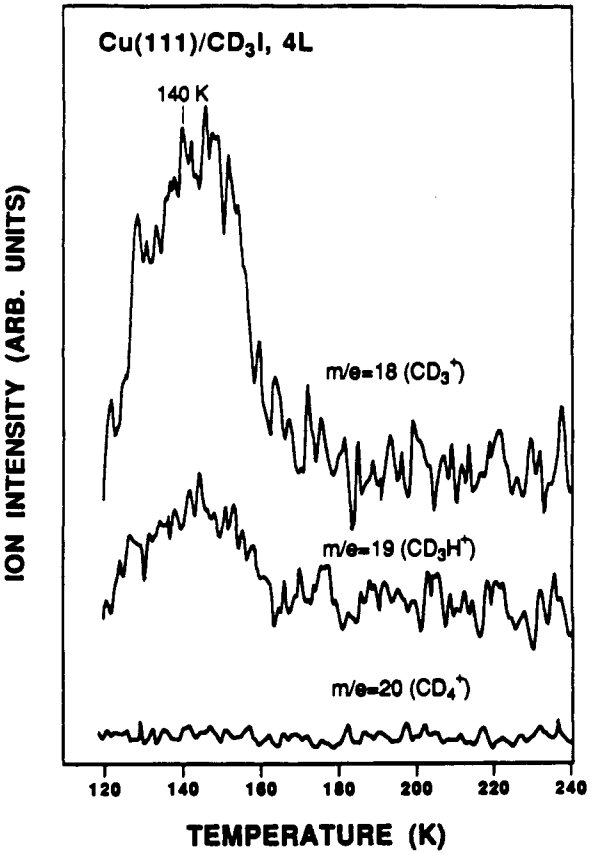

Figure 2. Temperature-programmed reaction spectra for m/e = 18, 19, and 20 after a 4-L exposure of deuterated iodomethane onto Cu(111) at 120 K. The presence of CD_3H^+ and the absence of CD_4^+ is indicative of hydrogen abstraction from the walls by methyl radicals.

intact on a Cu(111) surface which has been cooled to 110 K.[9] If the surface is then heated, carbon–iodine bond dissociation occurs at ~140 K to produce adsorbed methyl groups[9,10] and gas-phase methyl radicals. The evidence for methyl radicals is shown by the TPR spectra in Figure 1 for m/e = 15, 16, and 142 after a 4.0-L exposure (about 80% of monolayer saturation) of iodomethane to Cu(111) at 120 K. Other masses between 20 and 30 amu were also monitored, but no peaks were observed. While the detection of m/e = 142 (CH_3I^+) suggests molecular desorption, the m/e = 15:142 ratio of 21 is 8.5 times larger than that measured for CH_3I during desorption of multilayers from the surface. Similarly, the detection of m/e = 16 (CH_4^+) suggests methane evolution, but the observed m/e = 16:15 ratio of 0.3 is a factor of 4.1 less than that for methane. Mixtures of species are unlikely, because all three ions (m/e = 15, 16, and 142) have the same peak temperatures, shapes, and relative intensities for all exposures less than 5 L (the lowest exposure for which molecular desorption is detected).

We attribute all of the peaks in Figure 1 to evolution of methyl radicals. As methyl radicals enter the ionizer region of the mass spectrometer, some of them are ionized to produce m/e = 15 (CH_3^+), but others collide with surfaces inside the mass spectrometer shield and abstract H or I atoms to produce CH_4 and CH_3I, which are also detected. Such abstraction reactions by methyl radicals are well-documented,[12] and their interference in mass spectrometric detection of methyl radicals evolved from surfaces has been discussed previously.[13]

These abstraction reactions are supported by the results in Figure 2 for deuterated iodomethane. As shown, a small amount of m/e = 19 (CD_3H^+) is detected coincident with m/e = 18 (CD_3^+), consistent with hydrogen abstraction from the walls to form CD_3H. The presence of CD_3H is confirmed by the m/e 19:17 ratio (not shown) of 2.2, which is in agreement with the literature value of 2.0 for CD_3H.[14] The absence of m/e = 20 (CD_4^+) indicates that methane is not formed by a reaction between CD_3I molecules on the Cu(111) surface. Furthermore, since H_2 has a very low dissociative adsorption probability on Cu(111),[15] adsorption of hydrogen from the background gases is not the source of CD_3H. While it is possible that some CD_3H could be formed on the Cu(111) surface as a result of dissociative H_2 adsorption at defect sites, we believe that such a process does not play a role in our studies, since the m/e = 19:18 ratio is independent of surface coverage. In any event, the CD_3^+ peak in Figure 2 is a factor of 9.4 larger than that expected for cracking of CD_3H, supporting the presence of methyl radicals.

The evolution of methyl radicals at 140 K during CH_3I decomposition on Cu(111) is further substantiated by the measured mass spectrometer cracking pattern. After subtracting the methane and iodomethane daughter ion contribution to the m/e = 14 and 15 ion intensities, the 15:14 ratio for the product is 0.29 ± 0.07 for an electron-impact ionization energy of 70 eV. This value is consistent with the range 0.32–0.54 reported by others for methyl radicals[13b,16] and is substantially different from that of 0.11 for methane.

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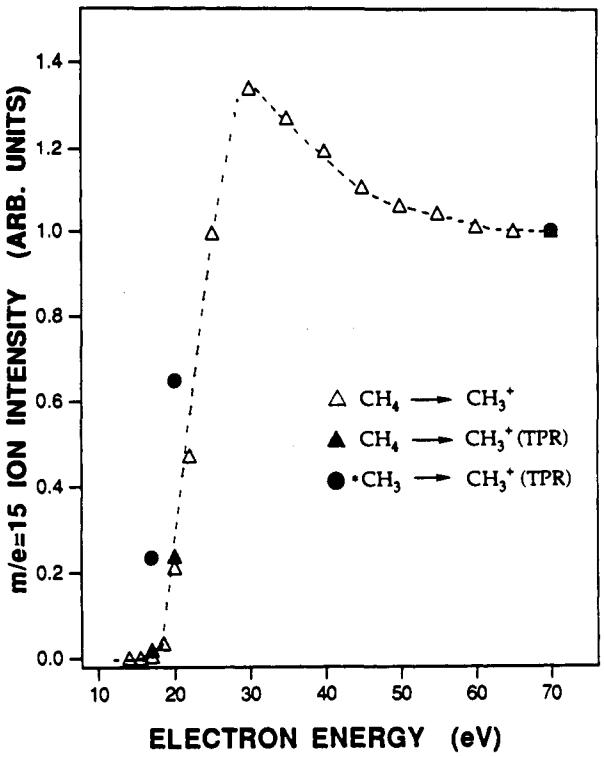

Figure 3. m/e = 15 intensity for methane and methyl radicals as a function of ionizer energy in the mass spectrometer. The open triangles are from calibration spectra for methane. The solid triangles and circles represent methane and methyl radicals, respectively, which are evolved during the temperature-programmed reaction of CH_3I with Cu(111). The intensities at 70 eV are normalized to 1. Methyl radicals have a lower ionization threshold and higher relative intensity at low ionizer energy, as compared to methane.

Methane and methyl radicals are also distinguishable by the appearance potentials for forming CH_3^+ by electron-impact ionization. For methyl radicals, the threshold to produce CH_3^+ is 9.8 eV, while for methane, 14.4 eV are required to ionize and crack CH_4 to CH_3^+.[17] In the case of CH_3I dissociation on Cu(111), we find that the dependence of the product mass spectrum on ionizer energy is consistent with CH_3 radicals as opposed to methane. The results are presented in Figure 3. The open triangles show the ionizer energy dependence of the m/e = 15 intensity for methane in our mass spectrometer. The apparent threshold of 18 eV is larger than that of 14.4 eV reported in the literature, but this value is reasonable given that fringing fields, contact potentials, mechanical offsets in the control panel, etc. are not taken into account in our measurement. We conclude that, relative to an absolute scale, the electron energy axis in Figure 3 is artificially shifted by ~3.6 eV to higher energy. As shown by the solid triangles in Figure 3, the same higher ionization energy threshold is found for the m/e = 15 TPR signal for methane evolved from Cu(111) at 470 K during decomposition of adsorbed methyl groups (see ref 9 for a discussion of this $CH_3 \rightarrow CH_4$ chemistry). By contrast, the threshold for the m/e = 15 TPR signal at 140 K from CH_3I decomposition on Cu(111) is at lower potential, as evidenced by the solid circles in Figure 3. The horizontal separation between these points and the dashed curve sketched for methane is ~3 eV, which is within a factor of 2 of that expected for methyl radicals.

On the basis of these results, we conclude that iodomethane decomposes at 140 K on Cu(111) to evolve methyl radicals. This is the same temperature, to within experimental uncertainty, determined previously for forming adsorbed methyl groups and iodine atoms by dissociative adsorption of CH_3I on Cu(111).[9,10]

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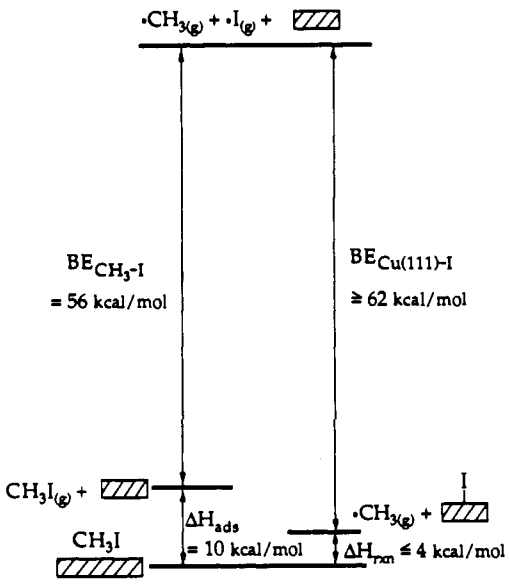
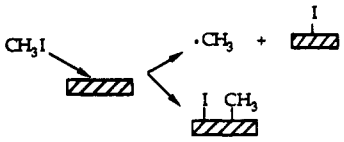


Figure 4. A thermochemical cycle for calculating the enthalpy change for dissociation of adsorbed iodomethane on Cu(111) to eject methyl radicals into the gas phase and leave iodine atoms on the surface.

Scheme II



In other words, the two processes shown in Scheme II occur concurrently. The relative yields of radical ejection and methyl adsorption (based on a carbon mass balance assuming that the CH_3I surface coverage increases linearly with exposure[18]) are about 0.25 and 0.75, respectively for a 4-L exposure. For reference, a 5-L exposure corresponds to one monolayer of CH_3I.[9,10] Assuming a first-order preexponential factor of 10^{13} s^{-1} for C–I bond scission, the activation energy for methyl radical formation is 8.5 kcal/mol.[19]

3.2. Thermodynamics of C–I Bond Scission on Cu(111). Radical ejection during C–I bond scission on Cu(111) is reasonable given the reaction thermodynamics. The enthalpy change for the reaction can be calculated from the thermochemical cycle shown in Figure 4. Although the heat of adsorption for CH_3I is not known because it dissociates as opposed to desorbing molecularly intact, ΔH_{ads} can be reasonably approximated as 10 kcal/mol,[20] slightly higher than both the C–I bond dissociation energy of ~8.5 kcal/mol and the CH_3Br desorption energy of ~8.2 kcal/mol.[10] The gas-phase C–I bond energy is 56 kcal/mol.[21] The Cu–I bond energy on Cu(111) is not accurately known, but the lower limit is 62 kcal/mol on the basis of the peak temperature of ~955 K for evolution of cuprous iodide (CuI) during temperature-programmed desorption experiments.[18] Given these approximations, the reaction to eject methyl radicals into the gas phase is 4 kcal/mol endothermic. The entropy change depends on the pressure of methyl radicals. Under vacuum conditions, ΔS will be large and positive. For example, with a $\cdot CH_3$ pressure of 10^{-10} Torr, the entropy change is ~83 cal mol^{-1} K^{-1} and $T\Delta S$ = 11.6 kcal/mol at 140 K (see Table I and discussion below).[22]

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Table I. Calculated Entropies (cal mol^{-1} K^{-1}) for the CH_3I/Cu(111) System

	S_{trans}	S_{vib}	S_{rot}
CH_3I(a)	21	~0	0.6
I(a)	0	7	0
CH_3(g)	35.4[a]	~0	8.2

[a] Calculated from ΔS_{rxn}, which is 29 cal mol^{-1} K^{-1}.

This value increases by 0.65 kcal/mol for each order of magnitude decrease in pressure, so the reaction is thermodynamically-allowed. The concern here is the rate at which the reaction occurs at 140 K.

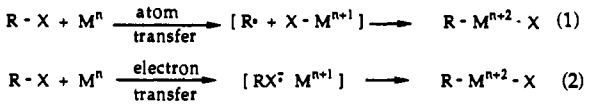
A thermodynamic limit to the rate of methyl radical evolution from CH_3I/Cu(111) can be determined by calculating the "equilibrium rate". At equilibrium, the rates for methyl ejection and adsorption are equal, so determining the equilibrium pressure of methyl radicals at 140 K provides the $^{\bullet}CH_3$/surface collision frequency as an upper limit to the rates of radical adsorption and desorption. To calculate the equilibrium methyl radical pressure, we use the fact that $\Delta H_{rxn} = T\Delta S_{rxn}$ at equilibrium. As determined from the thermochemical cycle in Figure 4, the enthalpy change is ~4 kcal/mol. The entropy change can be reasonably approximated by using statistical thermodynamics to calculate the entropies for adsorbed CH_3I, adsorbed I, and gas-phase $^{\bullet}CH_3$. In making this calculation, the entropy of mixing on the surface is neglected; adsorbed CH_3I is treated as completely mobile in two dimensions with unconstrained rotation about the C–I bond, and adsorbed I is treated as immobile with perpendicular and degenerate parallel vibrational frequencies of 230 and 50 cm^{-1}, respectively.[9] The calculated entropies are shown in Table I for a surface CH_3I concentration of 10^{14} molecules/cm^2. Note that the entropy contribution from vibrational motions is negligible except when the values of the vibrational frequencies are small; e.g., the ~50 cm^{-1} frustrated translational mode for adsorbed iodine atoms has an entropy of ~3.3 cal mol^{-1} K^{-1}. Furthermore the vibrational entropies for adsorbed CH_3I and gas-phase $^{\bullet}CH_3$ will tend to cancel each other in the calculation for ΔS_{rxn}, so the approximated values of zero will not cause a substantial error in the calculated ΔS_{rxn}.

The resulting translational entropy of 35.4 cal mol^{-1} K^{-1} for gas-phase methyl radicals at equilibrium corresponds to a pressure of 0.08 atm,[22] representing a collision frequency of 4.8×10^{22} molecules cm^{-2} s^{-1}. The measured rate of CH_3 radical evolution at 140 K from CH_3I/Cu(111) is $\sim 6.5 \times 10^{13}$ molecules cm^{-2} s^{-1}, as determined from a first-order Arrhenius expression:

$$\text{rate} = \nu \exp(-E_a/RT)\Theta$$

with $\nu = 10^{13}$ s^{-1}, $E_a = 8.5$ kcal/mol, $T = 140$ K, and $\Theta = 10^{14}$ molecules cm^{-2} s^{-1}. This value is ~10^9 smaller than the equilibrium rate, which is not surprising since the equilibrium rate assumes a reaction probability of 1 for methyl radicals incident on the surface. Given that the activation energy is 4.5 kcal/mol for $^{\bullet}CH_3$ addition to Cu(111)/I to form Cu(111)/CH_3I (the difference between the activation energy and the enthalpy change for radical formation), only 1 in 2.4×10^6 of the methyl radicals in a thermal distribution at 140 K will have energies in excess of the reaction barrier.[22c] The measured reaction rate of 6.5×10^{13} molecules cm^{-2} s^{-1} therefore implies a reaction probability of 0.003 for methyl radicals with energies in excess of the reaction barrier, a reasonable value given entropic effects. We conclude that methyl radical ejection at 140 K from CH_3I/Cu(111) is reasonable on the basis of the equilibrium reaction thermodynamics.

3.3. Implications for the Mechanism of C–I Bond Scission on Cu(111). In solution-phase organometallic chemistry, atom- and electron-transfer mechanisms have been proposed to account for alkyl radical formation during the oxidative addition of alkyl halides (eqs 1 and 2).[2] These two mechanistic possibilities are



difficult to discriminate experimentally. While there is circumstantial evidence[2] for one or the other in a few specific cases, these two reactions represent mechanistic extremes. In most cases, reality lies somewhere between the two. It is useful, however, to consider the extremes, because they illustrate most clearly the factors that determine the reaction barrier.

In the case of methyl radical evolution from CH_3I/Cu(111), the atom-transfer model provides the intuitive picture that C–I bond scission is compensated by formation of a Cu–I bond of comparable strength. The energy barriers for analogous hydrogen atom transfer reactions in the gas phase have been correlated with the reaction thermodynamics using bond energy–bond order (BEBO) models.[23] Similar approaches have also been employed for surface reactions.[24] For halogen atom transfer reactions, BEBO is known to be less effective,[25] but the measured activation energy of 8.5 kcal/mol (–1.5 kcal/mol relative to gas-phase CH_3I) is within the range of energy barriers expected for gas-phase hydrogen atom transfer reactions of comparable endothermicity.[23]

To the extent that adsorbed iodine atoms on Cu(111) are ionic, iodine atom transfer from the methyl group to the surface also involves electron transfer from the surface to the iodine atom. For the CH_3I coverages used in the studies here, the Cu(111) work function increases by 250 meV for the adsorbed iodine layer that remains on the surface.[9] This is a small value, corresponding to a charge of ~0.15 e 0.47 Å above the surface image plane.[26] Theoretical calculations for Cl on a copper cluster, however, indicate that the small net change in the surface dipole layer represents nearly complete electron transfer to the halogen, accompanied by compensating polarization of the halide/metal system.[27] It thus appears that substantial electron transfer occurs at some point during the iodine atom transfer reaction.

The energy (E_D) required to take an electron at the Fermi level in copper and transfer it to CH_3I adsorbed in its equilibrium geometry can be approximated by[18,28]

$$E_D = \Phi - \text{VEA}[CH_3I(g)] - E_{im} - E_{pol}$$

where Φ is the work function for the adsorbate-covered surface (4.3 eV for 2.5-L CH_3I on Cu(111)),[10] VEA[CH_3I(g)] is the vertical electron affinity for gas-phase CH_3I (–0.6 eV for the vibrational ground state[29]), E_{im} is the image charge attraction (~1.2 eV for a distance of 3 Å from the image plane[28]), and E_{pol} is the electronic polarization of the surrounding adsorbates (~0.6 eV for CH_3I adsorbed at monolayer coverage on Cu(111)).[28] The resulting value of 3.1 eV (~72 kcal/mol) for electron transfer is much larger than the measured activation energy of 8.5 kcal/mol for C–I bond scission. Stretching the C–I bond, however, dramatically lowers the energy barrier for electron transfer. This effect is illustrated by the one-dimensional potential energy curves for adsorbed CH_3I and CH_3I^- in Figure 5. The potential energy

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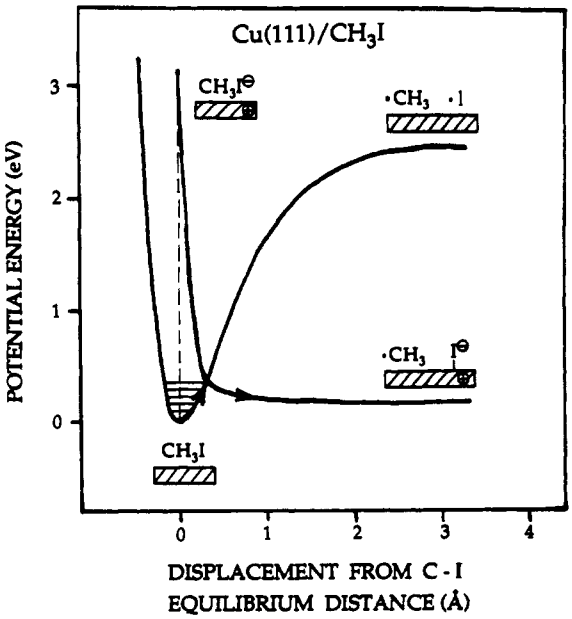


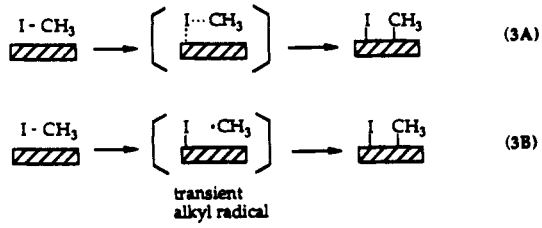
Figure 5. Potential energy curves for $CH_3I/Cu(111)$ and $CH_3I^-/Cu(111)$ as a function of C–I internuclear separation. For $CH_3I/Cu(111)$, no stabilization as a result of Cu–I bond formation is taken into account. For CH_3I^-, the potential energy curve includes Cu–I bond formation to achieve an overall endothermicity for the reaction of 4 kcal/mol (see section 3.2). As shown by the dashed line, ~3 eV are required to transfer an electron from the Fermi level of Cu(111) to adsorbed CH_3I. With elongation of the C–I bond in CH_3I^-, the potential energy drops dramatically so that a thermally-activated electron-transfer pathway becomes possible, as indicated by the arrows.

of adsorbed CH_3I^- decreases dramatically with increased C–I separation while that for neutral CH_3I increases approximately quadratically with internuclear distance.[29] The consequence is that, for vibrationally-excited CH_3I, the potential energy of $CH_3I/Cu(111)$ can become equivalent to that for $CH_3I^-/Cu(111)$ and electron transfer is thermoneutral. Such a thermall-activated electron-transfer process is indicated by the arrows in Figure 5. As discussed elsewhere,[18] simple harmonic potentials suggest that the degree of vibrational excitation required to achieve this energy-neutral electron transfer is within a factor of 2 of the measured energy barrier (8.5 kcal/mol) for CH_3 radical formation.

Such a mechanism of thermally-activated electron transfer contrasts with that recently proposed for methyl radical formation during the dissociative adsorption of CH_3Br on potassium-promoted Ag(111).[30] In that system, methyl radicals were evolved during adsorption at 100 K, and there was no evidence for an energy barrier in the process. As a result, it was suggested, by analogy with alkali metal/alkyl halide reactions in the gas phase, that dissociation of the C–Br bond occurs by electron harpooning.[30] In other words, the work function of potassium-promoted Ag(111) is sufficiently small [1.3 eV compared with 4.3 eV for the CH_3I-covered Cu(111) surface] that vertical electron transfer from the metal to CH_3Br in its ground-state equilibrium geometry becomes energetically feasible at physisorption or longer distances from the surface.[28] Such a process is clearly different from that

(30) Zhou, X.-L.; Coon, S. R.; White, J. M. *J. Chem. Phys.* **1991**, *94*, 1613.

Scheme III



for radical formation from $CH_3I/Cu(111)$, where electron transfer, if it occurs, requires thermal activation. The $CH_3I/Cu(111)$ system is probably more analogous to CH_2I_2/Al[31] and CCl_4/Fe,[32] where low-temperature carbene formation is observed via thermally-activated processes.

Finally, we address the question of whether methyl radicals also play a role in carbon–iodine bond dissociation to produce adsorbed methyl groups. The alternative, as shown in Scheme IIIA, is that there is partial copper–carbon bond formation in the transition state and that a true free radical as shown in Scheme IIIB never exists on the surface.

While we cannot rule out the possibility that C–I bond scission to form adsorbed CH_3 groups occurs via such a three- or four-center transition state, if this process happens, it must occur at a rate comparable to that for methyl radical formation; otherwise, radical formation would completely dominate. As a general rule, a difference of 1 kcal/mol in the activation energy for two competing reactions having the same preexponential factor changes the relative yields in a TPR experiment by an order of magnitude for typical surface heating rates of 1–10 K/s.[33] The fact that both radical ejection and methyl adsorption are detectable suggests, as shown in Scheme IIIB, that transient alkyl radicals are involved in the methyl adsorption pathway. Studies of intramolecular radical rearrangements and reactions are in progress to address this point.

4. Conclusions

Methyl radical ejection is detected by mass spectrometry during thermal dissociation of the carbon–iodine bond in CH_3I on a Cu(111) surface. A competing process is formation of adsorbed methyl groups. On the basis of the reaction temperature of 140 K and an assumed first-order preexponential factor of 10^{13} s^{-1}, the activation energy for C–I bond scission is 8.5 kcal/mol. Analogous to the solution-phase reactions of alkyl halides with metal compounds, carbon–iodine bond scission on a Cu(111) surface can be viewed as an oxidative addition that occurs by a thermally-activated atom- or electron-transfer mechanism. Thermodynamic and kinetic arguments indicate that both mechanisms are reasonable on the copper surface.

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